Synthesis and Spectroscopic Studies of New Bis(N-1-hydroxy-2,6-di-tert-butylphenyl-salicylideneaminato)cobalt(II) Complexes and their Oxidation with PbO₂

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A series of new bis[N-(1-OH-2,6-di-tert-butylphenyl)salicylaldiminato]cobalt(II) complexes possessing one or two HO- and CH₃O-substituents on the salicylaldehyde moiety were prepared, and their spectroscopic properties as well as their oxidation with PbO₂ 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 are influenced very little by the substituents and by coordination. The experimental observations indicate that the Co(Lₓ)₂ radicals are ligand-localized and that there is no notable contribution from the metal d-orbitals to the values of the g-factors. Satellite peaks from the ¹³C nuclei in the aromatic ring were also observed. The ESR spectra of some of the complexes showed partial conversion of primary radicals to secondary paramagnetic species exhibiting interaction with ⁵⁹Co(I = 7/2) and ¹⁴N nuclei.

Introduction

Oxidation processes catalyzed by transition-metal complexes capable to activate substrates and/or reactants by electron transfer reactions from the substrates to the metal centers are of current interest from viewpoints of synthetic problems [1, 2]. The ability of metal ions to control the oxidation potentials of organic molecules by complexation also plays a significant role in biological electron transfer systems. Examples are transition metal complexes containing sterically hindered phenol (SHP) fragments. The fact that SHP’s can undergo one- or two-electron oxidations, to the phenoxyl or quinone, respectively, offers the possibility of preparing chelates with unusual oxidation states [5–8].

Previously [5], we reported the unusual reactions of Cl-, Br-, NO₂-substituted bidentate salicylaldimines containing 2,6-di-tert-butyl-1-hydroxyphenyl fragments with Cu(II), which instead of the expected bis(salicylideneaminato)copper(II) complexes formed Cu(II) chelates with a tetradeinate salicylaldiminate ligand as a result of C-C oxidative coupling of phenols moieties. Complexation of these ligands with Co(II), VO(IV), Ni(II), Pd(II) and Zn(II), however, yielded the corresponding expected bis-salicylaldimimates. Their oxidation with PbO₂ leads to the formation of coordinated phenoxyl radicals with different ESR spectra. The ESR spectra of the radical intermediates generated by the oxidation of Co(II) complexes were quite different from those obtained for other metal complexes. The redox behaviour 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 the 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-hydroxynaphthalene and HO-, CH₃O-substituted salicylaldehyde derivatives.

Experimental

The elemental analyses were carried out in the Turkish Center of the Science and Technology Research Council (TÜBİTAK) 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 various solvents. Magnetic susceptibilities were measured by the Faraday technique at room temperature. The apparatus was calibrated using Hg[Co(NCS)4]. Effective magnetic moments were calculated by the equation, \( \mu_{\text{eff}} = 2.828 \sqrt{\chi_M \tau} \), where \( \chi_M \) is the molar magnetic susceptibility corrected for diamagnetism by the use of Pascal’s constants [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 \( g = 2.0036 \) of a DPPH sample. The errors for g- and A-parameters of radicals are ± 0.0002 and ± 0.005 G, respectively. Oxidation of Co(Lx)2 compounds was carried out by lead dioxide in a sealed, degassed system. The compound (dissolved in 4 ml of toluene) and PbO2 were transferred into separate glass tubes on a vacuum line. The solution was deoxygenated under vacuum (10⁻³ mm Hg) by repeated freeze-pump-thaw cycles. Then 90–110 mg of PbO2 was suspended in the solution of the sample and shaken for 30 s under vacuum. After the sedimentation of a 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, its hydroxy- and methoxy-substituted derivatives, Co(OAc)2·4H₂O, and all solvents were commercial (Merck, Fluka, Sigma) products and used without further purification. 1-Hydroxy-2,6-di-tert-butyl-aniline and ligands (LxH) were prepared as previously described [5, 10]. The analytical and spectroscopic data of LxH and their oxidation by PbO2 have been reported [10]. The electronic spectral data of LxH in dioxane are given in Table 1.

<table>
<thead>
<tr>
<th>LxH</th>
<th>Electronic spectra ( \lambda_{\text{max}} ) (log ε), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1H</td>
<td>244(4.26), 330*, 358(4.21), 375*, 480*</td>
</tr>
<tr>
<td>L2H</td>
<td>240(4.20), 254(4.14), 276(4.24), 338(4.39), 380(3.28), 420(2.44)</td>
</tr>
<tr>
<td>L3H</td>
<td>242(4.12), 254(4.01), 275(4.07), 340(4.26), 380(3.58), 460(1.95)</td>
</tr>
<tr>
<td>L4H</td>
<td>243(4.32), 279(4.18), 349(4.28), 430(3.52)</td>
</tr>
<tr>
<td>L5H</td>
<td>245(4.37), 282(4.22), 351(4.48), 420*</td>
</tr>
<tr>
<td>L6H</td>
<td>244(4.51), 271(4.18), 344(4.27), 368(4.29)</td>
</tr>
<tr>
<td>L7H</td>
<td>245(4.51), 272(4.17), 320(4.26), 343(4.31), 368(4.36), 395(3.54), 480*</td>
</tr>
<tr>
<td>L8H</td>
<td>253(3.89), 381(4.18)</td>
</tr>
</tbody>
</table>

* Shoulder.

Co(Lx)2 complexes were prepared by the following procedure: A slow stream of nitrogen was passed through a stirred solution of the 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 heated at ca. 60–65 °C with stirring for about 40–50 min under nitrogen and evaporation to 20–25 ml left to 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 an acetone-CHCl₃ mixture, yield 78–95%. Analysis for Co(L1)₂: M.p. 270 °C. –UV/vis (dioxane): \( \lambda_{\text{max}} = 208, 240, 333, 380, 508 \text{ nm} \). – IR (pellet): \( v = 1610 \text{ (CH=N)} \), 3610 cm⁻¹ (O-H). – \( \mu_{\text{eff}} = 4.47 \text{ B. M.} \). – C₄₂H₅₂N₂O₄Co: calcld. C 72.26, H 7.42, N 3.96; found C 71.15, H 7.57, N 3.47.

In the alternative method, the Co(II) complexes were prepared in a similar manner under atmospheric air conditions. In this case, except for the compound synthesized from L1H, all complexes were identical with those of the corresponding Co(Lx)₂ compounds obtained under nitrogen. The
Table 2. Physical and analytical data for the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>M.p.°C</th>
<th>Yield (%)</th>
<th>μ\text{eff} (B.M.)</th>
<th>Elemental analyses, found/calcd [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(dec.)</td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Co(L₁)₂</td>
<td>brown</td>
<td>270</td>
<td>80</td>
<td>4.49</td>
<td>71.15/72.26</td>
</tr>
<tr>
<td>Co(L₂)₂</td>
<td>reddish brown</td>
<td>(200)</td>
<td>90</td>
<td>5.25</td>
<td>66.92/68.19</td>
</tr>
<tr>
<td>Co(L₃)₂</td>
<td>green</td>
<td>275</td>
<td>88</td>
<td>4.30</td>
<td>67.20/68.82</td>
</tr>
<tr>
<td>Co(L₄)₂</td>
<td>brown</td>
<td>270</td>
<td>85</td>
<td>5.18</td>
<td>67.93/68.19</td>
</tr>
<tr>
<td>Co(L₅)₂</td>
<td>orange brown</td>
<td>289</td>
<td>95</td>
<td>4.95</td>
<td>69.23/68.82</td>
</tr>
<tr>
<td>Co(L₆)₂</td>
<td>reddish brown</td>
<td>(255)</td>
<td>78</td>
<td>5.12</td>
<td>69.25/68.19</td>
</tr>
<tr>
<td>Co(L₇)₂</td>
<td>brown</td>
<td>(190)</td>
<td>90</td>
<td>4.87</td>
<td>66.35/6882</td>
</tr>
<tr>
<td>Co(L₈)₂</td>
<td>reddish brown</td>
<td>275</td>
<td>70</td>
<td>4.25</td>
<td>64.28/65.36</td>
</tr>
<tr>
<td>Co(L₉)₂</td>
<td>brown</td>
<td>286</td>
<td>82</td>
<td>4.95</td>
<td>64.86/65.36</td>
</tr>
</tbody>
</table>

Results and Discussion

The elemental analyses, magnetic susceptibility measurements, IR and electronic absorption spectral data indicate that the Co(Lₓ)₂ complexes exist in the high-spin 1:2 metal:ligand stoichiometry. ESR spectra of the starting complexes confirmed that no Co(II) species is present even at liquid nitrogen temperature. All complexes can be obtained as orange-brown or red powders and are sparingly soluble in common organic solvents but dissolve appreciably in dioxane and toluene. The comparison of analytical, magnetic and spectral data indicates that the attempted complexation of LₓH with Co(OAc)₂ in air gives instead of the expected Co(L₁)₂ complex – a red organic compound identified as indophenol (I) [8] (Scheme 2). In the oxidative conversion of LₓH to I the Co(II) ion probably plays as catalytic role. The Co(L₁)₂ complex was finally prepared under nitrogen atmosphere.

The C=N stretching vibrations of the ligands are located in the region 1614–1649 cm⁻¹ and are shifted to lower frequencies (1598–1618 cm⁻¹) upon chelation, which is consistent with coordination through the azomethine nitrogen atoms of the ligands. The stretching frequency of the sterically hindered OH of LₓH and Co(L₅)₂ appears as a sharp strong peak in the range 3440–3637 cm⁻¹ and 3482–3648 cm⁻¹, respectively (Table 3). The appearance of two ν(OH) frequencies, observed for Co(L₂)₂ and Co(L₅)₂ - Co(L₇)₂, indicate the existence of sterically hindered OH in different environments, or of 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 and 3536 cm⁻¹ which can be attributed to νOH. In agreement with the data for other N-aryl-salicylaldimine complexes of Co(II) [11, 12], the bands at about 650–550 and 550–420 cm⁻¹ for the present compounds are assigned to νCo-O and νCo-N stretching frequencies, correspondingly.

The effective magnetic moments (4.25–5.25 B. M.) of the Co(L₅)₂ complexes at room temperature per molecule fall in the range 4–5 B. M., which suggest a spin quartet state S = 3/2. For Co(II) (d⁷) 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 and the fact that LₓH

![Scheme 2](image-url)
Table 3. IR and electronic spectral data for Co(Lx)2 complexes.

<table>
<thead>
<tr>
<th>Co(Lx)2</th>
<th>IR spectra (cm⁻¹)</th>
<th>Electronic spectra**, λmax (log ε), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>vC=N</td>
<td>vOH</td>
<td></td>
</tr>
<tr>
<td>Co(L1)2</td>
<td>1610 3614</td>
<td>208, 240, 333, 380, 508</td>
</tr>
<tr>
<td>Co(L2)2</td>
<td>1618 3629, 3646</td>
<td>249(4.66), 327(4.48), 400*, 480*, 750*, 900*, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L3)2</td>
<td>1619 3626</td>
<td>243(4.57), 317(4.29), 388(4.32), 600*, 690*, 750*, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L4)2</td>
<td>1598 3626</td>
<td>245(4.59), 317(4.42), 380(4.38), 600*, 690*, 890*, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L5)2</td>
<td>1612 3619, 3648</td>
<td>254(4.72), 301(4.42), 381(4.32), 640*, 735, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L6)2</td>
<td>1610 3625, 3566</td>
<td>246(4.62), 318(4.6), 432(4.27), 698, 870*, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L7)2</td>
<td>1602 3621, 3482</td>
<td>247(4.69), 317(4.38), 426(4.25), 500*, λ &gt;1100</td>
</tr>
<tr>
<td>Co(L8)2</td>
<td>1606 3625, 3578</td>
<td>250, 280*, 354, 500*</td>
</tr>
<tr>
<td>Co(L9)2</td>
<td>1612 3635, 3470</td>
<td>257, 330, 368, 490*</td>
</tr>
</tbody>
</table>

* Shoulder; ** in dioxine.

could be coordinated only as a bidentate ligand suggests that the tetrahedral geometry is most favored for Co(Lx)2.

The electronic spectra of the Co(Lx)2 complexes in dioxane show two or three peaks in the ultraviolet region. The bands beyond 400 nm are very intense (log ε = 4.27–4.72) and are observed only on complex formation. The band at 380–432 nm seems to be due to both the π→π* transitions of C=N and charge-transfer transition arising from π-electron interactions 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 are 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 easy oxidation of the cobalt(II) chelates. The spectra of some complexes show low intensity shoulders at ca.500–670 nm which are probably due to d-d transitions. The spectra of the Co(L2)2-Co(L7)2 complexes show another band in the near-IR region λmax >1100 nm, along with maximum at 900 and 735 nm (Table 1). Although the spectral region of the spectrophotometer does not allow us to determine the absorption bands higher than 1100 nm (Fig. 1), the μeff values of Co(Lx)2 and the similarity of the absorption spectra with those of known bis(N-aryl-salicylideneaminato)cobalt(II) complexes [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 tentatively be assigned to 4A2→4T2 and 4A2→4T1(P) transitions, respectively.

![Fig. 1. ESR spectra observed in the oxidation of Co(L1)2 with PbO2 in benzene at room temperature: (a) initial stage spectrum; (b) after 2h.](image-url)
tively [16]. Although the electronic spectra are in good agreement with tetrahedral geometry, the possibility of penta- and hexacoordinate adducts of the Co(L\textsuperscript{x})\textsubscript{2} complexes with dioxane cannot be ruled out completely. Comparison of the electronic spectra of the L\textsubscript{x}H ligands (Table 1) and their Co(L\textsubscript{x})\textsubscript{2} (Table 3) complexes measured in dioxane solution indicate that some bands in the ultraviolet region and all bands in the 400–460 nm range of the L\textsubscript{x}H have disappeared in the spectra of complexes.

**Oxidation of Co(L\textsuperscript{x})\textsubscript{2}**

No ESR signals were observed for powders and freshly prepared solutions of Co(L\textsubscript{x})\textsubscript{2} at 300 and at 77 K because rapid spin-lattice relaxation of Co\textsuperscript{2+} broadens the lines at higher temperatures [15]. The Co(L\textsubscript{x})\textsubscript{2} compounds are readily oxidized with lead dioxide in toluene/CHCl\textsubscript{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 no decrease was observed during 5–6 h. When the temperature was lowered, the intensity of the ESR spectra of Co(L\textsubscript{x})\textsubscript{2} decreased markedly and finally a slight asymmetric unresolved signal remained at 77 K. As the sample was heated to room temperature the original spectra was regenerated. The substantial decrease in the intensity of the ESR signal at lower temperature is probably caused by dimerization of the radicals. The ESR spectra of the reaction mixtures did not show any triplet state biradical species, for which the appearance of two sets of \( \Delta m = 1 \) lines, about \( g = 2 \) and a half-field \( \Delta m = 2 \) signal at ca. \( g = 4 \) signal, were expected.

The oxidation of Co(L\textsubscript{1})\textsubscript{2} with PbO\textsubscript{2} at room temperature in benzene solution immediately leads to the formation of the stable paramagnetic species and its spectrum is given in Fig. 1a. This spectrum consists of two superimposed signals with similar intensity. One has a triplet pattern spacing of 4.25 G in which each component shows additional less resolved hfsc 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 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 \( ^{59}\text{Co} = 7/2 \), one \(^{14}\text{N} = 1 \) and one azomethine proton nucleus with \( A_{\text{CH}} = A_{\text{N}} \) and \( A_{\text{Co}} = 3A_{\text{N}} \). In this case from the spectra the \( A_{\text{CH}} = A_{\text{N}} = 1.975 \) G, \( A_{\text{Co}} = 5.93 \) 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 was disappeared completely and only the 27-line signal with the unchanged ESR parameters remains (Fig. 1b). A low intensity asymmetric signal (\( g = 2.009 \)) without of hyperfine structure was observed at 77 K. No solid matter was found in ESR tubes excluding the possibility that the radical species might decay to a Co(salicylaldehyde)\textsubscript{2} type complex and another radical product.

Oxidation of the Co(L\textsubscript{2})\textsubscript{2}, Co(L\textsubscript{5})\textsubscript{2}, Co(L\textsubscript{6})\textsubscript{2} complexes in toluene/chloroform solutions immediately leads to the 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 1:4:7:8:8:7:4:1 ratio. The ESR spectra of these radicals are shown in Fig. 2. At both sides of these symmetric ESR spectra the low intensity five satellite lines arising from \( ^{13}\text{C} \) isotopes in natural abundance (Figs. 2 (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 \( A_{\text{CH}} = 1/2A_{\text{N}} \). At the same time, the simultaneous observation of a secondary radical without any evidence of primary

Fig. 2. ESR spectra of Co(L\textsubscript{2})\textsubscript{2} (a), Co(L\textsubscript{5})\textsubscript{2} (b) and Co(L\textsubscript{6})\textsubscript{2} (c) in toluene/chloroform solutions at 300K.
radicals seems to be less likely. In addition, unlike II, when the mentioned radicals standing in air and 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 phenoxyl ring and one proton in the 6-position of the salicylaldehyde ring) by assuming $A_{m}^H = A_{sal}^H = A_N = 1/3 A_{CH}^H$. The simulation of these spectra, which were obtained using a computer program of McKelvey [14c], is shown in Fig. 3. 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 (1 N) 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 $g = 2.0048$. 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 $A_{CH}^H = A_N = 2A_{m}^H = 2A_{sal}^H$ [A$^H_{CH} = 2.05$ G (1H), $A_{m}^H = 1.025$ G (2H), $A_{sal}^H = 1.025$ G and $A_N = 1.025$ G]. It is interesting that when the reaction mixture was allowed to stand at room temperature and under vacuum overnight (~20 h), the spectrum of this sample along with the above ten-line signal, also show 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 Co(L$^4$)$_2$ in 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. In the oxidation of this complex in toluene solution slightly asymmetric well-resolved nine-line spectrum centered at $g = 2.0044$ and hfsc $A^H = 1.1$ G was observed.

Oxidation of the complex Co(L$^7$)$_2$ with PbO$_2$ in toluene solution leads to the formation of radical species with an ESR spectrum which consists of nine well-resolved lines spacing of 1.125 G ($g = 2.0047$) with an intensity distribution close to 1:4:7:8:8:8:7:4:1 (Fig. 4a). 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 splitting pattern seems to suggest a ligand-based Co(L$^7$)$_2$ radical. The observed intensity distribution was analyzed in terms of an interaction of the unpaired electron with one nitrogen nucleus ($A_N = 1.125$ G) and three sets of four protons.

![Fig. 3. ESR spectrum of Co(L$^6$)$_2$: experimental (top) in toluene/chloroform at 300 K and its simulation (below).](image-url)
Fig. 4. ESR spectra observed in the oxidation of Co(L7)2 with PbO2 in toluene solution at room temperature: initial stage spectrum (a); spectrum recorded after 16 h under vacuum and at room temperature (b).

\[ \Delta H_{CH} = 4.5 \text{ G (1 H)}, \Delta H_{m} = 2.25 \text{ G (2H)} \] and \[ \Delta H_{Sal} = 1.125 \text{ G (H)}. \] 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 a new low intensity octet of triplets (1:1:1) centered at \( g = 2.00 \) (Fig. 4 b). The hyperfine splitting pattern of this signal is consistent with a coupling of the unpaired electron with 59Co (I = 7/2) and 14N (I = 1) nuclei (\( A^{\text{Co}} = 11 \text{ G}, A^{\text{N}} = 1.1 \text{ G} \)). 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 the oxidation of bis[N-(2,6-di-tert-butyl-1-methoxyphenyl)salicylaldiminato]Cu(II), which has nearly the same ligand as in Co(L*)2 complexes, shows that the twist angle between N-phenyl ring and -N=CH-Sal group is 82.7° [21]. 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*)2. The values of cobalt hyperfine coupling constants in the present Co(III)-phenoxy radical is the same range of the Co(III)-o-semiquinone system [22-28], 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 phenoxy radical anion as a result of the Co(II) → ligand electron transfer. An alternative structure for the Co(III)-stabilized radical intermediate may be shown as III (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 lower unpaired electron spin density. For all these radicals no half-field forbidden signal (\( zlM = 2 \)) 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-stabilizing phenoxyl radicals. The fact that the isotropic hyperfine coupling to $^{14}\text{N}$ and $^1\text{H}$ are almost identical and independent of the nature and position of the substituents on the salicylaldehyde moiety for a series $\text{Co}(L^x)_2$ 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 hfsc 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, 29], the appearance of $^{13}\text{C}$ hyperfine splitting in the ESR spectra of phenoxyl type radicals is observed in very few cases [29]. According to theory developed by Karpuls and Fraenkel [30], the magnitude of the $^{13}\text{C}$ splitting depends upon the spin density both at the carbon atom in question and at neighboring carbons in the $\pi$ system. The small values of the isotropic $^{14}\text{N}$-hfsc constants in a series $\text{Co}(L^x)_2$ is an indication that there is a very little direct spin density in the nitrogen $s$ orbital.

**Conclusions**

The 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 very little influenced by coordination or by the nature and positions of the substituents in salicylaldehyde moiety. ESR spectra of some complexes showed the partial conversion of primary radicals to secondary paramagnetic species exhibiting interaction radical center with $^{59}\text{Co}(I = 7/2)$ and $^{14}\text{N}(I = 1)$ nuclei and Copping's type phenoxyl radicals. There is not ESR evidence indicating the existence of a strong exchange interaction between two phenoxyl centers in $\text{Co}(L^x)_2$ radical complexes. Satellite peaks from the $^{13}\text{C}$ nuclei in the aromatic ring were also observed in the ESR spectra of some radicals.

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