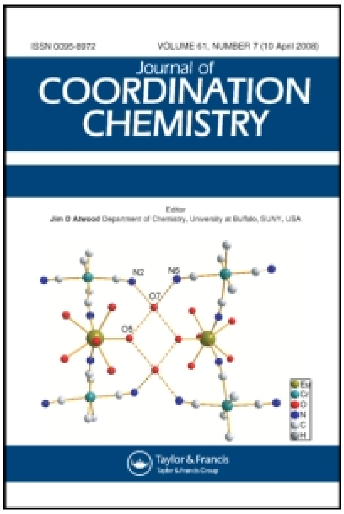

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND SPECTROSCOPIC STUDIES OF NEW BIS(N-1-HYDROXY-2, 6-DI-TERT-BUTYLPHENYL-SALICYLIDENEAMINATO)COBALT(II) COMPLEXES AND THEIR OXIDATION WITH PbO_2

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To cite this Article Kasumov, Veli T. , Karabulut, Bünyamin , Kartal, Ibrahim and Köksal, Fevzi(2001) 'SYNTHESIS AND SPECTROSCOPIC STUDIES OF NEW BIS(N-1-HYDROXY-2, 6-DI-TERT-BUTYLPHENYL-SALICYLIDENEAMINATO)COBALT(II) COMPLEXES AND THEIR OXIDATION WITH PbO_2', Journal of Coordination Chemistry, 52: 4, 289 — 304

To link to this Article: DOI: 10.1080/00958970108028179

URL: http://dx.doi.org/10.1080/00958970108028179

J. Coord. Chem., 2001, Vol. 52, pp. 289–304
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SYNTHESIS AND SPECTROSCOPIC STUDIES OF NEW BIS(N-1-HYDROXY-2, 6-DI-TERT-BUTYLPHENYL-SALICYLIDENEAMINATO)COBALT(II) COMPLEXES AND THEIR OXIDATION WITH PbO_2

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(Received 9 November 1999; In final form 5 April 2000)

A series of new bis(N-(1-OH-2,6-di-tert-butylphenyl)salicylaldiminato)cobalt(II) complexes possessing one or two HO- and CH_3O- substituents on the salicylaldehyde moiety were prepared, and their spectroscopic properties as well as oxidation with PbO_2 were examined. ESR data indicate that oxidation of the complexes produces stable phenoxyl radicals. All phenoxyl radicals have similar *g*-values and hyperfine coupling constants, which were less influenced by the substituents and coordination. The experimental observations indicate that some $Co(L_x)_2$ radical ligand complexes are ligand-localized and there is not much contribution from the metal *d*-orbitals to the values of the *g*-factors. We were also able to observe satellite peaks from the ^{13}C nuclei in the aromatic ring. ESR spectra of some complexes during the time showed the partial conversion of primary radicals to secondary paramagnetic species exhibiting interaction of the radical center with $^{59}Co(I = 7/2)$ and ^{14}N nuclei.

Keywords: Redox-reactivity; SalicylaldiminatesCo(II); ESR spectra; Optical spectra; Radical intermediates

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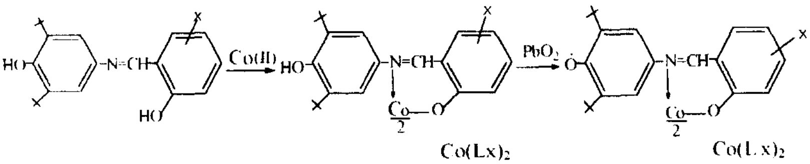
INTRODUCTION

Oxidation processes catalyzed by transition-metal complexes capable of activation of substrates and/or reactants by electron transfer reactions from the substrates to the metal centers are of current interest for synthetic problems and biological oxygenation [1, 2]. The ability of the metal ions to control the oxidation potentials of organic molecules by complexing may be significant in biological electron transfer systems.

The fact that sterically hindered phenol and its derivatives can, in principle, undergo a ligandcentered one- or two-electron oxidation, generating a coordinated phenoxyl, coordinated semiquinonate or *p*-quinone, respectively, offers the possibility of preparing chelates with unusual oxidation states [4 – 7].

Previously [5, 8], we reported the unusual reactions of Cl, Br, NO_2-substituted bidentate salicylaldimines containing 2,6-di-tert-butyl-1-hydroxyphenyl fragment with Cu(II), which in contrast to the expected bis(salicylidenaiminato)Cu(II) complexes formed Cu(II) chelates with a tetradentate salicylaldiminate ligand as a result of C – C oxidative coupling of phenols. But complexation of these ligands with Co(II), VO(II), Ni(II), Pd(II) and Zn(II) yielded the expected bis-salicylaldiminates. Their oxidation with PbO_2 leads to the formation of coordinated phenoxyl radicals with different ESR spectra. ESR spectra of the radical intermediates generated by the oxidation of Co(II) complexes were quite different from those obtained for other metal complexes. Nevertheless, the redox behavior of the complexes and their oxidized products are not fully understood. In order to obtain further information on the nature of these radical species we decided to investigate similar metal chelates bearing electron-releasing substituents on salicylaldehyde moiety.

In this paper we report the synthesis, spectroscopic characterization and oxidation behavior of the cobalt(II) complexes obtained from Schiff bases formed from 2,6-di-tert-butyl-1-hydroxyaniline and HO-, CH_3O-substituted salicylaldehide derivatives.



X = H(L_1H), 3-OH(L_2H), 3-OCH_3(L_3H), 4-OH(L_4H), 4-OCH_3(L_5H),
5-OH(L_6H), 5-OCH_3(L_7H), 4, 6-di-OH(L_8H), 3, 4-di-OH(L_9H)

SCHEME 1

EXPERIMENTAL

The elemental analyses were carried out in the Turkish Center Science and Technology Research Council (TÜBITAK) in Gebze. Infrared spectra were recorded on a MATTSON 1000 FTIR spectrophotometer in the region 4000–400 cm^{-1} using KBr discs. Electronic spectra were measured on a Shimadzu UV 160 A spectrophotometer in the 200–1100 nm region in the various solvents. Magnetic susceptibilities were measured by the Faraday technique at room temperature. The apparatus was calibrated by using $Hg[Co(NCS)_4]$. Effective magnetic moments were calculated by the equation, $\mu_{eff} = 2.828[(\chi_M - N_\alpha) \times T)]^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetism by the use of Pascal's constants and N_α-temperature independent paramagnetism $= 60 \times 10^{-6}$ [9]. The ESR spectra were recorded on a Varian E-109 C model X-band spectrometer with 100 kHz frequency modulation. The g-values were determined by comparison with a $g = 2.0036$ of the DPPH sample. The errors for g- and A-parameters of radicals are $\pm$ 0.0002 and $\pm$ 0.005 G, respectively. Oxidation of $Co(L_x)_2$ compounds were carried out by lead dioxide in a sealed, degassed system. The compound (dissolved in 4 mL toluene) and PbO_2 were transferred into separate glass tubes on a vacuum line. Solution was deoxygenated under vacuum (10^{-3} mm Hg) by repeated freeze-pump-thaw cycles. Then 90–110 mg of PbO_2 was suspended in the solution of sample and shaken for 30 under vacuum. After the sedimentation of heterogeneous phase, 1 mL of the solution was taken for ESR measurements. All ESR spectra of the reaction mixtures were recorded at room temperature under vacuum as the oxidation proceeded.

Preparation of the Compounds

Salicylaldehyde and its hydroxy-, methoxy-substituted derivatives and all solvents are commercial (Merck, Fluka, Sigma) products and were used without further purification. 1-hydroxy-2,6-di-tert-butyl-aniline and ligands (L_xH) were prepared as previously described [8, 10].

The analytical and spectroscopic data of L_xH and their oxidation by PbO_2 reported [10]. The electronic spectral data of L_xH in dioxane are given in Table II. The following procedure was used. A slow stream of nitrogen was passed through a stirred solution of corresponding salicylaldimine (3 mmole) refluxed at 65–75°C in ethanol (50–70 mL) and a deoxygenated solution of cobalt(II) acetate tetrahydrate (1.5 mmole) in methanol (10 mL) was added. The mixture was kept hot (60–70°C) with stirring for about 40–50 min under nitrogen and evaporated to 20–25 mL and then left to

TABLE I Physical and analytical data of the complexes

		M.p°C	*Yield*	μ_{eff}	*Elemental analyses, found/calcd, %*		
Compound	*Color*	*(dec.)*	(%)	*(B.M.)*	*C*	*H*	*N*
$Co(L_1)_2$	Brown	270	80	4.49	71.15/72.26	7.57/7.42	3.47/3.96
$Co(L_2)_2$	Reddish Brown	(200)	90	5.25	66.92/68.19	6.35/7.08	2.80/3.78
$Co(L_3)_2$	Green	275	88	4.30	67.20/68.82	6.16/7.35	2.65/3.64
$Co(L_4)_2$	Brown	270	85	5.18	67.93/68.19	6.71/7.08	3.12/3.78
$Co(L_5)_2$	Orange Brown	289	95	4.95	69.23/68.82	7.67/7.35	3.71/3.64
$Co(L_6)_2$	Reddish Brown	(255)	78	5.12	69.25/68.19	7.31/7.08	3.66/3.78
$Co(L_7)_2$	Brown	(190)	90	4.87	66.35/6882	7.32/7.35	3.55/3.64
$Co(L_8)_2$	Reddish Brown	275	70	4.25	64.28/65.36	6.28/6.73	3.78/3.62
$Co(L_9)_2$	Brown	286	82	4.95	64.86/65.36	7.16/6.73	3.26/3.62

TABLE II Electronic Spectral Data for the L_xH Salicylaldimines in dioxane

L_xH	*Electronic spectra* λ_{max} *(log* ε*), nm*
L_1H	244(4.26), 330*, 358(4.21), 375*, 480*
L_2H	240(4.20), 254(4.14), 276(4.24), 338(4.39), 380(3.28), 420(2.44)
L_3H	242(4.12), 254(4.01), 275(4.07), 340(4.26), 380(358), 460(1.95)
L_4H	243(4.32), 279(4.18), 349(4.28), 430(3.52)
L_5H	245(4.37), 282(4.22), 351(4.48), 420*
L_6H	244(4.51), 271(4.18), 344(4.27), 368(4.29)
L_7H	243(4.51), 272(4.17), 320(4.26), 343(4.31), 368(4.36), 395(3.54), 480*
L_8H	253(3.89), 381(4.18)

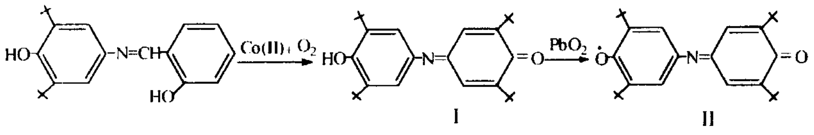
* Shoulder.

cool to room temperature. The precipitated brown-red complex, was filtered, washed with a small amount of methanol and finally with hexane. The crude product was crystallized from acetone–$CHCl_3$ mixture. In the alternative method, the Co(II) complexes also were prepared in a similar manner under atmospheric air conditions. In this case except for the compound synthesized from L_1H, all prepared complexes were identical with those of the corresponding $Co(L_x)_2$ obtained under nitrogen. The physical and analytical data of the complexes are summarized in Table I.

RESULTS AND DISCUSSION

The elemental analyses, magnetic susceptibility measurements, IR and electronic absorption spectral data indicate that the $Co(L_x)_2$ complexes exist as high-spin 1 : 2 metal:ligand stoichiometry. The starting complexes were confirmed by ESR spectroscopy that no Co(II) species was observed even at liquid nitrogen temperature. All complexes can be obtained as orange-brown or red powders and are less soluble in common organic solvents but dissolve appreciably in dioxane and toluene. Comparison of the analytical, magnetic and spectral data indicate that the complexation of L_1H with $Co(acet)_2$ under air, formed indophenol (I)[8] (Scheme 2) instead of the expected $Co(L_1)_2$ complex. More probably in the present oxidative conversion of L_1H to I the Co(II) ion plays catalytic role. The $Co(L_1)_2$ complex was prepared under nitrogen.

The C=N stretching vibrations in the ligands are located in the region 1614–1649 cm^{-1} and are shifted to lower frequencies (1598–1618 cm^{-1}) upon chelation indicating that the azomethine N atom is involved in the Co—N bond formation. The stretching frequency of the sterically hindered OH of L_xH and $Co(L_x)_2$ appears as a sharp strong peak in the range 3440–3637 cm^{-1} and 3482–3648 cm^{-1}, respectively (Tab. III). The appearance of two ν(OH) frequencies, observed for $Co(L_2)_2$ and $Co(L_5)_2$–$Co(L_7)_2$ indicate the existence of sterically hindered OH in different environments or isomers of these complexes. The IR spectra of complexes with hydroxy substituents in the 4- and 5-positions show a broad medium band at *ca.* 3428 cm^{-1} and 3536 cm^{-1} which could be attributed to νOH. In agreement with the data



SCHEME 2

TABLE III IR and Electronic Spectral Data for $Co(L_x)_2$Complexes

	IR spectra (cm^{-1})		
$Co(L_x)_2$	*$\nu C=N$*	*νOH*	*Electronic spectra**, $\lambda_{max}(\log \varepsilon)$, nm*
$Co(L_1)_2$	1610	3614	208, 240, 333, 380, 508
$Co(L_2)_2$	1618	3629, 3646	249(4.66), 327(4.48), 400*, 480*, 750* , 900, $\lambda > 1100$
$Co(L_3)_2$	1619	3626	245(4.57), 317(4.29), 388(4.32), 600*, 690*, 750*, $\lambda > 1100$
$Co(L_4)_2$	1598	3626	245(4.59), 317(4.42), 380(4.38), 600*, 690*, 890, $\lambda > 1100$
$Co(L_5)_2$	1612	3619, 3648	254(4.72), 301(4.42), 381(4.32), 640*, 735, $\lambda > 1100$
$Co(L_6)_2$	1610	3625, 3566^b	246(4.62), 318(4.6), 432(4.27), 698, 870*, $\lambda > 1100$
$Co(L_7)_2$	1602	3621, 3482^b	247(4.69), 317(4.38), 426(4.25), 500*, $\lambda > 1100$
$Co(L_8)_2$	1606	3625, 3578	250, 280*, 354, 500*
$Co(L_9)_2$	1612	3635, 3470	257, 330, 368, 490*

*Shoulder; **in dioxine; ^{b} –broad band.

for other N-aryl-salicylaldimine complexes of Co(II) [11, 12] the new bands at about 650–550 cm^{-1} and 550–420 cm^{-1} for the present compound are assigned to νCo—O and νCo—N stretching frequencies, correspondingly.

The effective magnetic moments (4.25–5.25 B.M.) of the $Co(L_x)_2$ complexes at room temperature per molecule fall in the range 4–5 B.M., which suggests a spin quartet state $S = 3/2$. For Co(II) (d^7) a spin quartet state $S = 3/2$ arises either in a weak field octahedral configuration or in a tetrahedral configuration [13–15]. The electronic spectra of the complexes discussed and the fact that L_xH could be coordinated only as a bidentate ligand suggests that the tetrahedral geometry is most favored for $Co(L_x)_2$.

The electronic spectra of the $Co(L_x)_2$ complexes in dioxane show two or three peaks in the ultraviolet region. The bands beyond 400 nm are very intense ($\log\varepsilon = 4.27-4.72$) and are observed only on complex formation. The band at 380–432 nm seems to be due to both the $\pi \rightarrow \pi^*$ transitions of C=N and a charge-transfer transition arising from π-electron interaction between metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer [14–16]. The observed bathochromic shift in the higher-energy spectral bands is probably caused by the electron transfer from the metal to the ligand [16]. This is in agreement with both the strong electron-acceptor properties of the imine group of the salicylaldimine ligand and the relative ease of oxidation of the cobalt(II) chelates. The spectra of some complexes show low intensity shoulders at *ca.* 500–670 nm that is probably due to *d–d* transitions. The spectra of $Co(L_2)_2-Co(L_7)_2$ complexes along with maximum at 900 and 735 nm, also show another band in the near-IR region $\lambda_{max} > 1100$ nm (Tab. II and Fig. 1). Although the spectral region of the spectrophotometer does not allow us to determine the absorption bands higher than 1100 nm (Fig. 1), the μ_{eff} values of $Co(L_x)_2$ and the similarity of their absorption spectra with those for known bis(N-aryl-salicylideneaminato)cobalt(II) [15, 16], probably indicate that all these complexes possess tetrahedral coordination around the Co(II) ion. The shoulders in the range 500–670 nm and absorption maximum at about 690–900 nm may be tentatively assigned as $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$ (P) transitions, respectively [16]. It is necessary to note that the electronic spectra are in good agreement with tetrahedral geometry, though the possibility of a penta- and hexacoordinated adduct structure of $Co(L_x)_2$ complexes with dioxane cannot be ruled out completely. Comparison of the electronic spectra of the L_xH ligands (Tab. II) and their $Co(L_x)_2$ (Tab. III) complexes measured in dioxane solution indicate that some bands in the

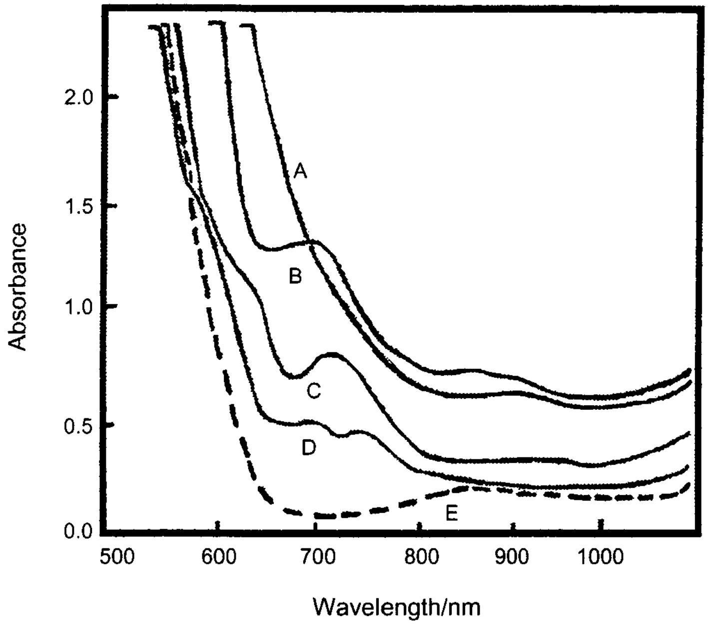


FIGURE 1 Absorption spectra of $Co(L_2)_2$ (A), $Co(L_6)_2$ (B), $Co(L_5)_2$ (C), $Co(L_3)_2$ (D) and $Co(L_7)_2$ (E) in dioxane.

ultraviolet region and all bands in the 400–460 nm range of the L_xH disappeared in the spectra of complexes.

Oxidation of $Co(L_x)_2$

No ESR signals were observed for powders and freshly prepared solutions of $Co(L_x)_2$ at room temperature and 77 K because rapid spin-lattice relaxation of Co^{2+} broadens the lines at higher temperatures [15]. The $Co(L_x)_2$ compounds are readily oxidized with lead dioxide in toluene/$CHCl_3$ solution at room temperature and under vacuum with the formation of stable phenoxyl radicals. In general, while oxidation proceeded the intensity of the signal increased and notable decreasing during 5–6 h was not observed. When the temperature decreased, the intensity of the ESR spectra of $Co(L_x)_2$ decreased markedly and finally a slight asymmetric signal remains at 77 K. In addition, as the sample was heated to room temperature the original spectra regenerated. The substantial decreasing in the intensity of the ESR signal at lower temperature is probably caused by dimerization of the radical centers. At the same time, the ESR spectra of the reaction mixture did not reveal a triplet state biradical species, for which the appearance of two sets of $\Delta m = 1$ lines, about $g = 2$, as well as a half-field $\Delta m = 2$ signal were expected.

The oxidation of $Co(L_1)_2$ with PbO_2 at room temperature in benzene solution immediately leads to formation of the stable paramagnetic species and its spectrum is given in Figure 2a. This spectrum consists of two superimposed signals with closer intensity. One has a triplet pattern spacing of 4.25 G in which each component shows additional less resolved hfs constant of 0.98 G and centered at $g = 2.0049$, probably, arising from the phenoxyl radical. Another signal centered at $g = 2.0094$ consists of 27 equidistant lines with spacing of 1.975 G. The observed hyperfine structure may be interpreted if it is assumed that the splitting arises from the interaction of the unpaired electron with $^{59}Co(I = 7/2)$, one $^{14}N(= 1)$ and one azomethine proton nucleus with $A^{H}_{CH} = A^{N}$ and $A^{Co} = 3\ A^{N}$. In this case from the spectra the $A^{H}_{CH} = A^{N} = 1.975\,G$, $A^{Co} = 5.93\,G$ values can be estimated. At the same time, when the spectrum of this sample was recorded after standing 3 h under vacuum, its phenoxyl part disappeared completely and only the 27-line signal with the practically unchanged ESR parameters remains (Fig. 2b). A low intensity asymmetric signal ($g = 2.009$) with the absence of hyperfine structure were observed at 77 K. No solid matter was found in ESR tubes excluding the possibility that the radical species might decay to a Co(salicylaldehide)$_2$ type complex and another radical product.

Oxidation of the $Co(L_2)_2$, $Co(L_5)_2$, $Co(L_6)_2$ complexes in toluene/chloroform solutions immediately leads to formation of the radical species having a well-resolved nine-line ESR signal ($g = 2.0045-2.0052$) of spacing 1.063 G with an intensity distribution approximately 1 : 4 : 7 : 8 : 8 : 8 : 7 : 4 : 1 ratio. The ESR spectra of these radicals are shown in Figure 3. At both sides of these symmetric ESR spectra the low intensity five satellite lines arising from ^{13}C isotopes in natural abundance (Figs. 3(a) – (c)) have been observed. It is interesting that these spectra were identical with spectrum II (Coppinger's radical), which was formed by the oxidation of indophenol I (Scheme 2). The observed nine-line spectrum may be easily analyzed by assuming that the unpaired electron spin density interacts with one nitrogen and four equivalent meta-protons of II with the values of hfsc related by $A^{H}_{m} = 1/2A^{N}$. At the same time, the simultaneous observation of a secondary radical without any evidence of primary radicals seems to be less likely. In addition, unlike II, when the mentioned radicals standing in air were shaken, the intensity of their spectra slightly decreases. We suggest that another alternative explanation for the observed spectral pattern may be interaction of the unpaired electron with one azomethine proton, one nitrogen nucleus and three equivalent (two *meta*-protons on the phenoxy

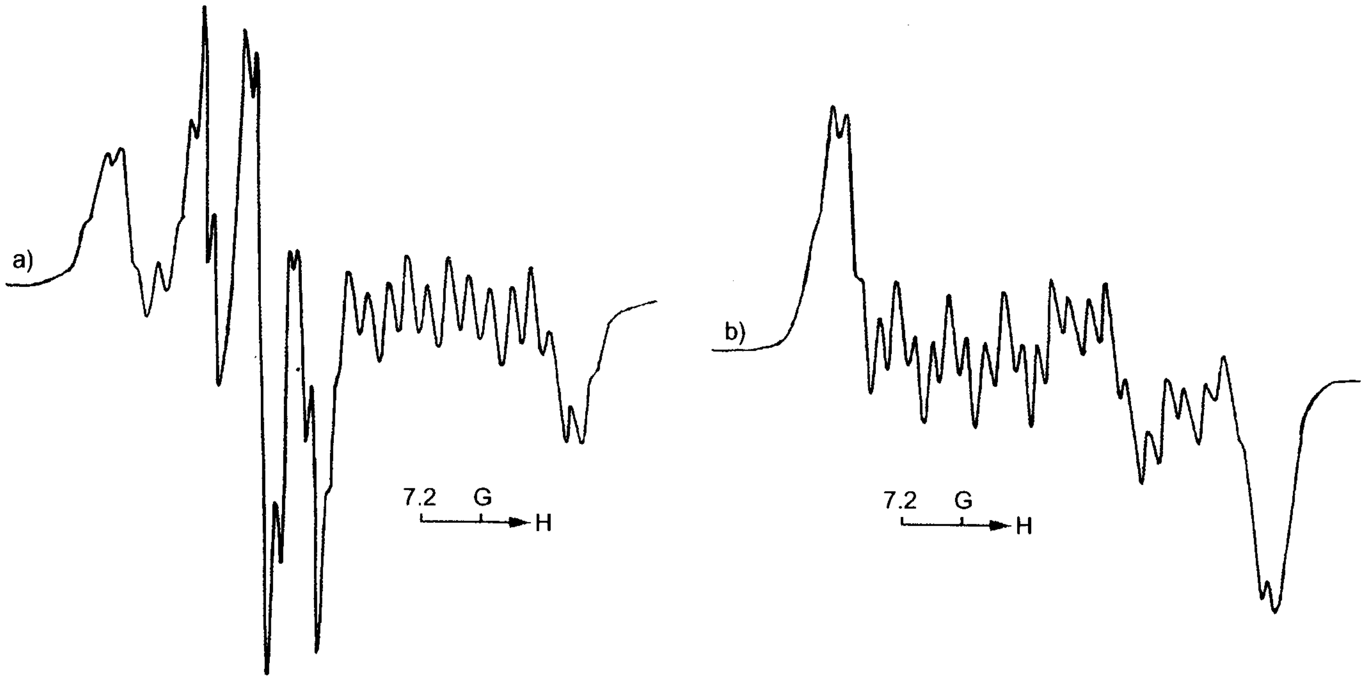


FIGURE 2 ESR spectra observed in the oxidation of $Co(L_1)_2$ with PbO_2 in benzene at room temperature: (a) initial stage spectrum; (b) after 2 h.

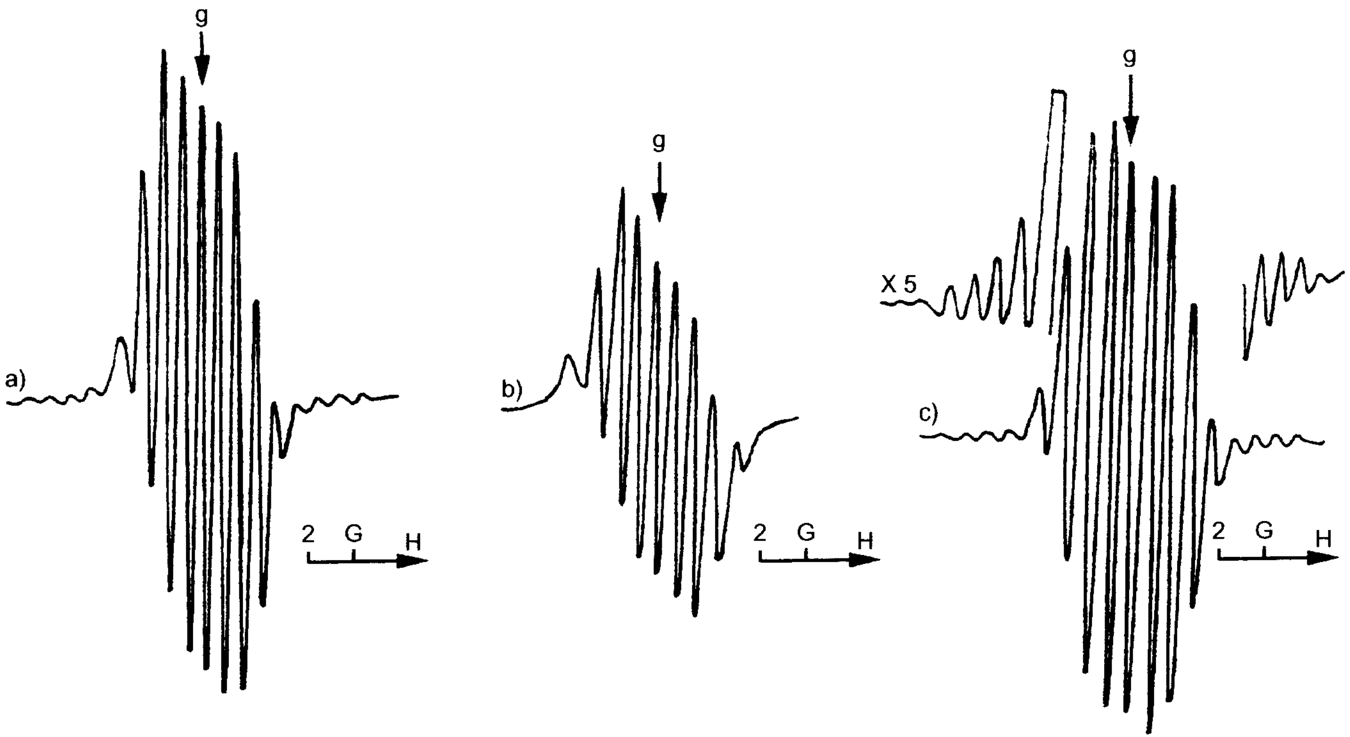


FIGURE 3 ESR spectra of $Co(L_2)_2$ (a), $Co(L_5)_2$ (b) and $Co(L_6)_2$ (c) in toluene/chloroform solutions at room temperature.

ring and one proton in the 6-position of the salicylaldehide ring) by assuming $A_m^H = A_{sal}^H = A^N = 1/3A_{CH}^H$. The simulation of these spectra, which were obtained using a computer program of McKelvey [14c], is shown in Figure 4. A match of the computed plot with the experimental spectra was obtained with the hfsc $A_{CH}^H = 3.075$ G (1H), $A_m^H = 1.025$ G (2H), $A_{Sal}^H = 1.025$ G (1H), $A^N = 1.025$ G (1N) and a line width of 0.2 G. The simulated spectrum does not reflect the observed satellite lines of ^{13}C coupling of 1.025 G. In the ESR spectra of these systems additional hyperfine coupling with the $^{59}Co(I = 7/2)$ nucleus from delocalization of the unpaired electron is not observed. No further change in the ESR spectra were noted on keeping these reaction mixtures under vacuum overnight.

The one-electron oxidation of Co(L$_3$)$_2$ with PbO$_2$ in toluene/CHCl$_3$ solution leads to formation of the coordinated phenoxyl radical centered at

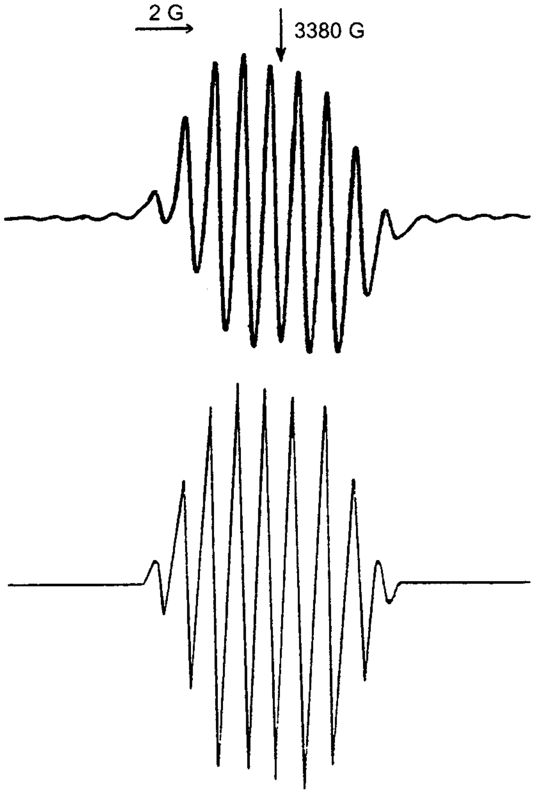


FIGURE 4 Experimental ESR spectrum of Co(L$_6$)$_2$ (top) in toluene/chloroform temperature 300 K and its simulation (below).

$g = 2.0048$. The ESR spectrum consists of 10 equidistant lines with spacing of 1.125 G. We did not observe additional lines when the modulation amplitude is varied over a range of 0.1 – 2 G. The spectrum was analyzed by assuming that the unpaired electron spin density interacts with one nitrogen and three sets of four hydrogens, which hfsc related as $A^{\mathrm{H}}_{\mathrm{CH}} = A^{\mathrm{N}} = 2A^{\mathrm{H}}_{m} = 2A^{\mathrm{H}}_{\mathrm{sal}}$($A^{\mathrm{H}}_{\mathrm{CH}} = 2.05$ G (1H), $A^{\mathrm{H}}_{m} = 1.025$ G (2H), $A^{\mathrm{H}}_{\mathrm{Sal}} = 1.025$ G and $A^{\mathrm{N}} = 1.025$ G). It is interesting that when the reaction mixture was allowed to stand at room temperature and under vacuum overnight (~20 h), the spectrum along with the above ten-line signal also shows a new low intensity octet centered at $g = 2.00$ with a ^{59}Co hyperfine coupling constant of 11G. No further splitting of this eight-line pattern from coupling of ^{14}N and proton was observed.

The spectrum of oxidized $\mathrm{Co(L_4)_2}$ in $\mathrm{CHCl_3}$ differs from all the other experimentally observed radical spectra and has an unresolved ESR signal centered at $g = 2.0049$ with $\Delta H = 6$ G. It is probable that the observed broadening of radical signal arises from intramolecular interaction of the radical centers with the unpaired electron of Co(II), and as a consequence of this the ESR spectrum of radical species occurs as a singlet. Another alternative reason of this phenomenon may be intermolecular exchange between radical centers. If interconversion rates of isomeric forms are much lower or comparable to the ESR time scale, a relative sharpening or broadening of the spectrum must be expected. At the same time, in the oxidation of this complex in toluene solution a slightly asymmetric well resolved nine-line spectrum centered at $g = 2.0044$ and hfsc $A^{\mathrm{H}} = 1.1$ G was observed.

Oxidation of the complex $\mathrm{Co(L_7)_2}$ with $\mathrm{PbO_2}$ in toluene solution leads to the formation of radical species with an ESR spectrum which consists of nine well resolved lines with spacing of 1.125 G ($g = 2.0047$) with an intensity distribution close to 1 : 4 : 7 : 8 : 8 : 8 : 7 : 4 : 1 (Fig. 5a). Five additional low intensity satellite lines are also observed at both ends of this spectrum, probably, arising from ^{13}C isotopes in natural abundance. The observation of a nine-line splitting pattern seems to suggest a ligand-based $\mathrm{Co(L_7)_2}$ radical. The observed intensity distribution was analyzed in terms of an interaction of the unpaired electron with one nitrogen nucleus ($A^{\mathrm{N}} = 1.125$ G) and three sets of four protons [$A^{\mathrm{H}}_{\mathrm{CH}} = 4.5$ G (1H), $A^{\mathrm{H}}_{m} = 2.25$ G (2H) and $A^{\mathrm{H}}_{\mathrm{Sal}} = 1.125$ G (H)]. When the reaction mixture was allowed to stand at room temperature under vacuum overnight (~16 h), the spectrum of this sample showed along with the nine-line signal new low intensity octet of triplets (1 : 1 : 1) centered at $g = 2.00$ (Fig. 5b). The hyperfine splitting pattern of this signal is consistent with a coupling of the unpaired electron

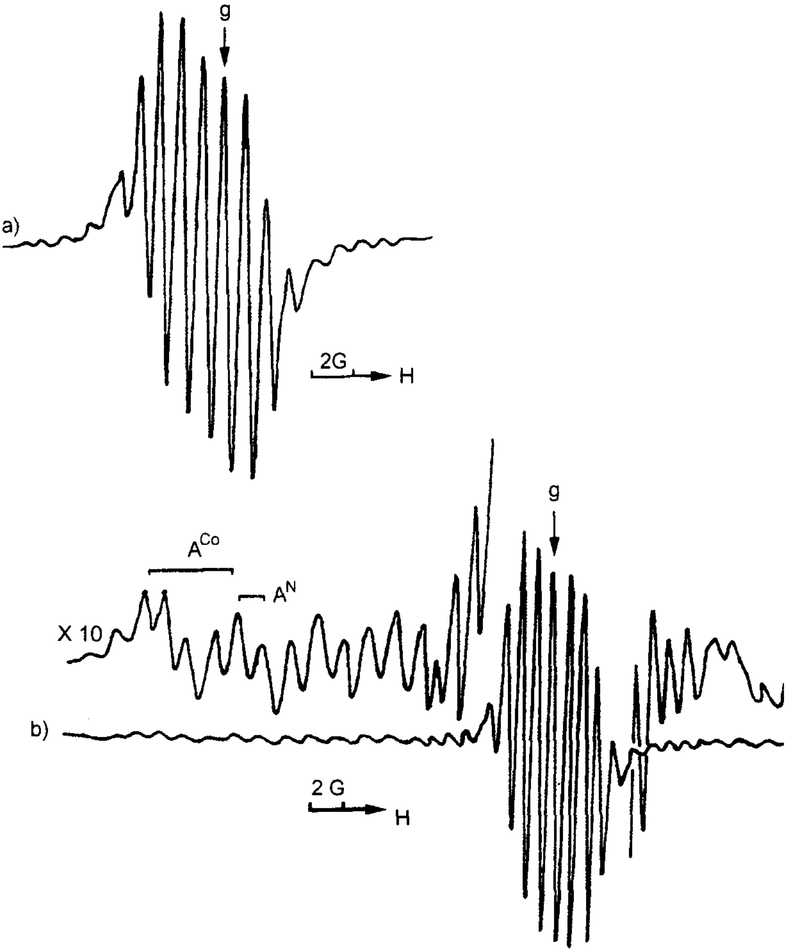
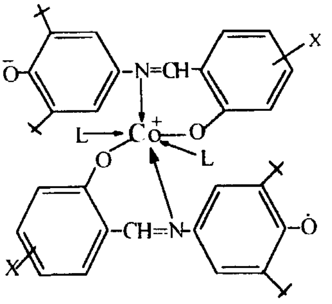


FIGURE 5 ESR spectra observed in the oxidation of $Co(L_7)_2$ with PbO_2 in toluene solution at room temperature: initial stage spectrum (a); spectrum recorded after 16 h under vacuum and at room temperature (b).

with $^{59}Co(I=7/2)$ and $^{14}N(I=1)$ nuclei ($A^{Co}=11\,G$, $A^N=1.1\,G$). The appearance of cobalt nucleus splitting of 11 G indicates that the highest occupied MO has approximately 20% metal character. Note that similar ESR spectra have also been observed in oxidation of bis(N-(1-hydroxy-2.6-di-tert-butyl-phenyl)-2-hydroxy-naphthaldiminato)Co(II) by PbO_2 ($g=1.998$, $A^{Co}=6.92$, $A^N=A^H=1.78$) [17]. No splitting was observed from the *tert*-butyl groups for any of the radicals. A possible explanation for the small coupling constant in $Co(L_x)_2$ radicals is a large twist angle. It is known that conjugation between the phenoxy ring and the *para* substituent depends on the twist angle, between the plane of the phenoxy ring and a plane projected through the N=CH-Sal group. If the twist angle is large, conjugation between these two moieties of the molecule is reduced [18, 19]. It should be noted that the x-ray structural analysis of bis[N-(2,6-di-tert-butyl-l-methoxyphenyl)salicylaldiminato]Cu(II), which has nearly the same ligand as in $Co(L_x)_2$ complexes, shows that the twist angle between N-phenyl ring and —N= CH-Sal group is 82.7° [20]. The conjugation of the C= N bond to the phenolic ring plays an important role in the interaction of the radical centers in $Co(L_x)_2$. The values of cobalt hyperfine coupling constants in the present Co(III)-phenoxyl radicals is the same range of the Co(III)-o-semiquinone system [21–27], and are much smaller than low-spin Co(II) complexes [3].

The octet signal arises from the complex of diamagnetic Co(III) ions coordinated with the phenoxyl radical anion as a result of the Co(II) → ligand electron transfer. An alternative structure for the Co(III) radical intermediate may be shown as III.



III

L-solvent

X= H, 3-OCH3, 5-OCH3

SCHEME 3

The generated radicals III are stable more than 2–3 days and did not disappear even after heating the reaction mixture to 340 K. No changes in the isotropic coupling constants for any of these radicals are observed at these temperatures. The nitrogen splitting in these radicals is smaller than nitroxide radicals and the major splitting is produced by the azomethine proton. The small coupling constant indicates that the phenoxy ring contains the largest unpaired electron spin density. For all these radicals no half-field forbidden signal ($\Delta M = 2$) which is characteristic for triplet state biradicals was observed. The absence of the characteristic triplet state signal, indicates that there is a weak spin-exchange interaction between radical centers in the present Co-containing phenoxyl radicals. The fact that the isotropic hyperfine coupling to ^{14}N and ^{1}H are almost identical and independent of the nature and position of the substituents on the salicylaldehyde moiety for a series $Co(L_x)_2$ radicals suggest that the unpaired electron is localized predominantly on the phenoxyl ring of the ligands. No splitting was observed from the tert-butyl groups for any of these radicals. On the other hand, the similarity in shape, number of lines and values of hyperfine coupling constants of the spectra under consideration with spectra obtained from the corresponding oxidized free ligands also confirmed the localization of unpaired electron on phenoxy ring. Although great numbers of phenoxyl radicals have been studied [4, 19, 28], the appearance of ^{13}C hyperfine splitting in the ESR spectra of phenoxyl type radicals is observed in very few cases [28b]. According to theory developed by Karpuls and Fraenkel [29], the magnitude of the ^{13}C splitting depends upon the spin density both at the carbon atom in question and at neighboring carbons in the π system. The small values of the isotropic ^{14}N-hfs constants in a series $Co(L_x)_2$ is an indication that there is a very little direct spin density in the nitrogen s orbital.

CONCLUSIONS

In conclusion we can state that chemical oxidation of bis(N-(1-hydroxy-2,6-di-tert-butylphenyl)salicylideneaminato)cobalt(II) complexes produces various stable free radical species. The unpaired electron is localized predominantly on the ligand in these kinds of radicals. The hyperfine coupling constants and g-factors of these radicals are less influenced by coordination or by the nature and positions of the substituents in salicylaldehide moiety. ESR spectra of some complexes showed the partial conversion of primary radicals to secondary paramagnetic species exhibiting interaction of the radical center with $^{59}Co(I = 7/2)$ and $^{14}N(I = 1)$ nuclei. There is not ESR evidence indicating the existence of a strong exchange interaction between two radical centers on phenoxyl rings in $Co(L_x)_2$ radical complexes. We were also able to observe satellite peaks from the ^{13}C nuclei in the aromatic ring.

Acknowledgments

We thank the Turkish Center Science and Technology Research Council (TÜBITAK) for financial support (Grant TBAG-1424) of this research.

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