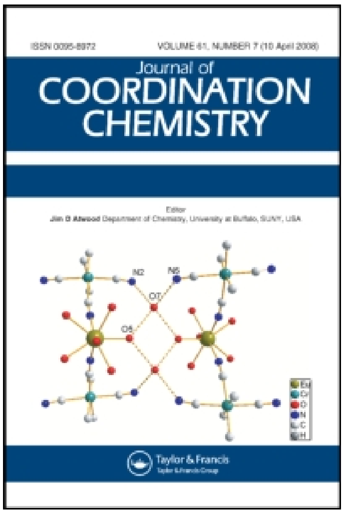

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NEW REDOX-ACTIVE BENZYLAMINE COMPLEXES OF COPPER(II) AND ESR STUDIES OF THEIR OXIDATIONREDUCTION PRODUCTS

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To cite this Article Kasumov, V. T.(2000) 'SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NEW REDOX-ACTIVE BENZYLAMINE COMPLEXES OF COPPER(II) AND ESR STUDIES OF THEIR OXIDATIONREDUCTION PRODUCTS', Journal of Coordination Chemistry, 52: 1, 57 — 71
To link to this Article: DOI: 10.1080/00958970008024563
URL: http://dx.doi.org/10.1080/00958970008024563

J. Coord. Chem., 2000, Vol. 52, pp. 57–71
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SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NEW REDOX-ACTIVE BENZYLAMINE COMPLEXES OF COPPER(II) AND ESR STUDIES OF THEIR OXIDATION–REDUCTION PRODUCTS

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(Received 28 May 1999; Revised 13 October 1999; In final form 2 February 2000)

New Cu(II) complexes Cu$(L'_x)_2$, where $L'_x = L'_1$, L'_2, L'_3, L'_4 are monoanion of unsubstituted, 5-Cl, 5-Br and 3,5-di-Br-substituted 2-hydroxybenzylamines of redox-active N-(3,5-*di-tert*-butyl-1-hydroxyphenyl)-2-hydroxybenzylamines were synthesized. Each compound of L'_xH and Cu$(L'_x)_2$ as well as products of their oxidation and reduction by PbO_2 and PPh_3, respectively, was characterized by IR, UV–visible and ESR spectroscopy. ESR results showed that one-electron oxidation of mononuclear tetrahedrally distorted Cu$(L'_x)_2$ chelates with PbO_2, *via* C–C coupling of the Cu(II)-stabilized ligand radical intermediates and by the oxidative dehydrogenation of amine-chelates, produce new Cu(II) complexes with square-planar geometry. The powder ESR spectra of these new Cu(II) complexes exhibit a triplet-state type pattern with the zero-field splitting due to interaction between the copper(II) pairs. Interaction of Cu$(L'_x)_2$ with PPh_3 *via* intramolecular ligand–metal electron transfer results in the formation of radical species and reduction of the metal center. All radical intermediates were characterized by ESR parameters.

Keywords: ESR spectrum; optical spectra; reactivity of Cu(II) complexes; redox-active; phenoxyl intermediates; oxidative C–C coupling

INTRODUCTION

The electron-transfer behavior of copper(II) complexes is a subject of considerable interest from the point of understanding and replicating

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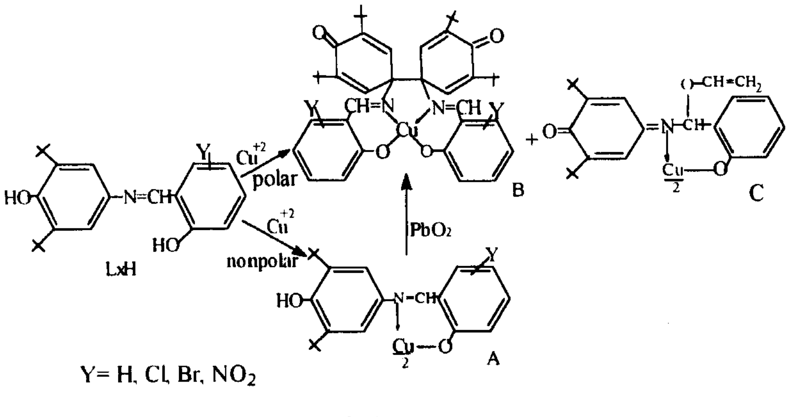
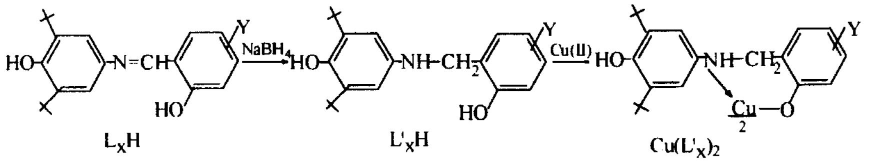
redox-function of 'type 3' copper proteins. The ability of the metal ions to control the oxidation potentials of organic molecules by complexing may be significant in biological electron-transfer systems such as photosynthesis. Specific questions concern the nature of the organic radical species, which are often the initial product of an electron-transfer process.[1,3] Phenols and their one- and two-electron oxidation products (phenoxyl and quinone) play an important role in many biological electron-transfer processes and sometimes function in conjunction with a redox-active metal center.[2,3] The fact that sterically hindered phenols can undergo one- or two-electron oxidations to the phenoxyl radicals or quinone, respectively, offers the possibility of preparing complexes with unusual oxidation states. In previous papers[4,5a,b] we reported that complexation of Cu(II) in polar solvents with bidentate salicylaldimines containing the 2,6-*di-tert*-butyl-1-hydroxyphenyl fragment yields, in contrast to the expected bis-salicylaldiminate of Cu(II) (A), unusual B and C types of salicylaldiminates of Cu(II). From the X-ray structural analysis of the X=H complex,[6] it was found that the phenol moieties of the B and C complexes which were synthesized in the polar solvents have quinolid and quinoid forms, as shown in the Scheme 1. Structure B indicates that synthesis occurs *via* oxidative C–C coupling by the sterically hindered phenol fragment. At the same time, it was found that in nonpolar solvents (or under vacuum in polar solvents) the bis-salicylaldiminates of Cu(II) (A) are formed and then transformed to the corresponding tetradentate salicylaldiminate complexes of Cu(II) upon interaction with PbO_2. It is interesting that, in contrast to other metal complexes such as Co(II), Ni(II), Zn(II), A reacts with PbO_2 without any detectable formation of the radical intermediates to yield complexes of type B.[5a,c,d]



SCHEME 1



Y= H (L'_1H); 3-Cl (L'_2H); 3-Br(L'_3H);3,5- di-Br(L'_4H)

SCHEME 2

The present investigation was undertaken to explore the role of $-CH_2-NH-$ as a linking group instead of azomethine in the ligand (L_xH). In particular, it is of interest to know to what extent the chemical properties of the L'_xH change upon coordination and how this structural change affects the redox reactivity of $Cu(L'_x)_2$ in relation to the formation of radicals and oxidative C–C coupling. We suppose that the difference in the redox reactivity of $Cu(L_x)_2$ and $Cu(L'_x)_2$ series should be related to the $-CH_2-NH-$ group. In this paper we report the preparation and characterization of new complexes $Cu(L'_x)_2$ on the basis of the redox-active ligand N-(3,5-*di-tert*-butyl-4-hydroxyphenyl)-2-hydroxybenzylamines (L'_xH) which contain a $-CH_2-NH-$ group instead of a CH=N group in its salicylaldimine analog (L_xH) prepared according to Scheme 2.

EXPERIMENTAL

Spectra

The IR spectra were obtained on a Carl Zeiss Jena Specord M 80 spectrophotometer in the range of 4000–400 cm^{-1} as KBr discs. Electronic spectra were recorded on a Carl Zeiss Jena Specord M 40 spectrophotometer in the range of 200–900 nm. Magnetic susceptibilities were measured by Faraday technique at room temperature ($25 \pm 2°C$). The apparatus was calibrated by the use of $Hg[Co(NCS)_4]$. Diamagnetic corrections were calculated from Pascal's constants.[7] The ESR spectra of $Cu(L'_x)_2$ were recorded on a Radiopan model SE/X-2547 (X-Band) in solution and in polycrystalline state at 300 and 77 K using DPPH ($g = 2.0036$) as the standard. The ESR parameters of the complexes were determined directly from the spectra. The magnetic field was calibrated using a standard Mn^{2+} sample. Reported values involve errors within ±0.005 for g-values and ±0.05 G for A-values of $Cu(L'_x)_2$. The errors for g-values and hfsc parameters of radicals are ±0.0005 and ±0.05 G, respectively.

Generation of Radicals

L'_xH and $Cu(L'_x)_2$ compounds were oxidized by the following procedure. The compound dissolved in 4 mL toluene or chloroform and lead dioxide were transferred into separate glass tubes on a vacuum line. The solution was deoxygenated under vacuum (10^{-3} mmHg) by repeated freeze–pump–thaw cycles. The 70–90 mg of PbO_2 was suspended in 2–3 mL of the solution and shaken for 1 min under vacuum. After the sedimentation of the heterogeneous phase, 1 mL of the solution was taken for ESR measurements.

Synthesis of Ligands and Complexes

Salicylaldimines L_xH were synthesized by the method described previously.[5a] N-(3,5-*di-tert*-butyl-4-hydroxyphenyl)-2-hydroxybenzylamines (L'_xH) were prepared by the following procedure. $NaBH_4$ (0.05 mol) was added slowly (small portions of about 10–15 mg) to 0.01 mol stirring solutions of L_xH in 40–50 mL of isopropanol for 15–20 min. Stirring was continued for another 30–40 min and the cooled mixture was then poured into 150–200 mL water. After cooling to room temperature the solution was stirred for 1 h and allowed to stand for 3–4 h. The precipitated white crystals were collected by filtration and then washed 6–8 times with water, dried under vacuum and recrystallized from hexane–acetone, yield 85–90%.

The complexes $Cu(L'_x)_2$ were synthesized by mixing hot methanol solutions of equimolar amounts of L'_xH (2 mmol) and copper(II) acetate (1 mmol) and heating at about 60°C with constant stirring for 40–50 min. The volume of the solution was concentrated to *ca.* 15 mL and left to stand overnight; the precipitated green crystals were collected, washed with water, dried under vacuum and recrystallized from methanol–acetone, yield 70–75%. Analytical and spectroscopic data for the compounds synthesized are given in the Tables I–III.

RESULTS AND DISCUSSION

The elemental analyses, magnetic susceptibility measurements, electronic, IR and ESR spectral data indicate that the copper(II) complexes of N-(3,5-*di-tert*-butyl-4-hydroxyphenyl)-2-hydroxybenzylamines exist as mononuclear bis(chelate) compounds.

The IR spectra (Table II) of $Cu(L'_x)_2$ complexes exhibit stretching vibrations due to ν(N–H) (3295–3310 cm^{-1}) which are shifted (~20–30 cm^{-1}) to

TABLE I The melting point and analytical data for L'_xH and $Cu(L'_x)_2$

Compound	*T* (°C)	*Formula*	*Elemental analyses* (%) (*Found*/*Calcd.*)		
			C	*H*	*N*
L'_1H	146	$C_{21}H_{29}NO_2$	78.44/78.98	8.27/8.85	4.78/4.28
L'_2H	149	$C_{21}H_{28}NClO_2$	70.43/69.71	7.12/7.76	3.34/3.87
L'_3H	156	$C_{21}H_{28}NBrO_2$	61.19/61.91	6.98/6.63	3.14/3.44
L'_4H	166	$C_{21}H_{27}NBr_2O_2$	52.43/51.74	5.87/5.53	2.42/2.87
$Cu(L'_1)_2$	> 250	$C_{42}H_{56}N_2O_4Cu$	70.78/71.43	8.56/7.93	4.66/3.95
$Cu(L'_2)_2$	> 250	$C_{42}H_{54}N_2Cl_2O_4Cu$	65.76/65.07	7.66/6.97	3.32/3.64
$Cu(L'_3)_2$	> 250	$C_{42}H_{54}N_2Br_2O_4Cu$	58.75/58.22	6.78/6.23	3.56/3.23
$Cu(L'_4)_2$	> 250	$C_{42}H_{52}N_2Br_4O_4Cu$	49.78/49.14	5.47/5.07	3.36/2.93

TABLE II IR, electronic spectral data and magnetic moments for the L'_xH and $Cu(L'_x)_2$

Compound	μ_{ef}	*IR spectra*, cm^{-1}		*Electronic spectra* λ_{max} (nm)
	BM	*νNH*	*νOH*	
L'_1H		3325	3620	230, 289, 308, 362, 454
L'_2H		3335	3620	232, 250, 289, 308, 365, 454
L'_3H		3320	3630	230, 289, 311, 364, 446
L'_4H		3345	3630	230, 289, 314, 364, 442
$Cu(L'_1)_2$	1.89	3305	3630	287, 316, 328, 387, 510, 670
$Cu(L'_2)_2$	2.12	3295	3625	277, 333, 378, 510, 690
$Cu(L'_3)_2$	2.16	3310	3635	240, 265, 274, 322, 339, 477, 427, 490, 715
$Cu(L'_4)_2$	2.08	3315	3620	235, 283, 319, 355, 445, 515, 790

lower frequencies compared with those of the free 2-hydroxy-benzylamine ligands and indicate coordination of the NH group to the copper(II) ion (Table II). The stretching frequency of the sterically hindered OH of L'_xH and $Cu(L'_x)_2$ appears as a sharp strong peak in the range 3620–3635 cm^{-1}. The far infrared indicates that νCu–O and νCu–N absorption bands would occur at 470–500 and 420–450 cm^{-1}, respectively. Compounds L'_xH and $Cu(L'_x)_2$ show no sign of ν(C=N) and ν(C=O) vibrations. Thus, the presence in the IR spectra of $Cu(L'_x)_2$ a narrow absorption band of the OH group in the region 3620–3640 cm^{-1} characteristic for sterically hindered phenols and the lack of a very strong C=O stretch in the region 1645–1675 cm^{-1},[5a] indicate that unlike $Cu(L_x)_2$ analogs, upon complexation of L'_xH by Cu(II) ions in polar media oxidative C–C coupling did not take place.

Room temperature magnetic moments of $Cu(L'_x)_2$ complexes are in the range 1.89–2.16 BM which were typical for mononuclear compounds of Cu(II) with a $S = 1/2$ spin-state and did not indicate antiferromagnetic coupling of spins at this temperature. The absorption bands in the electronic spectra in $CHCl_3$ show a group of identical asymmetric bands with λ_{max} at 490–515 and 670–790 nm (Table II) which may be attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ electronic transitions, respectively.[8]

ESR Spectra of $Cu(L_x)_2$

The ESR spectra of the complexes in the polycrystalline state at room temperature and 77 K show a strong broad asymmetric signal centered at *ca.* $g = 2.122$. No half-field (~ 1600 G) signals which may be associated with $\Delta M_s = 2$ forbidden transition arising from coupling between Cu(II) metal ions, were observed at 300 or 77 K. The ESR spin Hamiltonian parameters (Table III) and electronic absorption spectra (Table II) of the $Cu(L'_x)_2$ suggest tetrahedral distorted square-planar geometry around Cu(II) in these complexes. The room temperature and frozen glass solution (77 K) ESR spectra of $Cu(L'_x)_2$ did not show additional hyperfine splitting on the high-field $g_{\parallel}$ component or on $g_{\perp}$ arising from the interaction of the unpaired electron with ^{14}N nuclei. A probable mechanism for the absence of ^{14}N hyperfine splitting constants (hfsc) may be deviation of nitrogen atoms from square-planar configuration around the copper ion and the line-broadening effect of protons on nitrogen atoms of amine that can couple with an unpaired electron and ^{14}N-nuclei.[9] The $g_{\parallel}$ values (2.227–2.252), being less than 2.3 and the relatively small values of $A_{\parallel}$ (153–177 G) are typical of N,O-bonded Cu(II) in tetragonal stereochemistries.[8,10] All complexes exhibit ESR spectra consistent with nearly tetragonal symmetry $g_{\parallel} > g_{\perp} > 2.00$ and the G-values in the range 3.26–5.85 are consistent with a $d_{x^2-y^2}$ ground state having a small exchange coupling in the Cu $(L'_x)_2$.[8] The values (0.476–0.532) of the in-plane sigma bonding parameters (α^2), were estimated from the expression:[11] $\alpha^2 = A/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$. Much less than 1.0, which is expected for 100% ionic character of the bonds, indicates the presence of significant in-plane σ-bonding in these complexes.

TABLE III ESR parameters for $Cu(L'_x)$ complexes and their radical intermediates

Complex	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso} (G)	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	α^2	G	$^*g$	$^*A^H$ (G)
$Cu(L'_1)_2$	2.123	2.227	2.071	65.4	177.8	10.5	0.476	3.26	2.0034	1.11
$Cu(L'_2)_2$	2.125	2.236	2.069	69.34	167.5	29.2	0.495	3.50	2.0044	1.12
$Cu(L'_3)_2$	2.122	2.244	2.062	66.26	155.8	22.9	0.489	4.05	2.0041	1.13
$Cu(L'_4)_2$	2.118	2.252	2.045	63.5	153.5	18.5	0.532	5.847	2.0042	1.15

* The radical parameters.

Oxidation of L_xH

The oxidation of L'_xH with PbO_2 in toluene, $CHCl_3$ or THF leads to formation of phenoxy radical signals centered at *ca.* $g = 2.0044$ with similar hfsc. ESR spectra of radicals obtained upon oxidation of L'_1H and L'_2H in toluene and $CHCl_3$ consists of seven equidistant lines with an intensity distribution of 1 : 3 : 5.6 : 5 : 3 : 1 pattern and have the following parameters: $A^H_m = A^N = 1.85\,G$, $A^H_{NH} = 3.92\,G$ and, $A^H_m = A^N = 1.82\,G$, $A^H_{NH} = 3.95\,G$, respectively. The spectra of these radicals could be simulated assuming that the unpaired electron spin density interacts with two equivalent protons of the phenoxyl fragments ($A^H_m = 1.85\,G$), one nitrogen atom ($A^N = 1.85\,G$) and one hydrogen atom of the NH group ($A^H_{NH} = 3.92\,G$). At the same time, one-electron oxidation of the L'_3H in $CHCl_3$ solution leads to formation of a well-resolved nine line ESR spectrum with an intensity distribution of 1 : 2 : 3 : 4 : 4 : 4 : 3 : 2 : 1. The hfsc of the ESR spectrum of this radical arises from splitting at two equivalent *meta*-protons of the phenol ring, one proton at NH group and nitrogen atom with coupling constants as $A^N = A^H_{NH} = 2A^H_m$ ($g = 2.0049$, $A^H_m = 1.23\,G$, $A^N = A^H_{NH} = 2.46\,G$). A similar spectrum with close ESR parameters is also observed for oxidized L'_4H in $CHCl_3$ solution ($g = 2.0046$, $A^H_m = 1.26\,G$, $A^N = A^H_{NH} = 2.54\,G$). The radicals observed in the oxidation of L'_xH, unlike those obtained by the oxidation of salicylaldimines (L_xH), are unstable under vacuum.[5a]

Oxidation of $Cu(L'_x)_2$

The one-electron oxidation of the compounds $Cu(L'_x)_2$ with PbO_2 in toluene or $CHCl_3$ at room temperature, unlike their salicylaldiminate Cu(II) analogs (A), readily leads to formation of phenoxyl radicals. The spectra are shown in Figures 1–3. These spectra are similar to each other and have quite close *g*-factors and hfsc values but different from those observed for radicals generated from L'_xH. In addition, the number of lines and linewidth also were similar to each other. The oxidation products have been studied in detail only for $Cu(L'_1)_2$. The spectra of the reaction mixture which were recorded at 300 K after oxidation of $Cu(L'_1)_2$ with PbO_2 in $CHCl_3$ solution are shown in Figure 1. The initial spectrum (Figure 1(a)) consists of a radical signal centered at $g = 2.0034$ and copper(II) ESR parameters ($g_{iso} = 2.121$, $A_{iso} = 70.2\,G$) close to those for $Cu(L'_1)_2$. In addition, on the low-field and high-field sides of the intense radical signal, a very low-intensity hyperfine structure was observed. After 2–3 h the intensities of the radical and its hyperfine pattern were increased (Figure 1(b)). The spectrum of this radical

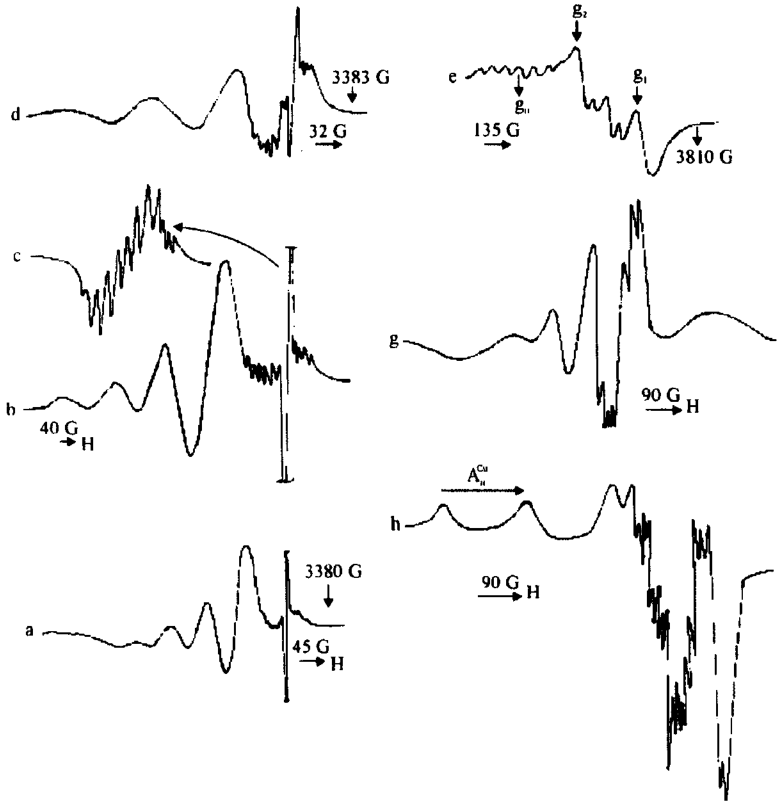


FIGURE 1 ESR spectra of the reaction mixture $Cu(L'_1)_2$ with PbO_2 in $CHCl_3$: the initial stage (a) and after 2 h (b) spectra recorded at 300 K under vacuum; the spectrum of radical part of (b) recorded in the scan range of 100 G (c); the spectrum recorded after 8 h (d); the solid-state spectrum of the oxidation product CuL'_1 at 77 K (e); spectrum of CuL''_1 at 300 K in toluene (g) and in $CHCl_3$ at 77 K (h).

signal which was recorded in the scan range of 100 G, exhibits a well-resolved hyperfine structure with nine equidistant lines of relative intensity of 1:4:7:8:9:8:7:4:1 and hfcs spacing of 1.1 G (Figure 1(c)). This spectrum was analyzed in terms of an interaction of the unpaired electron spin density with one nitrogen ($A^{\rm N} = 2.22$ G) and two sets of three protons [$A^{\rm H}_{\rm m} = 2.22$ (2H) and $A^{\rm H}_{\rm NH} = 2.22$ G (1H)] assuming that $A^{\rm N} = A^{\rm H}_{\rm NH} = 2A^{\rm H}_{\rm m}$. It has been observed that in the examination of the oxidation products on standing solutions of the reaction mixture at room temperature and under vacuum, the ESR spectrum undergoes further changes. The intensity of the radical signal gradually decreased and in parallel to this the radical signal was surrounded on each side by new hyperfine lines with a spacing of 8.6 G, which is attributed to the hfsc due to the ^{14}N nucleus of the newly formed Cu(II) complex with ESR parameters of $g_{iso} = 2.095$, $A_{iso}^{Cu} = 102$ G (Figure 1(d)). From these observations it is clear that the unpaired electron is localized predominantly on the ligand and the one-electron oxidation products may be formulated as radical complexes $Cu(L_1')_2$. On standing $Cu(L_1')_2$ radical intermediates undergo further changes, which are accompained by decreasing intensity of the radical signals and appearance of a new isotropic pattern which also shows ^{14}N-hyperfine splittings on the high-field component (Figure 1(d)). When the ESR spectrum of the reaction mixture $Cu(L_1')_2$ and PbO_2 was recorded after one day, in toluene at room temperature, it was found that ESR signals of the parent $Cu(L_1')_2$ complex and radical intermediates completely disappeared. The observed spectral changes indicate formation of a new complex. The powder ESR spectrum of this sample recorded at room temperature shows the allowed transitions $\Delta M_s = \pm 1$ resulting from the zero-field splitting of the triplet ground state, as well as the forbidden transition $\Delta M_s = \pm 2$ at 1550 G. The broad absorptions at $g_1 = 1.915$ and $g_2 = 2.298$, and the low-intensity absorption at $g = 4.18$, were attributed to a triplet-state dimeric complex with a dipole–dipole interaction between the two copper(II) ions.[12–14] Its powder ESR spectrum at 77 K shows six well-resolved copper hyperfine lines with an average spacing of 95 G, which is half of the $A_{\parallel}$ value expected for a copper monomer and centered at $g_{\parallel} = 2.544$ on the low-field side of the $\Delta M_s = \pm 1$ transition (Figure 1(e)). This absorption is assigned to the low-field parallel transition as designated by Wasserman *et al.*, and is indicative of a low-zero-field splitting parameter, D.[15–17] All these spectra, in which copper hyperfine structures were also resolved in the $\Delta M_s = \pm 1$ region, were typical triplet-state ESR signals with the zero-field splitting dominantly due to dipolar interactions between the copper(II) pairs.[11–13] It is interesting that when the polycrystalline sample was dissolved in $CHCl_3$ the room temperature ESR spectrum shows four copper hyperfine lines with $g_{iso} = 2.099$, $A_{iso} = 94.4$ G and $A_{iso}^{N} = 8.96$ G (Figure 1(g)). A broad band on the wings of the spectrum is attributed to a binuclear complex. The frozen solution spectrum (77 K) of this sample in $CHCl_3$ is characterized by $g_{\parallel} = 2.193$, $A_{\parallel} = 201$ G, $A_{\parallel}^{N} = 11.2$ G, $g_{\perp} = 2.052$, $A_{\perp} = 41$ G (Figure 1(h)). It is well known that the appearance of ^{14}N-hfs as well as the relatively high values of $A_{\parallel}$ and low values of $g_{\parallel}$ are characteristic for square-planar N_2O_2-bonded Cu(II) complexes with a $d_{x^2-y^2}$ ground state.[8,17,18] The electronic spectrum of the binuclear complex, which was isolated from the mononuclear impurity by recrystallization from toluene–$CHCl_3$ mixture, exhibited absorption bands with maxima at 256, 262, 264, 285, 393 and 556 nm. In the

IR spectrum of this sample the characteristic ν(OH) and ν(N–H) bands around 3600 and 3300 cm^{-1} were absent, but new bands at 1640 and 1670 cm^{-1}, characteristic for quinoid C=O, were observed. These spectral data are very similar to those observed for B type complexes.

Similar electron-transfer behavior is also observed for other Cu(L'_x)$_2$ complexes. Thus, in the interaction of Cu(L'_2)$_2$ and Cu(L'_3)$_2$ with PbO_2 in $CHCl_3$ at room temperature the ESR spectra of these reaction mixtures showed spectral patterns, which were substantially different from signals of parent complexes (Figures 2(a) and 3(a)). The higher field components of these spectra were superimposed with very intense radical signals with ESR parameters: $g = 2.0038$, $A^{\mathrm{H}}_{\mathrm{m}} = 1.143$ G, $A^{\mathrm{N}} = A^{\mathrm{H}}_{\mathrm{NH}} = 2.286$ (Figure 2(b)) and $g = 2.0044$, $A^{\mathrm{H}}_{\mathrm{m}} = 1.123$ G, $A^{\mathrm{N}} = A^{\mathrm{H}}_{\mathrm{NH}} = 2.286$ G (Figure 3(c)). Hyperfine structure appeared at the low field and high field side of radical signals attributed to ^{14}N-hfsc of the Cu(II) compounds abbreviated as Cu(L''_2)$_2$ and Cu(L''_3)$_2$. The ESR parameters of these compounds were quite different from those for the corresponding parent complexes. These compounds were attributed to reaction products, formed by the oxidation of Cu(L'_2)$_2$ and Cu(L'_3)$_2$, respectively. The ESR parameters of the products ($g_{\mathrm{iso}} = 2.085$, $A_{\mathrm{iso}} = 86.4$ G, $A^{\mathrm{N}}_{\mathrm{iso}} = 7.87$ G for Cu(L''_2)$_2$ and $g_{\mathrm{iso}} = 2.095$, $A_{\mathrm{iso}} = 100.7$ G,

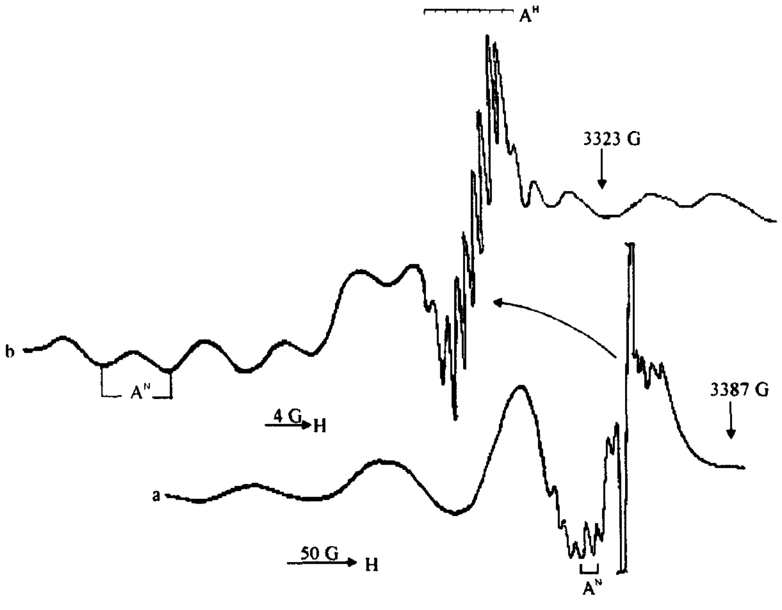


FIGURE 2 ESR spectra of the oxidation products of Cu(L'_2)$_2$ at 300 K under vacuum (a); the spectrum of radical part of (a) recorded in the scan range 100 G (b).

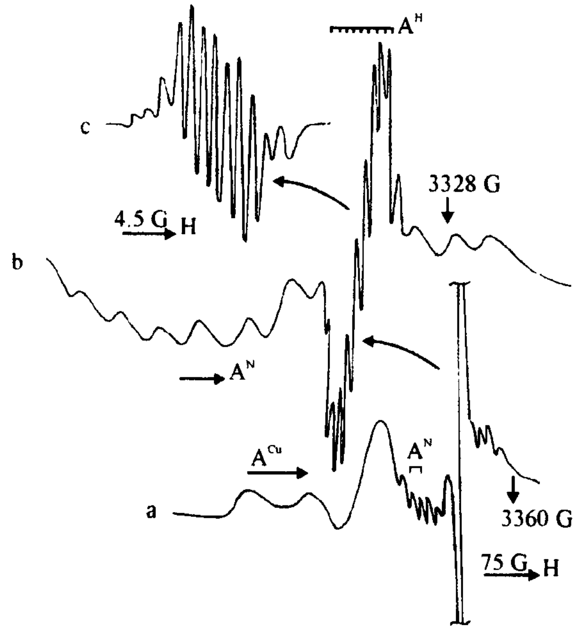
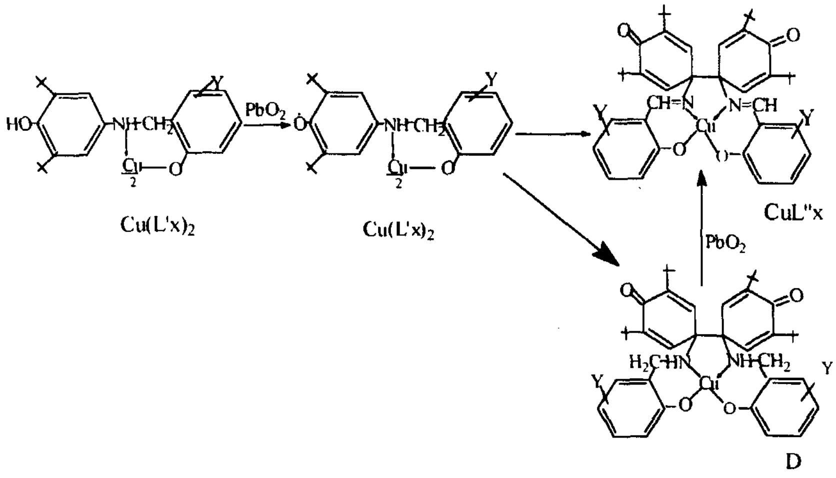


FIGURE 3 ESR spectra of the oxidation products $Cu(L'_3)_2$ at 300 K and under vacuum: initial stage spectrum (a); the highest component part of (a) recorded in the scan range 300 G (b); the radical signal of (b) recorded in the scan range 100 G (c).

$A_{iso}^{N} = 7.85$ G for $Cu(L''_3)_2$) are quite different from those for starting complexes (Table III). Note that in contrast to the $Cu(L'_1)_2$ complex, oxidation of $Cu(L'_2)_2$ and $Cu(L'_3)_2$, gives along with the radical signal, the spectra of new CuL''_2 and CuL''_3 complexes. The appearance of additional ^{14}N-hfsc on the highest field component of the Cu(II) spectra (Figures 2(a) and 3(a)), relatively high values of A_{iso} and a shift in g-factors allow us to suppose that all these observed spectra are due to square-planar Cu(II) complexes.

The observed conversions are very similar to the behavior of (A) upon oxidation by PbO_2.[5a,b] However, unlike salicylaldiminate complexes (A), in the oxidation of $Cu(L'_x)_2$ the relatively stable radical intermediates were observed which gradually disappeared with formation of the new Cu(II) complexes. The disappearance of the starting Cu(II) complexes and radical signals presumably proceeds by C–C dimerization of radicals containing $Cu(L'_x)_2$ to the corresponding CuL''_x complexes.

The ESR, IR, and electronic spectral data of CuL''_x are very similar to those obtained for square-planar salicylaldiminate Cu(II) (B) complexes. A proposed oxidation mechanism of $Cu(L'_x)_2$ is shown in Scheme 3. As seen



SCHEME 3

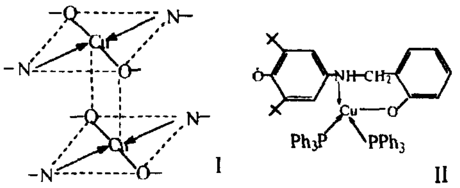


FIGURE 4 The proposed structure of binuclear complex CuL'_1 (I) and bis(triphenylphosphine) Cu(I)-stabilized radical complex $[(PPh_3)_2Cu(I)L'_1]$ (II).

from this scheme, formation of the N–H containing structure type D might be expected, but the characteristic ν(N–H) band is absent in the IR spectrum of the oxidation product (CuL''_x). This observation allows us to suppose that, in the oxidation process, the N–H containing complexes D were formed as unstable intermediates and are further rapidly dehydrogenated by PbO_2 to the corresponding relatively stable salicylaldiminate complexes of CuL''_x. Note that the similar oxidative dehydrogenation of 1,2-diamine or polyamine chelated complexes by chemical (O_2, Br_2, H_2O_2, *etc.*) and/or anodic oxidation to corresponding imine containing complexes has been the focus of a number of studies.[20–22]

The appearance of a characteristic triplet-state ESR spectrum due to dipolar interaction between the copper(II) pairs indicates that the oxidation products contain binuclear Cu(II) complexes in the polycrystalline state as structure I in Figure 4. This type of dimerization of planar Cu(II) complexes is common in copper coordination chemistry.[19] Note that in toluene solution at 300 and 77 K both monomer and dimer ESR spectra were observed superimposed on each other. It is possible that the monomer and dimer are in equilibrium in toluene solution. On the other hand, in the ESR spectrum of this sample in $CHCl_3$ solution (300 K) the dimer structure was not observed at all; only monomer signal was observed. These observations indicate that dimer was completely dissociated to monomer in $CHCl_3$.

Reduction of $Cu(L'_1)_2$

In previous papers[23,24] we reported a number of Cu(II) salicylaldimine, naphthaldiminate, β-ketoamine and azoligand complexes which contain sterically hindered phenols. It has been found that interaction of these complexes with PPh_3, unlike their unhindered analogs, leads to formation of radical-containing $Cu(I)L(PPh_3)_2$ complexes. Reduction of copper(II) complexes by triphenylphosphines is well known,[25–29] but, in some cases the radical character of this reaction remains uncertain. We have studied reduction of $Cu(L'_1)_2$ with excess PPh_3, carried out by mixing degassed toluene solutions in the molar ratio of 1:5 in the ESR tubes, and spectrum of the reaction mixture was immediately recorded under vacuum at 300 K. Upon mixing degassed toluene solutions of $Cu(L'_1)_2$ and PPh_3 the reaction mixture becomes deep red and in the ESR spectrum, along with starting complex signal, a new complicated multiplet radical signal was observed. The radical part of this spectrum is given in Figure 5. After 1 h the spectrum of the parent $Cu(L'_1)_2$ complex completely disappears. The radical part of the spectrum consists of two superimposed signals due to phenoxyl and bis(triphenylphosphine)Cu(I)-stabilized radicals II $[(PPh_3)_2Cu(I)L'_1]$ (Figure 5). The radical II is centered at $g = 2.012$ and consists four equidistant slightly broad lines of equal intensity seperated by 7.57 G. Each component of this spectrum shows additional 5-line splitting with a relative intensity ratio of 1 : 3 : 4 : 3 : 1 (Figure 5). This spectrum was analyzed in terms of an interaction of the unpaired electron with the copper nucleus, one nitrogen and two magnetically equivalent $^{31}P(I = 1/2)$ nuclei. This spectrum could be simulated by using hfsc: $A^{Cu} = 7.58$ G, $A^{N} = 1.52$ G and $A^{P} = 1.52$ G (2P). We were unable to interpret the second spectrum ($g = 2.0052$ and hfsc $A =$ 1.27 G) because of overlap with the first spectrum. Note that these radical species are stable in the absence of oxygen over a period of one week. In the presence of O_2 the radical signals immediately disappeared and a new very stable quartet signal at $g = 2.005$ with intensity ratio of 1 : 2 : 2 : 1 and spacing of 2.32 G was observed. The formation of a similar quartet spectrum

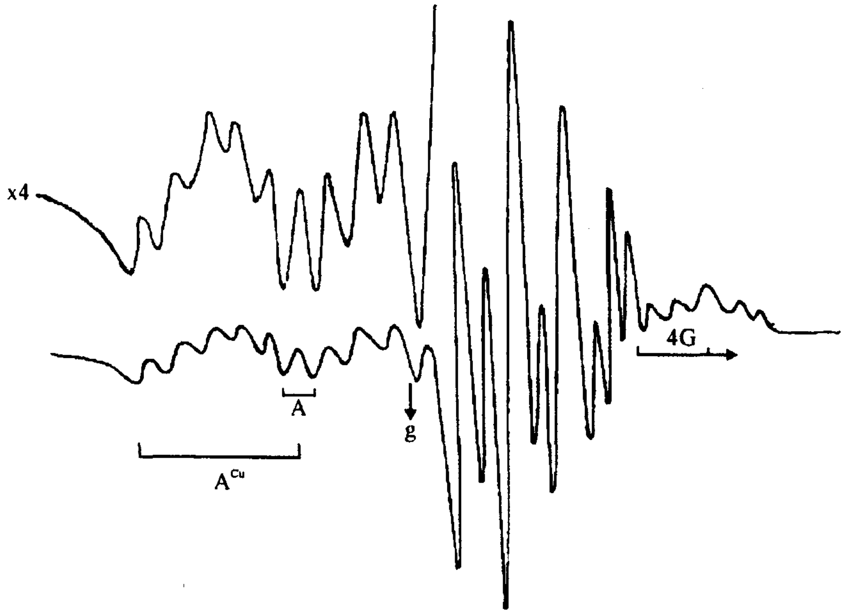


FIGURE 5 ESR spectra of the reduction products $Cu(L'_1)_2$ with PPh_3 in toluene at 300 K and under vacuum.

with identical magnetic-resonance parameters under air was also observed for other bis(chelate)Cu(II)–PPh_3 systems.[23,24]

Thus, our examination indicates that elimination of the resonance system of the salicylaldimines containing sterically hindered phenol fragments by replacement of the azomethine group by a $-NH-CH_2-$ linkage changes the redox-reactivity of the ligands and their Cu(II) complexes towards oxidation by PbO_2. It was found that complexation of Cu(II) with sterically hindered benzylamines under air, unlike their salicylaldimine analogous, did not lead to oxidative C–C coupling conversions. At the same time, one-electron oxidation of bis(benzylaminato)Cu(II) complexes with PbO_2, *via* radical intermediates, produces new Cu(II) complexes. Spectroscopic studies of the oxidation products indicates that oxidation of bis(benzylaminato)Cu(II) complexes yield tetradentate (aminate) Cu(II) chelates *via* C–C dimerization of radical-containing Cu(II) complexes. These complexes, in the presence of PbO_2, produces corresponding tetradentate salicylaldiminate Cu(II) compounds by oxidative dehydrogenation. In addition, the prepared benzylamine Cu(II) complexes unlike their salicylaldiminate analogs, are easily reduced by PPh_3 to give Cu(I) coordinated radical intermediates.

Acknowledgments

The author thanks the International Sciences Foundation (Grant No. MVZ 000) and the Scientific and Technical Research Council of Turkey (TUBITAK) (Grant No. TBAG-1424) for financial support of this research.

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