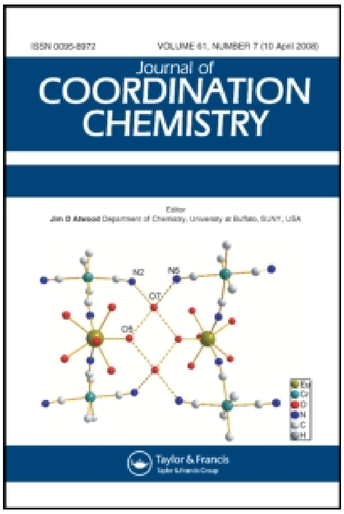

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Synthesis, spectroscopy and redox chemistry of bis(*n*-aryl-3,5-di-*tert*-butylsalicylaldiminato)copper(II) complexes

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SYNTHESIS, SPECTROSCOPY AND REDOX CHEMISTRY OF bis(*N*-ARYL-3,5-DI-*tert*-BUTYLSALICYLALDIMINATO)-COPPER(II) COMPLEXES

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A series of new bis(*N*-aryl-3,5-di-*tert*-butylsalicylaldiminato)copper(II) complexes (**I**), prepared from 3,5-di-*tert*-butylsalicylaldehyde and mono-substituted anilines, X-$C_6H_4NH_2$ (X = H, *o*-F, Cl, Br, CH_3, CH_3O; *p*-F, Cl, Br, CH_3, CH_3O, *t*-Bu and 5,6-benzo), and their spectroscopic properties as well as electrochemistry and reactivity toward PPh_3 are described. Comparison of $g_{\parallel}$ (2.223–2.249), $A_{\parallel}$ (150–170 G) tensors and the axial symmetry parameter, $g_{\parallel}/A_{\parallel}$, (140–155 cm) of **I** with those of model Cu(II) complexes reveals that the coordination site is distorted from square planar toward tetrahedral geometry. The di-*tert*-butyl groups on the salicylaldehyde moiety unlike those introduced on the aniline rings do not facilitate reactivity toward PPh_3. Electrochemical studies of **I** in acetonitrile solutions reveal highly irreversible behavior, due to chemical or stereochemical changes subsequent to electron transfer. In the oxidation of some complexes with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile at 300 K, along with decreasing ESR signals of Cu(II), the appearance of coordinated phenoxyl radical signals centered at $g = 2.004$ were detected. The CV studies on acetonitrile solutions of **I** revealed well-resolved *quasi*-reversible redox waves at $E_{1/2}^{1} = 0.61–0.99$ V and $E_{1/2}^{1} = 1.09–1.23$ V (*vs.* Ag/AgCl) attributable to ligand-centered oxidation processes to yield corresponding coordinated phenoxyl radical species such as Cu(II)(phenoxyl)(phenolate) and Cu(II)$(phenoxyl)_2$.

Keywords: Bis(*N*-aryl-3,5-di-*tert*-butylsalicylaldiminato)copper(II) complexes; Optical and ESR spectra; Redox reactivity; Cyclic voltammetry

INTRODUCTION

The design, synthesis and structural characterization of salicylaldimine complexes continues to be a subject of interest, not only because they can be useful models for metalloenzymes and metalloproteins [1–3], but also due to their interesting structural, magnetic, spectral, chemical, electrochemical, nonlinear optical and catalytic properties which are often strongly dependent on the detailed ligand structure [4–9]. Our interest

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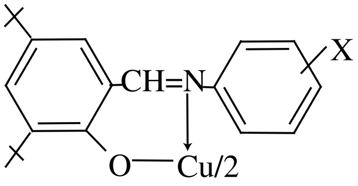

$CuLx_2$

SCHEME 1 $X = H$, L^1H; $X = 2\text{-}F$, L^2H; $X = 4\text{-}F$, L^3H; $X = 2\text{-}Cl$, L^4H; $X = 4\text{-}Cl$, L^5H; $X = 2\text{-}Br$, L^6H; $X = 4\text{-}Br$, L^7H; $X = 2\text{-}CH_3$, L^8H; $X = 4\text{-}CH_3$, L^9H; $X = 2\text{-}OCH_3$, $L^{10}H$; $X = 4\text{-}OCH_3$, $L^{11}H$; $X = 4\text{-}t\text{-}Bu$, $L^{12}H$; $X = 5,6\text{-benzo}$, $L^{13}H$.

in these compounds was associated with the redox activity of the bis(*N*-aryl-salicylaldimine)metal(II) complexes, containing peripheral sterically-hindered phenol (SHP) fragments and their potential for the generation of phenoxyl radical complexes upon one-electron oxidation [10]. In particular, it was of interest to investigate the stability and redox reactivity, as well as the nature of intramolecular exchange, which can occur between paramagnetic centers of the coordinated phenoxyl radical systems. While metal complexes with various *N*-aryl-salicylaldimine ligands are well known, the transition metal chelates with bidentate *N*-aryl-3,5-di-*tert*-butylsalicylaldimine ligands have not been reported.

As a part of a study on the stereochemistry and redox reactivity of bulky *tert*-butylated ligand complexes, we report herein a new series of *N*-aryl-3,5-di-*tert*-butylsalicylaldimine copper(II) complexes, CuL_2^x, derived from 3,5-di-*tert*-butyl-salicylaldehyde and mono-substituted aniline derivatives (Scheme 1).

EXPERIMENTAL

Materials

All solvents, naphthylamine, aniline derivatives and $Cu(ac)_2 \cdot H_2O$ (reagent grade, Aldrich) were used without further purification. 3,5-di-*tert*-Butylsalicylaldehyde was prepared from commercially available 2,4-di-*tert*-butylphenol according to the literature [11]. All salicylaldimines, L^xH, were prepared in high yields (80–96%) via condensation of the 3,5-di-*tert*-butylsalicylaldehyde with the corresponding mono-substituted aniline (1 : 1 molar ratio) in methanol at reflux for 2–6 h and recrystallized from methanol or hexane. The complexes CuL_2^x were prepared by refluxing methanolic solutions of $Cu(ac)_2 \cdot H_2O$ and L^xH in 1 : 2 molar ratio for 1–2 h. Analytical and spectroscopic data for the L^xH and CuL_2^x are presented in the Tables I–IV.

Physical Measurements

Elemental analyses (C, H, N) were carried out at the Department of Chemistry, Fırat University, Turkey. 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. Diamagnetic corrections for ligand susceptibility were evaluated using Pascal's constants. IR spectra

TABLE I The melting point and analytical data for CuL_2^x complexes

Complex	*T (°C)*	*Yield (%)*	*Found (Calcd.) (%)*		
			C	*H*	*N*
CuL_2^1	205–207	76	73.89 (74.14)	7.51 (7.70)	3.85 (4.12)
CuL_2^2	> 260	87	70.12 (70.41)	6.79 (7.03)	4.15 (3.91)
CuL_2^3	> 260	89	69.87 (70.41)	69.66 (7.03)	4.23 (3.91)
CuL_2^4	> 260	82	64.95 (64.72)	6.78 (6.46)	3.68 (3.59)
CuL_2^5	> 260	78	65.06 (64.72)	6.78 (6.46)	3.89 (3.59)
CuL_2^6	> 260	74	59.56 (60.18)	5.67 (6.01)	3.75 (3.34)
CuL_2^7	224–226	85	60.68 (60.18)	6.34 (6.01)	3.74 (3.34)
CuL_2^8	251	88	74.87 (74.59)	8.24 (7.97)	4.23 (3.95)
CuL_2^9	> 260	90	74.18 (74.59)	8.24 (7.97)	4.23 (3.95)
CuL_2^{10}	257	79	71.66 (71.31)	7.45 (7.62)	3.96 (3.78)
CuL_2^{11}	215	89	71.42 (71.31)	7.34 (7.62)	3.56 (3.78)
CuL_2^{12}	> 260	76	74.89 (75.76)	8.23 (8.64)	3.12 (3.53)
CuL_2^{13}	252–254	86	77.85 (76.94)	7.78 (7.23)	3.23 (3.58)

TABLE II IR and electronic spectral data for the L^xH

Ligand	*ν(CH=N) (cm⁻¹)*	*λ_{max} (nm) ($\log \varepsilon\, M^{-1}L^{-1}$)*
L^1H	1614	225 (4.65), 278 (4.42), 307 (4.51), 353 (4.25), 450 (1.69)
L^2H	1622	212*, 233 (4.29), 279 (4.20), 311 (4.14), 358 (4.06), 460*
L^3H	1618	210*, 226 (4.40), 277 (4.26), 308 (4.21), 353 (4.11), 460*
L^4H	1617	212 (4.49), 229 (4.46), 283 (4.25), 359 (4.06)
L^5H	1617	207 (4.65), 229 (4.62), 281 (4.45), 312 (4.44), 357 (4.31)
L^6H	1615	206 (4.65), 227 (4.56), 281 (4.39), 312 (4.38), 357 (4.25), 460 (1.76)
L^7H	1616	206 (4.68), 225 (4.68), 280 (4.55), 330*, 355 (4.42)
L^8H	1616	211 (4.39), 230 (4.43), 275 (4.25), 329 (4.14), 353 (4.12)
L^9H	1620	227 (4.61), 277 (4.37), 312 (4.39), 354 (4.33), 450*
$L^{10}H$	1616	210 (4.65), 234 (4.57), 276 (4.34), 344 (4.31), 450*
$L^{11}H$	1619	206 (4.51), 228 (4.51), 277 (4.21), 331 (4.33), 358 (4.32), 460*
$L^{12}H$	1619	206 (4.77), 227 (4.73), 278 (4.34), 312 (4.34), 355 (4.3), 440 (1.98)
$L^{13}H$	1614	212 (4.78), 227 (4.79), 274 (4.46), 290*, 365 (4.48)

*Shoulder.

TABLE III IR, electronic spectral and magnetic moment data for the CuL_2^x complexes

Complex	*ν(CH=N) (cm⁻¹)*	*ν(OH) (cm⁻¹)*	*μ_{eff} (BM)*	*Solvent*	*λ_{max} (nm)*
CuL_2^1	1605	–	2.03	$CHCl_3$	294, 320*, 416, 500*, 680*
				Toluene	315, 422, 500*, 680*
CuL_2^2	1618	3447	1.71	$CHCl_3$	295, 330, 410, 416, 680*
CuL_2^3	1604	3436	1.71	$CHCl_3$	287, 340*, 354, 415, 500*, 680*
CuL_2^4	1615	3438	1.84	$CHCl_3$	290, 330*, 420, 673
CuL_2^5	1610	–	1.94	$CHCl_3$	297, 423, 500*, 680*
CuL_2^6	1615	3433	1.86	$CHCl_3$	293, 310*, 421, 682
CuL_2^7	1616	–	2.06	$CHCl_3$	300, 320*, 424, 500*, 680*
CuL_2^8	1612	–	1.97	$CHCl_3$	289, 330, 410, 490*, 480*
CuL_2^9	1617	–	1.91	$CHCl_3$	289, 320*, 359, 402, 490*, 680*
CuL_2^{10}	1614	–	1.97	$CHCl_3$	290, 386, 435, 470*, 650*
CuL_2^{11}	1615	–	2.06	$CHCl_3$	313, 450, 688
CuL_2^{12}	1614	3437	1.84	$CHCl_3$	293, 416, 500*, 680*
CuL_2^{13}	1612	–	2.06	$CHCl_3$	257, 330*, 350, 416, 500*, 700*

*Shoulder.

TABLE IV ESR parameters for the CuL_2^x complexes

Complex	*Solid state*		*Solution spectra**							
	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso}	$A_{\parallel}$	$A_{\perp}$	$g_{\parallel}/A_{\parallel}$	G
CuL_2^1	2.137	2.060	2.116	2.231	2.059	65	169.5	12.8	140.7	4.03
CuL_2^2	2.129	2.037	2.118	2.238	2.058	68	170	17.0	140.8	4.23
CuL_2^3	2.088	2.012	2.118	2.232	2.061	66	162.5	17.8	146.8	3.94
CuL_2^4	2.144	2.050	2.121	2.239	2.062	62	162.5	11.8	147.3	4.03
CuL_2^5	2.092	2.015	2.116	2.238	2.055	59.4	160	9.1	149.5	4.47
CuL_2^6	2.142	2.041	2.122	2.224	2.073	62.7	165	11.6	144.4	3.12
CuL_2^7	2.134	2.046	2.117	2.236	2.058	62.5	170	8.8	140.1	4.19
CuL_2^8	2.064	2.037	2.124	2.230	2.064	66	158.8	19.6	150.2	3.69
CuL_2^9	2.108	2.045	2.121	–	–	67	–	–	–	–
CuL_2^{10}	2.092	2.041	2.130	2.249	2.071	64.8	155	19.3	155.1	3.59
CuL_2^{11}	2.113	2.049	2.122	2.223	2.072	64	158.8	16.6	149.7	3.17
CuL_2^{12}	2.142	2.041	2.118	2.228	2.063	68	165	19.5	144.4	3.72
CuL_2^{13}	2.077	2.038	2.129	2.234	2.077	60	164	8.0	145.6	3.10

*The values of A are expressed in Gauss (G).

were recorded in KBr pellets using a Perkin-Elmer FT-IR spectrophotometer. ESR spectra were recorded on a Varian model E 109 C spectrometer in X-band with 100 kHz modulation frequencies. The g-values were 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, platinum working and platinum counter electrodes and an Ag/AgCl (1 mol dm^{-3} NaCl) as reference electrode. Cyclic voltammetry experiments were performed in degassed acetonitrile solutions of *ca.* 10^{-3}–10^{-4} M L^xH and CuL_2^x, and n-Bu_4NClO_4 (TBAP) as the supporting electrolyte (0.04 M) in the potential range +2.0 to −1.0 V.

RESULTS AND DISCUSSION

All of the *N*-aryl-3,5-di-*tert*-butylsalicylaldimine ligands studied were prepared in good yields as yellow to orange crystalline solids by condensation of 3,5-di-*tert*-butylsalicylaldehyde with the appropriate aniline in refluxing methanol in the presence of a catalytic amount of formic acid. We were unsuccessful in preparing salicylaldimine ligands from 2-NO_2, 4-NO_2 and 4-OH substituted anilines even after refluxing for 16 h, although these aniline derivatives are easily condensed with salicylaldehyde. This indicates that 3,5-di-*tert*-butylsalicylaldehyde has a lower condensing ability than its salicylaldehyde analog. Satisfactory elemental analyses were obtained for all L^xH ligands. The analytical data of the CuL_2^x complexes indicate 2 : 1 ligand to metal stoichiometry (Table I). The solid state and solution samples of ligands and complexes are quite stable in air and are soluble in common organic solvents. Our repeated attempts to prepare ML_2^x complexes with M = Ni(II), Mn(II), VO(II), Zn(II) and Cd(II), were unsuccessful except for NiL_2^1, ZnL_2^1 and ZnL_2^{10}. The lack of binding to these metal ions originates from the steric effect of the bulky *tert*-butyl group in the 3-position of the salicylaldehyde ring which hinders intramolecular rotation of the unidentate coordinated ligand about the phenyl(C)–N bond by diminishing unfavorable nonbonding steric interactions. It should be pointed that none of the L^xH ligands underwent hydrolysis in complexation of the above metal ions.

The ν(C=N) bands of the ligands observed at 1614–1622 cm^{-1} are red shifted (1604–1617 cm^{-1}) in the spectra of the complexes (Tables II and III) pointing to the involvement of the azomethine nitrogen in coordination. Narrow intense bands at *ca.* 2868–2957 cm^{-1} for the free ligands and their complexes are assigned to ν(C–H) stretching modes of the *t*-Bu groups. The disappearance of weak, intense broad bands at around 2600–2800 cm^{-1} due to intramolecularly H-bonded OH in the spectra of free ligands and the appearance of new sharp bands at 1300–1330 and 1500–1546 cm^{-1} regions in the spectra of the complexes due to ν_{sym}(C–O, phenolic) and ν_{asym}(C–O–Cu), respectively, indicate bonding through the phenolic oxygen by copper(II) ions [4c]. Coordination through azomethine nitrogen and phenolic oxygen is further supported by the appearance of new bands at 420–650 cm^{-1} for the complexes, which are assigned to the ν(Cu–O) and ν(Cu–N) vibrations [12]. Medium intensity broad bands at 3433–3447 cm^{-1}, detected in the IR spectra of some complexes, are assigned to ν(OH) of lattice water.

Electronic Spectra

Electronic absorption spectral data of L^xH in ethanol are given in Table II. The bands observed below 290 nm and in the range 329–365 are assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [13]. The bands observed as maxima or shoulders in the 440–460 nm region in ethanol solutions, are more sensitive to the polarity of the solvent (in hexane or toluene they appeared as a very low intensity bands) and are attributed to $n \rightarrow \pi^*$ transitions in a dipolar zwitterionic structure or keto–amine tautomer of HL^x [14]. No absorption was observed for L^4H, L^5H, L^7H, L^8H and $L^{13}H$ ligands within the 400–460 nm regions in EtOH (Table II). Electronic spectra of the complexes CuL^x_2 in chloroform show a group of broad, asymmetric, visible bands at *ca.* 400–450, 470–500 and 650–700 nm (Table III), the last two of which are attributed to $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions in a nearly planar geometry, respectively [15]. The high-energy $d_{x^2-y^2} \rightarrow d_{xx,yz}$ band is obscured by the more intense metal-to-ligand charge-transfer (MLCT) bands. The bands at shorter wavelengths (400–460 nm) with larger intensities ($\varepsilon \sim 10.000$–$25.000\ M^{-1}\,cm^{-1}$) can be assigned to the MLCT transition ($Cu^{II} \rightarrow$ phenolate π^* transition; a CT band from filled d (d_{xz}, d_{yz}) orbitals of copper(II) to the antibonding π^* orbitals of the salicylic residue) [5a,13a,16].

Magnetic Moments

The room temperature magnetic moments of CuL^x_2 (1.84–2.06 BM) (Table III) except CuL^2_2 and CuL^3_2 are typical for mononuclear Cu(II) compounds with a $S = 1/2$ spin state in square-planar and tetrahedrally distorted N_2O_2Cu geometry and did not indicate the presence of significant exchange coupling between Cu^{II} centers at this temperature. The 1.71 μ_B for CuL^2_2 and CuL^3_2 suggests the existence of a weak intermolecular antiferromagnetic interaction between copper(II) ions in the solid state for these complexes. Note that the μ_{eff} for CuL^2_2 and CuL^3_2 evaluated using the expression $\mu_{eff} = 1/2(g_{\parallel}^2 + 2g_{\perp}^2)^{1/2}$, where *g*-factors were obtained in toluene glass ESR spectra at

130 K (Table IV), was 1.84 BM indicating much less exchange coupling between Cu^{II} centers in their frozen glass samples.

ESR Spectra

The spin Hamiltonian parameters of CuL_2^x complexes are listed in Table IV. The ESR spectra of polycrystalline samples of all compounds were obtained at 300 and 113 K. None of these compounds exhibits $\Delta M_s = \pm 2$ forbidden transitions at half-field of *ca.* 1600 G. The ESR parameters and electronic absorption spectra of the CuL_2^x complexes suggest pseudo-tetrahedral coordination geometry (C_{2v}) around Cu^{II} in these complexes.

The powder ESR spectra of the present complexes at room temperature have a wide variety of line shapes, as shown in Fig. 1. Polycrystalline samples of CuL_2^x exhibit a

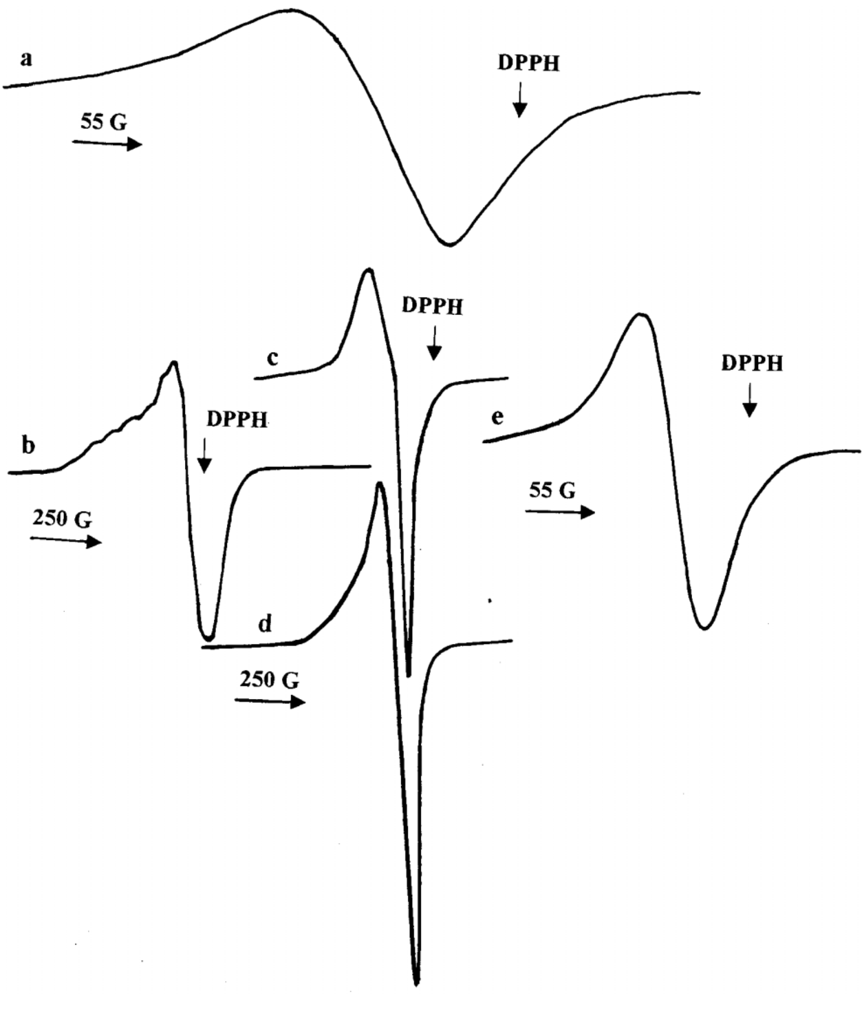

FIGURE 1 ESR spectra of solid state samples of some CuL_2^x complexes at 300 K: (a) CuL_2^6 (green); (b) CuL_2^5; (c) CuL_2^6 (brown); (d) CuL_2^{11}; (e) CuL_2^7.

strong axial symmetry with the trend, $g_{\parallel} > g_{\perp} > 2.03$ (Table IV), indicating that the unpaired electron is located in the $d_{x^2-y^2}$ orbital [17]. Except for CuL_2^3 and CuL_2^5, all solid state spectra at 300 K have the exchange interaction parameter, ($G = g_{\parallel} - 2/g_{\perp} - 2$), with $G < 3.5$, suggesting the presence of exchange coupling between two adjacent Cu^{II} centers in the solid state [17]. In the case of CuL_2^1 a rhombic spectrum ($g_x = 2.045$, $g_y = 2.075$, $g_z = 2.137$ and $\langle g \rangle = 2.086$) was observed, which might be due to misalignment of the local molecular axes [17,18]. The powder ESR spectra of CuL_2^3, CuL_2^5 (Fig. 1b) and CuL_2^{10} at 300 K, clearly exhibit a six-line hyperfine feature, separated by 77.5, 78.2 and 68.8 G, respectively, indicating an appreciable interaction between the two copper(II) ions in the solid state. It is well known that coupling two copper nuclei ($I = 3/2$) brings two sets of seven hyperfine lines whose separation ($A_{\parallel}$) is one-half of that of hyperfine lines of the mononuclear species constituting the binuclear complex [19]. For all other complexes the powder ESR spectra are so broad that g anisotropies are barely observed. This line-broadening effect is attributable to dipolar broadening and enhanced spin lattice relaxation [20a,b].

The room temperature toluene or $CHCl_3$ solution ESR spectra of these complexes in general show four-line hyperfine patterns with various line widths and without ^{14}N-shfs resolutions on the high-field copper components (Fig. 2). For CuL_2^9, CuL_2^{11} and CuL_2^{12} complexes containing *para*-electron donating constituents in the aniline ring, two of the low-field components of the four copper hyperfine lines have become so broadened that they cannot be resolved. In the anisotropic frozen (130 K) glass toluene solution ESR spectra of CuL_2^x an additional ^{14}N-shfs resolution was observed only for 2-F, 2-Br, 2-CH_3, 4-OCH_3, 4-*t*-Bu substituted complexes in the $g_{\perp}$ region of the spectra (Fig. 3). The appearance of ^{14}N-shfs resolutions for *o*-substituted complexes contrasts with the fact that the steric effect of *o*-substitutents creates a tetrahedral distortion of the planar configuration around copper and, as a result, the resolution of ^{14}N-shfs must be reduced. A mechanism for the appearance of ^{14}N-shf splitting may be blocking by *ortho*-substitutents of the axial coordination sphere from the attack of solvent molecules, inducing good resolution of the ESR line-width in these compounds [21]. All complexes in frozen solution exhibit ESR spectra with axially symmetric relation $g_{\parallel} > g_{\perp} > 2.03$ (Table IV), which indicates that the unpaired electron most likely resides in the $d_{x^2-y^2}$ orbital having $^2B_{1g}$ as a ground state term [17,22]. The values (0.48–0.52) of the in-plane σ-bonding parameter, α^2, evaluated using the expression [23] $\alpha^2 = |A|/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$, indicates the presence of significant in-plane σ-bonding in these complexes. The G-values [17] determined from the frozen glass spectra, except for CuL_2^6, CuL_2^{11} and CuL_2^{13} complexes, lie in the range 3.59–4.47 (Table IV) indicating that there is no appreciable exchange interaction between the copper centers in solution for these complexes [17]. According to Sakaguchi and Addison, for N-, O- and S-donor ligand Cu(II) complexes, the quotient $g_{\parallel}/A_{\parallel}$ may be considered as a convenient empirical index of tetrahedral distortion [24]. This quotient ranges from *ca.* 105 to 135 cm for square-planar structures. The quotient increases markedly on the introduction of tetrahedral distortion to the chromophore, for example, as in bis(*N*-*tert*-butylsalicylaldiminato)copper(II) (157 cm) [24] and bis(*N*-*tert*-butyl-pyrrol-2-carbaldiminato)copper(II) (210 cm) [24]. As seen from Table IV, the $g_{\parallel}/A_{\parallel}$ values ranged from 141 to 155 cm for CuL_2^x complexes and are higher than 135 cm indicating that CuN_2O_2 units are distorted from square planar to *pseudo*-tetrahedral geometry. Thus, the absence of ^{14}N-shf structure on the high field components of room temperature ESR spectra and relatively low values of $A_{\parallel}$ and

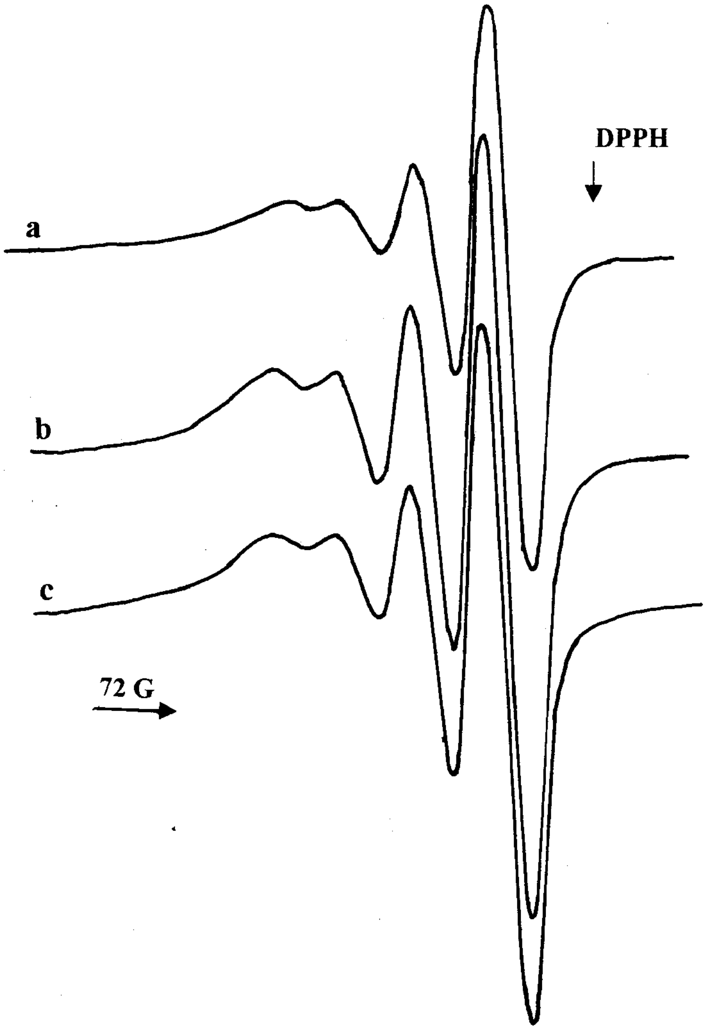

FIGURE 2 Toluene solution ESR spectra of CuL_2^x at 300 K: (a) CuL_2^{12}; (b) CuL_2^4; (c) CuL_2^5.

high values of the $g_{\|}/A_{\|}$ ratio suggest that tetrahedral distortion dominates in these complexes.

Reduction of CuL_2^x with PPh_3

Although the reduction of some Cu(II) complexes with PPh_3 is well known [25–30], the *N*-aryl-salicylaldimine Cu^{II}-complexes prepared from salicylaldehyde derivatives bearing F, Cl, Br, NO_2, CH_3, OCH_3, OH, mono-*tert*-butyl substituents and mono-substituted anilines show no sign of reduction or adduct formation on treatment with PPh_3. When we investigated the adduct formation ability of Cu^{II}-X-salicylaldiminates (X = H, Cl, Br, NO_2, OH, CH_3O) prepared from 1-hydroxy-2,6-di-*tert*-butylaniline, 2,5-di-*tert*-butylaniline, 3,5-di-*tert*-butylaniline [10i] as well as bis(2-oxy-3,5-di-*tert*-butylphenylarylazo)copper(II) chelates with triarylphosphines, unexpectedly, without

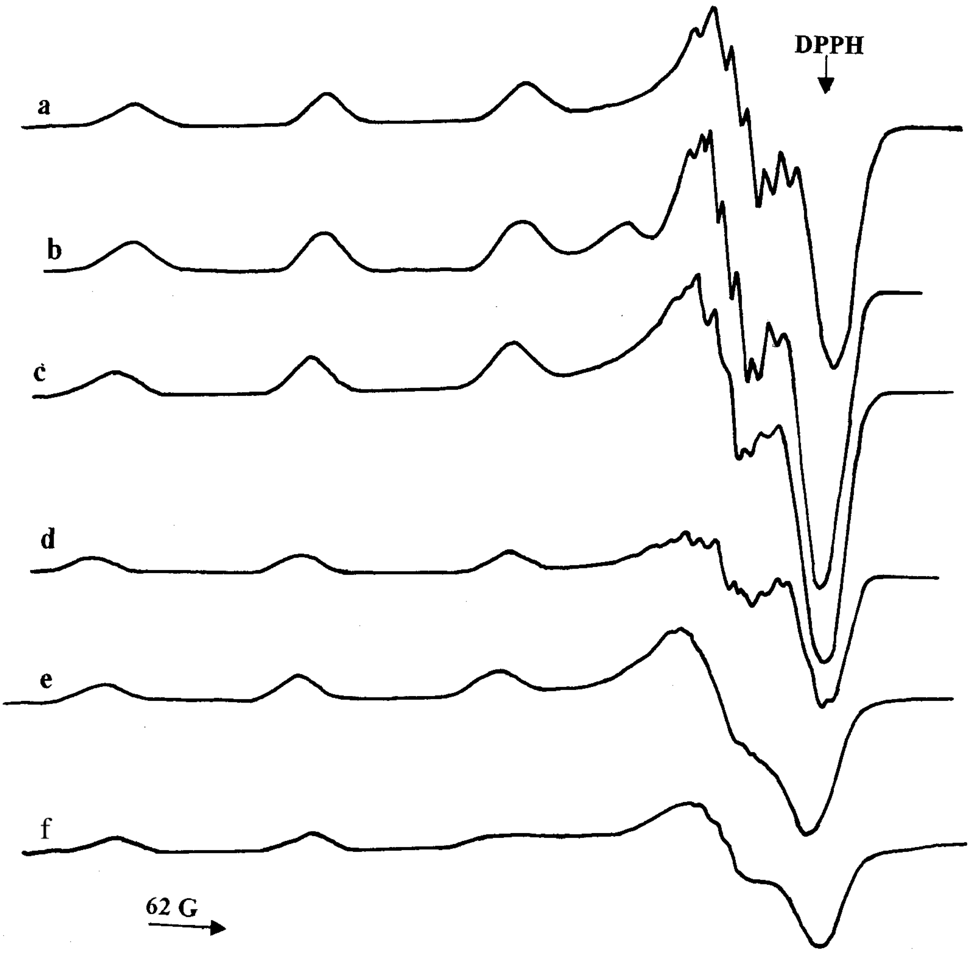

FIGURE 3 Frozen glass toluene ESR spectra of some CuL_2^x at 133 K: (a) CuL_2^9; (b) CuL_2^{11}; (c) CuL_2^5; (d) CuL_2^2; (e) CuL_2^4; (f) CuL_2^3.

any sign of adduct formation, the disappearance of Cu^{II} lines and the appearance of radical signals in their ESR spectra were observed [10c–e,g]. In the present study addition of a four–five-fold excess of PPh_3 to $CHCl_3$ solutions of CuL_2^x compounds resulted in a very slow color change from black-brown to orange-yellow (for 4-*t*-Bu and 2,4-di-CH_3 substituents) or brown-red (for 4-CH_3 and 4-OCH_3) and slow decreases of copper ESR signal intensities were observed. For complexes with an electron-withdrawing 4-F, 4-Cl, 4-Br substituents and all *ortho*-substituted complexes, even in the presence of a ten-fold excess of PPh_3 no change in color or in ESR and electronic spectra were observed. The rate of reduction with PPh_3 follows the order: 4-$OCH_3 \leq$ 4-$CH_3 <$ 4-*t*-Bu. In the spectra of $CuL_2^x + PPh_3$ mixtures no other changes in the ESR spectra of starting CuL_2^x or formation of a new signal assignable to radical species were observed. Note that bis(*N*-aryl-3,5-di-*tert*-butylsalicylaldiminato)copper(II) complexes prepared from 1-OH-2,6-di-*tert*-butylaniline [10d] and 1-OH-2,6-diphenylaniline [31], unlike CuL_2^x, are immediately reduced by treatment with PPh_3 via intramolecular electron transfer from ligand to copper(II) to give radical intermediates. Thus, the introduction of electron donating di-*tert*-butyl groups to the salicylaldehyde, unlike those introduced into the aniline-ring, does not facilitate the electron transfer ability of the copper(II) salicylaldimine complexes toward PPh_3.

Electrochemistry

The electron transfer properties of L^xH and CuL_2^x were studied in MeCN solution under anaerobic conditions at a scan rate of $0.2\,V\,s^{-1}$ over the potential range from $+2.25$ to $-1.0\,V$ *versus* Ag/AgCl by cyclic voltammetry (CV) using a platinum working electrode. The CV data are summarized in Tables V and VI. The ligands exhibit *quasi*-reversible and irreversible redox waves (Fig. 4a,b) (peak-to-peak separation, $\Delta E_p = 95$–$579\,mV$, $E_{1/2} = 1.125$–$1.235\,V$) (Table V), which are assigned to phenolate/phenoxyl radical couple. The $E_{1/2}$ redox potential of F substituted ligands (L^2H and L^3H) are larger in comparison to L^1H or electron-donating $-CH_3$ groups (L^8H and L^9H) indicating that the former are harder to oxidize due to the strong electron-withdrawing ability of the substituents. The unsubstituted *N*-phenylsalicylaldimine and *N*-*para*-tolylsalicylaldimine ligands under the same conditions exhibit only one irreversible oxidation wave at $E_{pa} = 1.502\,V$ and a *quasi*-reversible redox wave at $E_{1/2} = 1.38\,V$,

TABLE V Cyclic voltammetric data for some of the ligands

Compound	E_{pa} *(V)*	E_{pc} *(V)*	ΔE_p *(mV)*	$E_{1/2}$ *(V)*
L^1H	1.258	1.119	139	1.188
L^2H	1.303	1.132	171	1.217
L^3H	1.463	1.014	449	1.238
L^4H	1.432	0.839	579	1.224
L^5H	1.337	–	–	–
L^6H	1.325	–	–	–
L^7H	1.305	–	–	–
L^8H	1.205	1.088	117	1.146
L^9H	1.173	1.078	95	1.125
$L^{10}H$	1.149	0.518		
$L^{11}H$	1.173	0.546		

TABLE VI Electrochemical data for the CuL_2^x complexes in acetonitrile

Complex	E_{pa} *(V)*	E_{pc} *(V)*
CuL_2^1	0.743, 1.044, 1.225, 1.591	−0.589, −0.409, −0.0104
CuL_2^2	0.581, 1.074, 1.269, 1.699	−0.362, 0.117, 0.905, 1.162
CuL_2^3	0.672, 1.058, 1.236, 1.602	−0.384, 0.184, 0.953
CuL_2^4	0.618, 1.095, 1.302	0.135, 0.978, 1.163
CuL_2^5	0.553, 1.051, 1.231, 1.615*	0.013, 0.908, 1.119
CuL_2^6	−0.035, 0.583, 1.122, 1.383	0.011, 0,768, 1.205
CuL_2^7	0.499, 1.088, 1.295, 1.974	−0.377, 0.799, 1.139
CuL_2^8	1.075, 1.297	1.084
CuL_2^9	0.533, 0.855, 1.559	−0.209, 0.675, 1.202
CuL_2^{10}	0.475, 0.966, 1.271, 1.776	0.143, 0.781
CuL_2^{11}	0.533, 1.026, 1.209	0.073, 0.725, 1.011
CuL_2^{12}	1.046, 1.258, 1.644*	0.169, 0.916
CuL_2^{13}	−0.736, −0.175, 0.877*, 1.187*	−0.961, −0.473, 0.867*

*Shoulders.

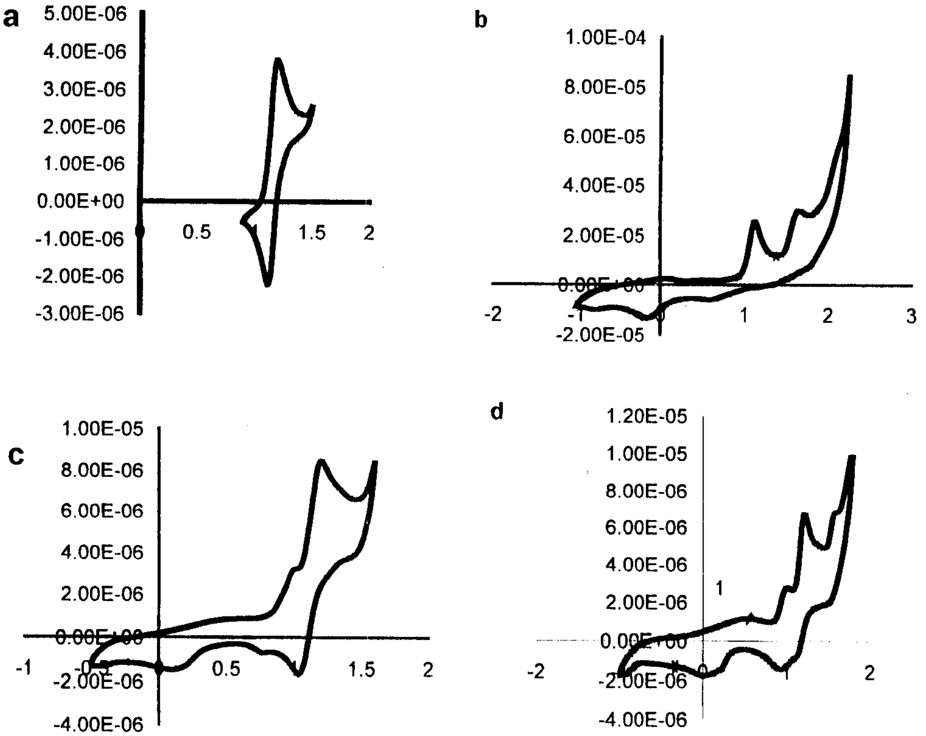

FIGURE 4 Cyclic voltammograms of some ligands and complexes in acetonitrile: (a) L^8H; (b) $L^{10}H$; (c) CuL^x_2 (where $x = 4$); (d) CuL^x_2 (where $x = 5$). The scan rate was $0.2\,V\,s^{-1}$.

respectively. This clearly indicates that the 3,5-di-*tert*-Bu groups in the salicylaldehyde moiety stabilize the electrochemically generated cation radicals by a $+I$ effect [32]. The CV curves of L^5H and L^6H are very similar to each other and exhibit, along with *quasi*-reversible couples around 0 V, an irreversible oxidation wave at *ca.* $E_{pa} = 1.38$ V *versus* Ag/AgCl. Surprisingly the CVs of 4-Br, 4-*t*-Bu, OCH_3 and 5,6-benzo substituted ligands under the same conditions are characterized by two irreversible anodic waves in the potential ranges of 1.193–1.303 and 1.643–1.798 V *versus* Ag/AgCl. Although the first irreversible response can be attributable to a phenoxide/phenoxyl radical couple, an unambiguous interpretation of the second irreversible oxidation peak is difficult. The second response may be associated with the products of disproportionation or polymerization of the phenoxyl radicals.

The electrochemistry of the CuL^x_2 complexes is complicated and the correct assignment of redox waves is not easy. One interesting feature of the electrochemistry of the CuL^x_2 complexes is that they undergo anodic irreversible and *quasi*-reversible redox processes in MeCN (Fig. 4c,d). The voltammograms of some CuL^x_2 complexes exhibit four anodic waves, while other complexes exhibit two or three anodic waves (Table VI). It is probable that for former complexes along with the Cu(II)/Cu(III) couple at lower anodic potential, the ligand-centered sequential one-electron oxidation of phenolate to coordinated phenoxyl radicals (L^x_2–$L^x[L^x]^{\bullet+}$ and $L^x[L^x]^{\bullet+} - [L^x]^{\bullet+}[L^x]^{\bullet+}$) with E_{pa} within in the range 1.0–1.38 V *versus* Ag/AgCl region also takes place. Interestingly, for some complexes at potentials $> +1.5$ V the CV reveals irreversible oxidation waves, probably due to the further irreversible oxidation of the coordinated phenoxyl arms or decomposition products. In the chemical oxidation of *p*-CH_3 [$(Cu(L^9)_2]$ and *p*-*tert*-butyl [$Cu(L^{12})_2$] substituted complexes with an excess of $(NH_4)_2Ce(NO_3)_6$ in acetonitrile at 300 K, along with a decrease in the Cu(II) signal intensity the appearance of radical signal at $g = 2.004$ was observed. The decrease of the Cu(II) ESR signal intensity can be interpreted by pairing of the unpaired electron in $d_{x^2-y^2}$ with a coordinated phenoxyl radical, generated by the oxidation of the complexes with $(NH_4)_2Ce(NO_3)_6$. Similar ligand-centered oxidations recently were reported for complexes prepared from ligands containing 2,4-di-*tert*-butylphenol pendant arms [33]. No correlation between the redox potentials of CuL_2^x and the electronic effects of the substituents in the aniline ring were found. This behavior probably originates from the nonplanarity of the pendant aniline ring planes with the plane of the six-membered metallocyclic ring. For example, the molecular structure of [3,5-Bu^t_2-2-(O)C_6H_2CH=N-2,6-$Me_2C_6H_3$]$AlMe_2$ [34] shows that the 2,6-di-Me-phenyl ring is oriented virtually orthogonally (89°) to the plane of the six-membered metallocyclic ring. A similar orthogonality of the 3,5-di-*tert*-butylaniline ring plane to the plane defined by CH=N and salicylic fragment has been observed in the crystal structure of bis(4-OCH_3-3,5-di-*tert*-butylphenyl-1-*N*-salicylaldiminato)Cu(II) [35]. The voltammograms of some CuL_2^x complexes also contain ill-defined irreversible reduction waves, occurring within the range −0.7 to 0 V *versus* Ag/AgCl, which we ascribe to the Cu^{II}/Cu^I couple.

In summary, *N*-arylsalicylaldimines prepared from 3,5-di-*tert*-butylsalicylaldimine ligands compared to those formed through non-di-*tert*-butylsalicylaldehyde derivatives, possess lower complexation ability towards Co(II), Ni(II), Mn(II), VO(II) and Zn(II). The 3,5-di-*tert*-butyl groups on the salicylic frame, unlike those introduced on the aniline ring, do not facilitate redox reactivity of the copper(II) complexes toward PPh_3. We have shown that the bulky butylated salicylaldimine copper(II) complexes can be chemically oxidized, generating relatively stable phenoxyl radical complexes. While the $E^1_{1/2}$ values of free ligands are anodically shifted in accordance with increasing electron-withdrawing ability of the substituents, the redox potential of their copper(II) complexes is governed predominantly by geometric factors. The CV studies on acetonitrile solutions of the present complexes revealed well-resolved, *quasi*-reversible, oxidation waves at $E^1_{1/2} = 0.61$–0.99 V and $E^2_{1/2} = 1.09$–1.23 V *versus* Ag/AgCl attributable to ligand-centered oxidation processes yielding corresponding coordinated phenoxyl radical species such as Cu(II)(phenoxyl)(phenolate) and $Cu(II)(phenoxyl)_2$.

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