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# Synthesis, spectroscopic characterization and EPR studies on electron transfer reactions of bis[N-(2,5-di-*tert*-butylphenyl)salicylaldiminato]copper complexes with PPh<sub>3</sub>

Veli T. Kasumov<sup>a,\*</sup>, Fevzi Köksal<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Arts and Sciences, Harran University, Sanliurfa, Turkey <sup>b</sup> Physics Department, Faculty of Arts and Sciences, Ondokuz Mavis University, Samsun, Turkey

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#### Abstract

New bidentate *N*-(2,5-di-*tert*-butylphenyl)salicylaldimines bearing X = H, HO, CH<sub>3</sub>O, Br, NO<sub>2</sub>, 3,5-di-Br, 3-NO<sub>2</sub>-5-Br and 5,6-benzo substituents on the salicylaldehyde moiety, L<sup>x</sup>H, and their mononuclear bis[*N*-(2,5-di-*tert*butylphenyl)salicylaldiminato]copper(II) complexes, Cu(L<sup>x</sup>)<sub>2</sub>, have been prepared and investigated by IR, UV–Visible, <sup>1</sup>H NMR, ESR spectroscopy, magnetic measurements, as well as reactions of Cu(L<sup>x</sup>)<sub>2</sub> with PPh<sub>3</sub> were studied. It has been found that some complexes with X = HO and CH<sub>3</sub>O unlike their electron-withdrawing and unsubstituted analogues are readily reduced by PPh<sub>3</sub> via intramolecular electron transfer from ligand to copper(II) to give Cu-stabilized radical intermediates. The spectra of the primary radicals interpreted in terms of couplings of unpaired electron with <sup>63,65</sup>Cu, <sup>31</sup>P, <sup>14</sup>N nuclei and aromatic protons. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The introduction of bulky groups in ligands influences the overall catalytic and redox properties of the complexes [1,2]. Increased steric hindrance about the metal center of the complex affects its reactivity, but the effects are not always straightforward. In some cases sterically hindered complexes have been shown to react faster in catalytic reactions compared to less bulky ones [3].

Previously we reported [4–16] a number of copper(II) complexes with salicylaldimine, 2-hydroxybenzylamine  $\beta$ -ketoamine and 2-hydroxyarylazo ligands containing sterically hindered phenols in which unlike their unhindered analogous in the treatment with (XPh)<sub>3</sub>P or oxidation with PbO<sub>2</sub>, the formation of various radical intermediates (or oxidative C–C coupled

<sup>\*</sup> Corresponding author. Fax: + 90-414-314-6984

E-mail address: vkasumov@harran.edu.tr (V.T. Kasumov).

copper(II) complexes) were observed. Although the reduction of some copper(II) bischelates by triphenylphosphine are well documented [17–28], the copper(II) complexes in which reduction of Cu(II) complexes with PPh<sub>3</sub> proceeds via radical intermediates are very limited [28]. At the same time, the introduction of two *tert*-butyl groups in the above-mentioned ligands promote the proceeding of the intramolecular electron transfer in copper(II), palladium(II) and cobalt(II) complexes, as well as the catalytic activity of the palladium(II) salicylaldiminates in the hydrogenation of nitrocompounds and alkenes [7–16,29–31].

As a continuation of our earlier work on copper(II) complexes with redox-active ligands, we report the synthesis, spectral properties and redox behavior toward PPh<sub>3</sub> of a series of new Cu( $L^x$ )<sub>2</sub> salicylaldimine complexes, where  $L^x$  represents the monoanions of bidentate *N*-(2,5-di-*tert*butylphenyl)salicylaldimine ligands (Scheme 1).

#### 2. Experimental

The elemental analyses were carried out in the Turkish Center of the Science and Technology Research Council (TÜBITAK) in Gebze and in the Analytical Center of Chemistry Department, Firat University. Infrared spectra were recorded in a Mattson 1000 FTIR spectrophotometer in the region 4000-400 cm<sup>-1</sup> using KBr discs. Electronic spectra were measured in a Shimadzu UV 1601 and Cary 1E spectrophotometers in various solvents. Magnetic susceptibilities of powdered samples were determined in a Sherwood Scientific Magnetic Susceptibility Balance (Model MK 1) magnetometer at room temperature and the molar susceptibili



X = H (L<sup>1</sup>H), 3-OH (L<sup>2</sup>H), 3-OCH<sub>3</sub> (L<sup>3</sup>H), 4-OH(L<sup>4</sup>H), 4-OCH<sub>3</sub>(L<sup>5</sup>H), 5-OH(L<sup>6</sup>H), 5-OCH<sub>3</sub>(L<sup>7</sup>H), 5-Br (L<sup>8</sup>H), 5-NO<sub>2</sub> (L<sup>9</sup>H), 3,5-di-Br (L<sup>10</sup>H), 3-NO<sub>2</sub>-5-Br (L<sup>11</sup>H), 5,6-Benzo (L<sup>12</sup>H)

Scheme	1
Derrerite.	•

ities were corrected for ligand diamagnetism using Pascal's constants. The effective magnetic moments were calculated using the expression  $\mu_{eff} =$  $2.828(\chi_m \times T)^{1/2}$ . EPR spectra of the complexes were measured in a Varian E-109 C model X-band spectrometer with 100 kHz frequency modulation in solution and polycrystalline state at 300 K and in frozen solution at 113 K. The spectra were calibrated with the diphenylpicrylhydrazyl (DPPH) free radical of g = 2.0036. The EPR parameters of the complexes and radicals were determined directly from the spectra. Reported values involve errors within +0.0005 for g-values and +0.005 G for hyperfine coupling constants (hfcc) of  $Cu(L^{x})_{2}$ and radicals, respectively. Reductions of  $Cu(L^{x})_{2}$ with 2-4-fold excess of PPh<sub>3</sub>, were carried out by mixing their deoxygenated toluene or chloroform solutions in the EPR tubes at room temperature under vacuum. The EPR spectra of the reaction mixtures were immediately recorded under vacuum at room temperature.

## 2.1. Preparation of ligands

Salicylaldehyde, its hydroxy- and methoxy-substituted derivatives, 2,5-di-tert-butylaniline, copper(II) acetate monohydrate and all solvents were obtained commercially and used as received. Solvents used for analytical purposes were spectrograde. Brand NO<sub>2</sub>-substituted scopic salicylaldehyde derivatives were prepared according to the reported method [32,33]. All ligands  $L^{x}H$  were prepared using standard procedures involving the condensation of 2.5-di-tert-butylaniline with the appropriate salicylaldehyde in methanol (MeOH). The yellow imines were purified by recrystallization from MeOH (yields 85-92%). A solution of 2,5-di-tert-butyl-aniline (10.5 mmol) in MeOH (10 ml) was added to a solution of 3-methoxy salicylaldehyde (10 mmol) in MeOH (50 ml). The resulting mixture was stirred for 50 min at 45-50 °C. After reducing the volume to 10 ml and cooling to room temperature, the precipitate yellow-orange crystals were filtered off and crystallized from chloroform-MeOH (1:3 v/v) mixture, yield 92%. Elemental analyses, melting points, yields of L<sup>x</sup>H are summarized in Table 1.

Table 1 Analytical data for the  $L^{x}H$  and  $Cu(L^{x})_{2}$  complexes

Compound	Yield (%)	M.p. (°C)	Stoichiometry	Elemental analyses (found/calculated) (%)			
				С	Н	N	
L <sup>1</sup> H	85	102	C <sub>21</sub> H <sub>27</sub> NO	81.38/81.51	8.62/8.179	4.48/4.52	
L <sup>2</sup> H	88	126	$C_{21}H_{27}NO_2$	77.32/77.54	7.56/7.75	4.67/4.31	
L <sup>3</sup> H	92	129	$C_{22}H_{29}NO_2$	77.43177.88	7.62/7.78	4.32/4.13	
L <sup>4</sup> H	86	189	$C_{21}H_{27}NO_2$	77.34/77.54	7.43/7.75	4.45/4.31	
L⁵H	89	119	$C_{22}H_{29}NO_2$	77.63/77.88	7.98/7.78	4.23/4.13	
L <sup>6</sup> H	88	215	$C_{21}H_{29}NO_2$	77.31/77.54	7.87/7.70	4.12/4.31	
$L^{7}H$	93	132	$C_{22}H_{29}NO_2$	77.65/77.88	7.56/7.78	4.42/4.13	
L <sup>8</sup> H	87	165	C <sub>21</sub> H <sub>26</sub> NOBr	65.12/64.76	6.46/6.73	3.34/3.59	
L <sup>9</sup> H	93	163	$C_{21}H_{26}N_2O_3$	70.87/71.16	7.73/7.39	7.78/7.89	
$L^{10}H$	96	152	C <sub>21</sub> H <sub>25</sub> NOBr <sub>2</sub>	53.76/53.73	5.57/5.36	2.86/2.98	
$L^{11}H$	95	212	$C_{21}H_{25}N_2O_3Br$	57.96/57.92	5.58/5.78	6.21/6.43	
$L^{12}H$	87	143	$C_{25}H_{29}NO$	83.78/83.52	8.45/8.13	4.05/3.89	
$Cu(L^1)_2$	91	241	C42H22N2O2Cu	74.27/74.14	7.59/7.70	3.84/4.11	
$Cu(L^2)_2$	86	> 300	$C_{42}H_{52}N_2O_4Cu$	71.08/70.81	7.56/7.35	4.18/3.93	
$Cu(L^3)_2$	85	242	C44H56N2O4Cu	70.17/70.41	7.56/7.62	3.45/3.78	
$Cu(L^4)_2$	76	167	$C_{42}H_{52}N_2O_4Cu$	71.12/70.81	7.13/7.35	4.15/3.93	
$Cu(L^5)_2$	85	226	C44H56N2O4Cu	69.94/70.41	7.32/7.62	3.46/3.78	
$Cu(L^7)_2$	79	245	C44H56N2O4Cu	71.21/70.81	7.43/7.62	3.56/3.78	
$Cu(L^8)_2$	82	> 300	$C_{42}H_{50}N_2O_2Br_2$	58.79/60.01	5.78/6.02	3.12/3.33	
$Cu(L^9)_2$	86	200	$C_{42}H_{50}N_4O_6Cu$	65.45/65.48	6.23/6.54	7.32/7.27	
$Cu(L^{10})_2$	88	> 300	C42H48N2O2Br4Cu	54.04/53.73	5.12/5.36	2.23/2.79	
$Cu(L^{11})_2$	86	233	$C_{42}H_{48}N_4O_6Br_2Cu$	54.26/54.11	5.32/5.19	5.86/6.01	
$Cu(L^{12})_2$	90	> 300	$C_{50}H_{56}N_2O_2Cu$	75.82/76.94	7.48/7.23	3.47/3.58	

#### 2.2. $Cu(L^x)_2$ complexes

These complexes were prepared by following general procedure. A solution of 200 mg (1 mmol) of copper(II) acetate monohydrate in 15 ml of MeOH was added to a magnetically stirred and heated solution of 2 mmol of the appropriate ligand in 80-90 ml of MeOH. The reaction mixture was stirred at about 45-50 °C for 1-1.5 h. The solution volume was decreased to ca. 15 ml. After standing for 1-1.5 h at room temperature, the precipitated product was filtered off and washed with a small amounts cold MeOH, n-hexane, dried in air and recrystallized from acetone/n-hexane mixture, yield 76–91%. Analytical, spectroscopic and magnetic moments data for the  $Cu(L^x)_2$  are given in Tables 1, 4 and 5.

#### 3. Results and discussion

The analytical data of the  $Cu(L^x)_2$  complexes indicate 2:1 ligand to metal stoichiometry. The synthesized complexes are found to be sufficiently soluble in chloroform, toluene, dioxane, acetone, N,N-dimethylformamide (DMF) and pyridine for spectral measurements. The complexes were obtained in good yields and high purity by slow evaporation of the solvent mixture at atmospheric pressure. None of the EPR spectra of polycrystalline samples of  $Cu(L^x)_2$  obtained at 298 and 113 K show any detectable half-field absorption associated with a  $\Delta M_s = \pm$ 2 transition. The room temperature EPR spectra of Cu(L<sup>6</sup>)<sub>2</sub> complex, along with copper hyperfine patterns also exhibit low intensity radical signal at g = 2.0038.

## 3.1. Magnetic moments

The room temperature magnetic moments of  $Cu(L^x)_2$  fall in the range 1.89–2.19 BM which are typical for tetrahedrally distorted mononuclear of Cu(II) compounds with a S = 1/2 spin state and did not indicate any antiferromagnetic coupling of spins at this temperature.

## 3.2. IR spectra

The v(C=N) stretching frequencies of the ligands (Table 2) are located in the region 1615-1635  $\text{cm}^{-1}$  and are shifted to lower frequencies  $(1604-1625 \text{ cm}^{-1})$  upon chelation, which is consistent with coordination through the azomethine nitrogen atoms of the ligands (Table 4). A medium intensity broad band at 2600-2800 cm<sup>-1</sup> and a strong absorption in the 1280-1320 cm<sup>-1</sup> range caused by the intramolecular OH...N in the IR spectra of  $L^{x}H$  are absent in the spectra of  $Cu(L^{x})_{2}$  and suggests the coordination of the ligand to the metal ion through the deprotonated hydroxyl group in these complexes. These data illustrate the monoanionic bidentate behavior of the L<sup>x</sup>H ligands in the  $Cu(L^x)_2$  complexes. The IR spectra of ligands and their complexes containing OH in the 3-, 4- and 5-positions show a strong bands at 3433, 3242, 3310 cm<sup>-1</sup> for L<sup>2</sup>H, L<sup>4</sup>H,

Table 2

IR and electronic spectral data for $L^{x}H$ ligand
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L<sup>6</sup>H and 3438, 3259 cm<sup>-1</sup> for Cu(L<sup>2</sup>)<sub>2</sub>, Cu(L<sup>4</sup>)<sub>2</sub>, respectively. Thus in the complexation of L<sup>2</sup>H, L<sup>4</sup>H, L<sup>6</sup>H, no coordination of 3- and 4-hydroxy groups took place. New bands observed in the IR spectra of Cu(L<sup>x</sup>)<sub>2</sub> at ca. 420–470 and 490–580 cm<sup>-1</sup> regions, were assigned to the  $\nu$ (Cu–N) and  $\nu$ (Cu–O) modes, respectively, according to Ref. [34,35].

## 3.3. Electronic spectra

Electronic absorption spectral data of  $L^{x}H$  in ethanol are given in Table 2. All  $L^{x}H$  in ethyl alcohol solutions show three group bands at about 217-285, 324-366, and 410-480 nm regions as maximum or a shoulder bands (Table 2). The bands at the first region are assigned to intraligand  $\pi \rightarrow \pi^*$  transitions. The band at 324– 366 nm are attributed to  $n \rightarrow \pi^*$  transitions. The bands observed as a maxima or a shoulder in the 410-480 nm region in ethanol solutions, are more sensitive to the polarity of the solvents (this band was absent in hexane and toluene) and is attributed to dipolar ketoamine tautomer forms of  $L^{x}H$  [36–38]. The electronic spectra confirm that the  $L^{x}H$  compounds exist in the phenolimine form in non-polar solvents and as equilibrium mixtures of phenolimine and ketoamine forms in ethanol. All  $Cu(L^x)_2$  complexes show a group of identical a

Compound	IR spectra (	$cm^{-1}$ )	Electronic spectra $\lambda_{\max}$ (log $\epsilon$ , M <sup>-1</sup> l <sup>-1</sup> )			
	vCH=N	vOH	—			
L <sup>1</sup> H	1620	_	268 (4.86), 337 (4.67), 430 (2.14)			
L <sup>2</sup> H	1625	3438	224 (5.0), 277 (4.76), 324 (4.51), 447 (2.09)			
L <sup>3</sup> H	1617	_	218 (5.01), 274 (4.81), 330 (5.54), 444 (2.23)			
L <sup>4</sup> H	1617	3247	239 (4.68), 285 (4.59), 333 (4.74), 410*(2.54)			
L⁵H	1615	_	210 (4.36), 218*, 236 (4.24), 245*, 282 (4.16), 330 (4.11), 420 (3.67)			
L <sup>6</sup> H	1625	3310	240 (6.3), 272 (3.6), 366 (2.3), 480* (0.008)			
L <sup>7</sup> H	1628	_	237 (9.1), 271 (5.1), 362 (3.5), 470* (0.015)			
L <sup>8</sup> H	1625	_	217 (12), 230 (12.5), 268 (5.9), 349 (4.4)33, 440* (0.012)			
L <sup>9</sup> H	1625	_	210(4.1), 215*, 237 (2.5), 285 (2.1), 318*, 334 (1.6), 445*			
$L^{10}H$	1612	_	206 (3.0), 219 (2.9), 230 (2.9), 271 (1.5), 350 (1.1), 450*			
$L^{11}H$	1604	_	212 (8.9), 246 (5.6), 268 (4.2), 331 (4.1), 423 (2.4)			
$L^{12}H$	1622	_	232 (11.8), 260*, 316 (3.2), 364 (2.6), 434 (2.2)			

\* Shoulder.

Compound	OH/NH	CH=N	ОН	OCH <sub>3</sub>	Sal.(H)	Phen (H)	t-Butyl (H)
L <sup>1</sup> H	13.09	8.44	_	_	7.33–7.45, 6.05–7.02	7.25 d, 7.23 d, 6.84 d	1.29, 1.41
L <sup>2</sup> H	13.60	8.41	5.78	_	7.37 d, 7.08–7.04 td, 6.85 m	7.27 d, 7.23 d, 7.02 d	1.34, 1.41
L <sup>3</sup> H	13.42	8.44	_	3.95	7.36 d, 7.04 m	6.85–6.99 m	1.31, 1.37
L <sup>6</sup> H	12.95	8.31	4.85	_	7.34, 7.26, 6.88	7.22, 7.18, 6.78	1.25, 1.34
$L^{7}H$	12.63	8.39	_	3.82	7.37, 7.34, 9.55 m	7.26, 7.23, 6.85	134, 1.41
L <sup>8</sup> H	13.10	8.36	-	_	7.55 d, 7.54 d, 7.48 d 7.38, 7.34, 7.26, 6.94 d	7.27 d, 7.24 d, 6.81 d	134, 1.39
L <sup>12</sup> H	15.33	9.21	-	_	8.14d, 7.77q	7.5 t, 7.14–7.72 m, 7.01 d	1.37, 1.46
	15.35	9.19					

<sup>1</sup>H NMR chemical shifs ( $\delta$  in ppm) of some L<sup>6</sup>H in CDCl<sub>3</sub>

Table 3

broad asymmetric visible bands at ca. 470-500 and 645-730 nm (Table 4) which are attributed to  $d_{x^2-y^2} \rightarrow d_{xy}$  and  $d_{x^2-y^2} \rightarrow d_{xz, yz}$  transitions in tetragonal ligand field, respectively [39,40]. For square planar complexes, the lower energy d-dband is usually observed in the region 550-630 nm. The complexes reported in the present work show the lower energy d-d band in the region 645-730 nm, and this red shift may be due to the tetrahedral distortion from square planar environment of the Cu<sup>II</sup> ion [41]. This behavior probably due to the steric effects of the bulky tert-butyl group in the 2-position of the ligands. The bands in the 340-385 nm range and a shoulders at ca. 400 nm are attributed to  $e_g \rightarrow \pi^*_{azomethine}$  metal-toligand transitions and ligand-to-metal chargetransfer transitions from the phenolate groups to the copper center, respectively [42,43].

#### 3.4. <sup>1</sup>H NMR

The ligands structure is supported by <sup>1</sup>H NMR spectra, recorded in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub>. The <sup>1</sup>H NMR spectral results obtained for L<sup>x</sup>H in CDCl<sub>3</sub>, together with the assignments are given in Table 3. All L<sup>x</sup>H salicylaldimines show a sharp intense singlet in the low field  $\delta$  12.63–13.60 ppm region, which is due to the exchangeable hydrogenbonded hydroxyl/aminyl (OH/NH) proton. It disappears upon exchange with D<sub>2</sub>O and can be associated with the –OH protons doubtlessly involved in intramolecular hydrogen bonding with iminic nitrogen atom. Note that the linewidth at half-peak height of OH/NH proton signal in the spectra of L<sup>x</sup>H is very narrow ( $\Delta H = 1-2$  Hz) than that in the analogues salicylaldimines derived from 2,6-di-tert-butyl-1-hydroxy-aniline (14-25 Hz) [44]. This effect may be due primarily to  $^{14}N$ quadruple relaxation and broadening by intermediate proton exchange between oxygen and nitrogen in tautomeric structures in the  $L^{x}H$ . It is interesting that the resonances of hydrogenbonded OH and CH=N group of N-(2,5-di-tertbutylphenyl-2-hydroxy-naphthaldimine  $(L^{12}H)$ were appeared as a doublet at  $\delta$  15.33–15.35 ppm (J = 4 Hz) and 9.19-9.21 ppm (J = 6 Hz) in CDCl<sub>3</sub>, respectively, suggesting the existence of two isomers for this compound in CHCl<sub>3</sub>. But, the resonances of these groups appeared as a singlet at  $\delta$  15.43 and 9.18 ppm in C<sub>6</sub>D<sub>6</sub>. All the 3-OH, 4-OH and 5-OH-substituted salicylaldimines show a broad and low intensity singlet in the range  $\delta$ 4.85–5.78 ppm assigned to salicylic OH protons. The CH=N and OCH<sub>3</sub> protons resonances appeared as a sharp singlet in the ranges  $\delta$  8.31– 8.44 and 3.82–3.95 ppm, correspondingly. The aromatic protons appeared as a multiplet in the 6.66–7.54 ppm range. The protons of the tert-butyl groups of all  $L^{x}H$  exhibit two sharp singlet peaks in the ranges  $\delta$  1.25–1.34 and 1.34–1.46 ppm indicating that tert-butyl protons in the 2and 5-positions of the aniline moieties of  $L^{x}H$  are magnetically non-equivalent.

## 3.5. EPR spectra

The spin-Hamiltonian parameters of  $Cu(L^{x})_{2}$ complexes are listed in Table 5. The EPR spectra of polycrystalline samples of all compounds were obtained at 300 and 113 K. None of the spectra show resolvable metal hyperfine coupling or any detectable half-field absorption associated with  $\Delta M = \pm 2$  forbidden transition indicating a small zero field splitting effect. All the complexes show a strong broad asymmetric signal centered at ca. g = 2.1. The spin-Hamiltonian parameters, electronic absorption spectra and magnetic moment values for the  $Cu(L^x)_2$  complexes suggest a tetrahedral distorted square planar geometry around Cu(II) in these complexes. The X = 3-OH, and 3-CH<sub>3</sub>O substituted complexes displays a five-line superhyperfine structure on high field copper hyperfine component with  $A_{iso}(N) = 12-14$  G due to

Table 4 IR and electronic spectra for  $Cu(L^x)_2$  complexes

coupling with two <sup>14</sup>N (I = 1) nuclei. But spectra other complexes neither at 300 nor 113 K did not observe any additional <sup>14</sup>N hyperfine splitting on the high-field  $g_{\parallel}$  component or at  $g_{\perp}$ . A probable mechanism for the absence of <sup>14</sup>N hfsc may be a relatively higher tetrahedral distortion from square planar configuration around the copper ion for these complexes. All complexes exhibit EPR spectra corresponding to axial symmetry with  $g_{\parallel} > g_{\perp} > 2.03$  and  $A_{\parallel} \gg A_{\perp}$ , 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 [45-49] in a distorted tetragonal copper site. The value of the in-plane  $\sigma$ -bonding parameter,  $\alpha^2$ , evaluated using the expression  $\alpha^2 = |A|/|$  $0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$ [45,46], fall in the 0.48–0.52 range and indicate the presence of significant in-plane  $\sigma$ -bonding in these complexes [50]. For  $Cu(L^2)_2$ ,  $Cu(L^8)_2$ ,

Compound	$\mu_{\rm eff}$ (BM)	IR spectra (cm <sup>-1</sup> )		Solvent	Electronic spectra	
		vCH=N	vOH	-		
$\overline{Cu(L^1)_2}$	2.03	1605	_	CHCl <sub>3</sub>	246, 270, 307, 362, 600 <sup>a</sup> , 700 <sup>a</sup>	
				Dioxane	246, 270, 306, 364, 610 <sup>a</sup> , 710 <sup>a</sup>	
$Cu(L^2)_2$	2.18	1618	3433 <sup>ь</sup>	CHCl <sub>3</sub>	289, 375, 400 <sup>a</sup> , 510 <sup>a</sup> , 740	
				Dioxane	249, 265 <sup>a</sup> , 292, 374, 747 <sup>a</sup>	
$Cu(L^3)_2$	1.99	1604	-	CHCl <sub>3</sub>	278, 325, 350 <sup>a</sup> , 410 <sup>a</sup> , 500 <sup>a</sup>	
				Dioxane	248, 287, 400 <sup>a</sup> , 600 <sup>a</sup> , 700 <sup>a</sup>	
$Cu(L^4)_2$	1.92	1615	3259°	CHCl <sub>3</sub>	290, 345, 650	
				Dioxane	248, 260 <sup>a</sup> , 287, 350, 374, 645	
$Cu(L^5)_2$	1.94	1610	-	CHCl <sub>3</sub>	260, 290, 310 <sup>a</sup> , 376, 410 <sup>a</sup> , 730 <sup>a</sup>	
				Dioxane	256, 288, 354, 600 <sup>a</sup> , 700 <sup>a</sup>	
$Cu(L^7)_2$	1.89	1620	_	EtOH	240, 265, 360, 730	
				Dioxane	248, 378, 402, 727	
$Cu(L^8)_2$	1.93	1612	_	CHCl <sub>3</sub>	370 <sup>a</sup> , 305, 365, 390 <sup>a</sup> , 700 <sup>a</sup>	
				Dioxane	250, 265 <sup>a</sup> , 309, 361, 400 <sup>a</sup> , 700 <sup>a</sup>	
$Cu(L^9)_2$	2.19	1617	_	CHCl <sub>3</sub>	370, 365, 600 <sup>a</sup>	
				Dioxane	258, 362, 400 <sup>a</sup> , 609	
$Cu(L^{10})_2$	2.18	1614	_	CHCl <sub>3</sub>	254, 310 <sup>a</sup> , 381, 400 <sup>a</sup> , 610 <sup>a</sup> , 730 <sup>a</sup>	
				Dioxane	252, 270 <sup>a</sup> , 330 <sup>a</sup> , 379, 500 <sup>a</sup> , 600 <sup>a</sup>	
$Cu(L^{11})_2$	2.08	1615	_	CHCl <sub>3</sub>	265, 360, 450 <sup>a</sup> , 620 <sup>a</sup>	
				Dioxane	245 <sup>a</sup> , 265, 358, 618	
$Cu(L^{12})_2$	2.14	1618	_	CHCl <sub>3</sub>	265 <sup>a</sup> , 317, 384, 400, 450 <sup>a</sup> , 700 <sup>a</sup>	
				Dioxane	265, 290, 315, 390, 420 <sup>a</sup> , 700 <sup>a</sup>	

<sup>a</sup> Shoulder.

<sup>b</sup> Broad.

<sup>c</sup> Narrow.

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Compound	$g_{\rm iso}$	$g_{\parallel}$	$g_{\perp}$	$A_{\rm iso}$	$A_{\parallel}$	$A_{\perp}$	$\alpha^2$	G	$g_{\parallel}/A_{\parallel}$
$Cu(L^1)_2$	2.107	2.208	2.057	78.8	178	29.2	0.49	3.75	133
$Cu(L^2)_2$	2.114	2.229	2.057	75	174	45.5	0.50	4.02	137
$Cu(L^3)_2$	2.109	2.216	2.056	77.5	180	26.3		3.85	132
$Cu(L^4)_2$	2.090	2.189	2.041	66.3	172	13.5		4.61	136
$Cu(L^5)_2$	2.106	2.214	2.052	80	184	28	0.49	4.12	129
$Cu(L^6)_2$	2.083	2.242	2.004	_	172	_			140
$Cu(L^7)_2$	2.109	2.217	2.055	75	176	24.5	0.48	3.95	135
$Cu(L^8)_2$	2.101	2.211	2.046	83.8	184	33.7	0.50	4.58	127
$Cu(L^9)_2$	2.109	2.231	2.048	82.5	166	40.8	0.52	4.37	144
$Cu(L^{10})$	2.113	2.216	2.061	72.5	178	19.8	0.48	3.54	133
$Cu(L^{11})_2$	2.116	2.251	2.048	70	156	27	0.50	5.23	156
$Cu(L^{12})_{2}$	2.103	2.226	2.042	85	166	44.5	0.52	5.38	143

Table 5 ESR parameters<sup>a</sup> for the  $Cu(L^x)_2$  complexes

<sup>a</sup> Copper hyperfine constants are given in Gauss.

 $Cu(L^9)_2$ ,  $Cu(L^{11})_2$  and  $Cu(L^{12})_2$  complexes the axial symmetry parameter,  $G = (g_{\parallel} - 2.0023/g_{\perp} -$ 2.0023), lie in the 3.54-5.38 range and indicates that there is no exchange interaction between the copper centers (G > 4) [45,46,50]. 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 [51]. This quotient ranges from ca. 105 to 132 cm for square-planar geometry with no appreciable tetrahedral distortion. The  $g_{\parallel}/A_{\parallel}$  quotient increases markedly on the introduction of tetrahedral distortion to the chromophore, for example, as in bis(N-tert-butylsalicylaldiminato)copper(II) (157 cm) [52] and bis(N'-tert-butyl-pyrrol-2-carbaldiminato)copper(II) (210 cm) [53]. As seen from Table 5, the  $g_{\parallel}/A_{\parallel}$  quotients except Cu(L<sup>5</sup>)<sub>2</sub> and  $Cu(L^8)_2$ , for all other complexes are slightly higher than those for a square-planar geometry (Table 5) suggesting that the steric hindrance of the o-tert-butyl group induces a relatively higher tetrahedral distortion.

#### 3.6. Reactivities of $Cu(L^x)_2$ toward PPh<sub>3</sub>

In our early works it has been demonstrated that the copper(II) complexes with salicylaldimine, 2-hydroxy-benzylamine, 2-hydroxy-arylazo and  $\beta$ -ketoaminate ligands containing sterically hindered 2,6-di-*tert*-butylphenyl and

2,4-di-tert-butylphenyl units unlike their unhindered analogous, undergo one- or two-electron transfer reactions in the interactions with triarylphosphines and lead dioxide giving corresponding metal-stabilized radical complexes [7-16,29-31]. Attempts to generate radical species by treatments of the free L<sup>x</sup>H ligands and their  $Cu(L^x)_2$  complexes with PbO<sub>2</sub> were unsuccessful. When the HO- and CH<sub>3</sub>O-substituted  $Cu(L^{x})_{2}$  was treated with a 2-4-fold excess of PPh<sub>3</sub> in various solvents (dioxane, CHCl<sub>3</sub>, THF, toluene) at room temperature under vacuum or in air the decreasing of the intensities of copper hyperfine lines and immediate appearance of radical signals centered at g = 2.0056 - 2.0082 were observed (Figs. 1-3). Surprisingly in the EPR spectra of these systems any sign of adduct formation with PPh<sub>3</sub> and noticeable changes in g-factors and copper hyperfine constants were not observed. Upon treatment of  $Cu(L^2)_2$  with a 2.5fold excess of PPh<sub>3</sub> in toluene at 300 K in air along with spectrum of the complex, a well-resolved seven-line pattern at g = 2.0095 spacing of 11 G with an intensity distribution of ca. 1:1:1:2:1:1:1 was observed (Fig. 1a). The observed 7-fold pattern with intensities of 1:1:1:2:1:1:1 may be interpreted in terms of coupling of the unpaired electron to one  ${}^{63,65}$ Cu (I = 3/2) and  ${}^{31}$ P (I = 1/2) nuclei with hfcc  $\langle A^{P} \rangle = 3 \langle A^{Cu} \rangle$ . It can be easily simulated with an isotropic coupling constants  $A_{iso}(P) = 33$  G and  $A_{iso}(Cu) = 11$  G.

When this reaction is carried out by the mixing deoxygenated solutions of  $Cu(L^2)_2$  and PPh<sub>3</sub> under vacuum, each component of this septet exhibits additional triplet superhyperfine splitting (shfs) with a coupling constant of 2.5 G to the <sup>14</sup>N nucleus (I = 1) (Fig. 1b). This sample upon standing under vacuum or in air about 12 h showed the copper hyperfine components disappearance and a five-line pattern (Fig. 1c) which can be consid-

ered to reflect the superimposed triplet and doublet due to <sup>14</sup>N and <sup>31</sup>P nuclei having hfcc  $A_{iso}(N) = 32$  and  $A_{iso}(P) = 35$  G, and centered at g = 2.0089 and 2.0096, respectively. The similar septet pattern radical spectrum with an intensity ratios of 1:1:1:2:1:11 spacing of 11.5 G is also observed in the reduction of Cu(L<sup>4</sup>)<sub>2</sub> with an excess amount of PPh<sub>3</sub> (Fig. 2a and b). As seen from Fig. 2c, the deoxygenated samples of this



Fig. 1. EPR spectra of  $Cu(L^2)_2 + PPh_3$  system: the initial stage spectrum of the reaction mixture  $Cu(L^2)_2 + PPh_3$  in toluene at 300 K (a); radical part of (a) under vacuum (b); spectrum detected after 12 h under vacuum (c).



Fig. 2. Changes of the EPR spectra of  $Cu(L^3)_2 + PPh_3$  system: the initial stage spectrum immediately recorded after mixing of toluene solutions of  $Cu(L^3)_2$  and PPh<sub>3</sub> at 300 K (a); radical part of (a) in air (b); spectrum of (b) under vacuum (c); spectrum of (c) after 16 h under vacuum in toluene at 300 K at modulation 1 G and scan 100 G (d).



Fig. 3. The initial stage EPR spectrum  $Cu(L^6)_2 + PPh_3$  system recorded immediately after mixing of deoxygenated dioxane solutions of  $Cu(L^6)_2$  and PPh<sub>3</sub> under vacuum at modulation 1.6 G and scan 200 G (a); spectrum of (a) under vacuum at modulation 1.6 G and scan 100 G (b).

mixture shows additional superhyperfine structure on each component arising from the <sup>14</sup>N nucleus of the ligand. In addition, weak couplings arising probably from the azomethine proton were also observed on some components. The spin-Hamiltonian parameters for this radical are: g = 2.0082,  $A_{iso}(Cu) = 11.5 \text{ G}, A_{iso}(P) = 34.5 \text{ G}, A_{iso}(N) = 3.5$ G,  $A_{iso}(H) = 0.85$  G. After 16 h in air a septet line pattern disappeared and only very stable quartet signal centered at g = 2.0035 remained, with intensity ratios 1:2:2:1 spacing of 1.875 G (Fig. 2d). It is interesting to note that the similar quartet pattern with an intensity ratios of 1:2:2:1 and unreactivity towards atmospheric  $O_2$  (this signal remains unchanged more than 3 weeks in air) previously also were observed in the reduction of bis(β-ketoaminato)copper(II) [9], bis(salicylaldiminato)palladium(II) [29-31,54], bis(salicylaldiminato)copper(II) [10,11,15], and 2-hydroxyaryl-azo ligands chelates of Cu(II) [7,8] containing sterically hindered phenols fragments. The detection of stable secondary radical species exhibiting identical quartet pattern and g- and A-factors in the reduction of various complexes by PPh<sub>3</sub>, suggests that these radical species probably contain one <sup>31</sup>P and <sup>14</sup>N nuclei with hfcc  $A^{P} = A^{N}$ . Note that the generation of  $Ph_3P^{+\bullet}$  cation radicals in the process of reduction which can readily bond to PPh<sub>3</sub> to give corresponding  $\sigma^*$ -radicals  $Ph_3P^{\bullet}-PPh_3^+$  with two equivalent <sup>31</sup>P nuclei have been reported by Symons [55]. Similarly, in our system the generated  $Ph_3P^{+\bullet}$  cation radicals can bond to ligand molecules giving  $Ph_3P^{\bullet}-NR_2^+$  with close hfcc of <sup>31</sup>P and <sup>14</sup>N nuclei can be considered as one possible alternative. The EPR spectral data suggest that the salicylate moiety is oxidized yielding a phenoxyl coordinated radical ligand complex,  $[(PPh_3)_2Cu(I)L^{x\bullet}]$ , as primary radical intermediates in the reduction. It is thought that the attack of PPh<sub>3</sub> to  $Cu(L^x)_2$  molecule one ligand removed as an anion radical and the afforded  $(PPh_3)_2Cu^{II}L^x$  intermediate, via one-electron transfer from coordinated  $L^x$  to Cu(II) ion, converts to oxidized forms.

In the reduction of  $Cu(L_4)_2$  and  $Cu(L_5)_2$  in THF, which was used from their solubility, with an excess of PPh<sub>3</sub>, without appearance any radical species simultaneous disappearance of copper(II)

signals were observed. Although the solid state EPR spectrum of  $Cu(L^6)_2$  did not exhibit any radical signal, the dioxane solution of this complex reveals the presence a less intensity radical singlet centered at g = 2.0044 ( $\Delta H = 10$  G). Upon addition of a 3-fold excess of PPh<sub>3</sub> to dioxane solution of this sample in air, the appearance of a seven-line pattern with a hyperfine splitting of about 9.75 G at g = 2.0063 was observed. The presence a strong singlet centered at the center of the spectrum complicated the accurate determination of the relative intensity ratios of hyperfine lines. The complicated ESR spectra of this sample in toluene under vacuum at 300 K are presented in Fig. 3. It is assumed that these spectra result from the overlapping signals due to the presence at least two type of radicals. The central more intense part of the spectra probably reflects contributions arising from the phenoxyl type radical presented in the starting complex (g = 2.0042, $\Delta H = 10$  G). It is thought that a less intense patterns at high field and low field parts of the spectra (g = 2.0063) can be assigned to radical species generated by the reduction with PPh<sub>3</sub>. Some lines on wings of this pattern (Fig. 3b) exhibit additional a triplet (3.5 G) of doublets (1.125 G) splittings. We suppose that this spectrum is similar to above spectral features and may be readily simulated assuming  $\langle A_{iso}^{P} \rangle = 3 \langle A_{iso}^{Cu} \rangle$ , with an additional shfs to one <sup>14</sup>N and azomethine proton. From the spectra spin-Hamiltonian parameters:  $A_{iso}(P) = 33.6$  G,  $A_{iso}(Cu) = 11.175$ G,  $A_{iso}(N) = 3.5$  G and  $A_{iso}(H) = 1.125$  G can be calculated. Upon treatment of  $Cu(L^7)_2$  with PPh<sub>3</sub> in toluene, although the decreasing of the intensities of copper hyperfine lines takes place, but the formation of any radical signal was not observed. It is interesting that under the above-mentioned conditions the reduction of  $Cu(L^1)_2$  (X = H) and  $Cu(L^{x})_{2}$  (X = Br, NO<sub>2</sub>, 5,6-benzo) complexes with a 5-10-fold excess of PPh<sub>3</sub>, even on heating, did not take place.

Thus EPR examination of the reaction mixture of 2,5-di-butylated Cu(II)bis(salicylalimine) complexes—PPh<sub>3</sub> systems shows that some Cu(II) chelates were readily reduced giving stable radical ligand Cu(I) complexes and other stable secondary radical species. It has been found that the reduction of some 2,5-di-*tert*-butylated bis(salicylalimine)copper(II) complexes with PPh<sub>3</sub> proceeds via Cu-stabilized phosphine containing radical intermediates. The electron transfer ability of these complexes is dependent upon both the position and the nature of the substituent on the salicylic fragment.

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