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Spectroscopic studies of metal complexes with redox-active hydrogenated Schiff bases

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Abstract

Synthesis and spectroscopic (IR, UV-visible, ESR) characterization of metal(II) complexes $M(L'_x)_2$, (where M = Co(II), NI(II), VO(II), Pd(II), $L'_x = L'_1$, L'_2, L'_3 are monoanion of unsubstituted, 5-Cl and 5-Br substituted-2-hydroxybenzylamine) with redox-active *N*-(3,5-ditert-butyl-4-hydroxyphenyl)-2-hydroxybenzylamine ligands as well as radical species generated from these compounds by the oxidation with PbO_2 are reported. ESR studies indicate that the $VO(L'_x)_2$ and $Ni(L'_x)_2$ complexes, in opposite to their salicylaldimine precursors, are more readily oxidized with lead dioxide and results in the formation of the indophenoxyl type stable radical. The formed radical species are very similar to each other and quite different from those of the salicylaldimine analogous according to their *g*-factors and hyperfine coupling constants. The nine line radical spectra observed in the oxidation of $Co(L'_x)_2$, on standing under vacuum, gradually converted to the signals characteristic of the low-spin Co(II) ($g_{x,y} = 2.276$, $g_z = 1.998$, $A^{Co}_{xy} = 122.7$ G, $A^{Co}_z = 150$ G) and radical containing Co(III) intermediate with $g_{x,y} = 2.015$, $A^{Co}_{xy} = 4.66$ G, $g_z = 1.989$, $A^{Co}_z = 10$ G were also observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Redox-active benzylamine-complexes; Radical species; IR; UV-visible; ESR

1. Introduction

Intramolecular electron transfer is a fundamental chemical phenomenon and relates specifically to biological and catalytic redox processes which occur in natural and synthetic electron transfer systems [1]. The ability of the metal ions to control the oxidation potentials of organic molecules by complexing are significant in redox processes. A particularly interesting class of redox system is provided by chelates of transition metal ions which are capable of oxidizing a coordinated organic figand to the neutral radical. From this viewpoint, one interesting redox-active system consists of transition metal complexes containing sterically hindered phenol fragments. It is well known that sterically hindered phenol derivatives are effective antioxidants against photo-destruction of materials such as polymers, petroleum products, and in the rancidification of fats and oils [2,3]. The fact that sterically hindered phenols can readily undergo one or two-electron transfer offers the possibility of preparing chelates with unusual oxidation states [4].

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Although there have been intensive studies on coordination compounds of salicylaldimines with transition metal ions, relatively little is known about Schiff base chelates containing redox-active fragments. The coordination chemistry of some transition metals with potentially redox-active chelating ligands such as bi-, tri- and tetradentate salicylaldimines, naphthaldi mines, azoligands, β-ketoiminates and other species containing sterically hindered phenol fragments has been studied [4–6]. The present investigation was undertaken to explore the changes which can occur in redox reactivity of L_xH and $M(L_x)_2$ when the –CH = N–group was replaced by saturated –CH_2–NH– linkage in the structure of salicylaldimine. In particular, it is of interest to know to what extent and how this structural change affects the redox properties of free and coordinated benzylamine ligands (L'_xH).

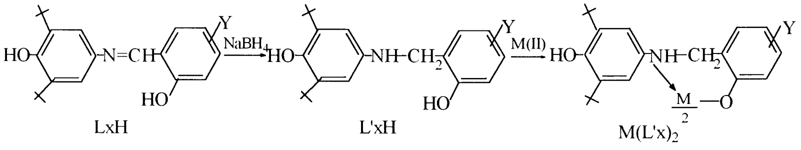
In this paper we describe the coordination and redox chemistry of new complexes of $M(L'_x)_2$ [M = Ni(II), Pd(II), VO(II)] on the basis of the redox-active *N*-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxybenzylamines (L'_xH) ligands, prepared according to Scheme 1.

2. Experimental

Elemental analyses were performed by the Science and Technical Research Council of Turkey (TUBITAK) in Gebze. IR spectra were obtained using a Carl Zeiss Jena Specord M 80 spectrophotometer in the 4000–400 cm^{-1} region as KBr discs. Electronic spectra were recorded on a Carl Zeiss Jena Specord M 40 spectrophotometer in the 200–900 nm region. Magnetic susceptibilities were measured by the Faraday technique at room temperature (25 ± 2°C). The apparatus was calibrated by the use of Hg[Co(SCN)$_4$]. The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants [7]. The ESR spectra of $M(L_x)_2$ 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 A-values of $VO(L_x)_2$. The errors for radical g-factors and hyperfine splitting constant (hfsc) parameters are ± 0.0005 and ± 0.005 G, respectively.

3. Synthesis of ligands and complexes

Salicylaldimines L_xH were synthesized by the method described previously 4a. *N*-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-hydroxybenzylamines (L'_xH) were prepared by using the following procedure: $NaBH_4$ (0.05 mol) was added slowly with 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 continued for another 30–40 min and the mixture, cooled to room temperature, was then poured into 150–200 ml water. The resulting solution was vigorously stirred for 1–1.5 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 vac-



Y= H (L'$_1$H); 5-Cl (L'$_2$H); 5-Br(L'$_3$H)

M= Ni(II), VO(II), Pd(II)

Scheme 1.

Table 1
Analytical data for L'_xH and $M(L'_x)_2$ compounds

Compound	Yields (%)	Color	M.p. (°C)	Elemental analyses, found/calc'd (%)		
				C	H	N
L'_1H	91.5	White	146	74.44/74.71	8.27/8.66	3.78/8.30
L'_2H	92.8	White	149	70.43/67.78	7.42/7.86	7.44/7.53
L'_3H	85.5	White	156	61.19/60.54	6.98/7,02	6.57/6.73
Co(L'_1)$_2$	56.4	Brown	>250	71.56/70.85	7.64/7.93	3.45/3.93
Co(L'_2)$_2$	62.4	Brown	>250	64.35/64.59	6.96/7.23	3.32/3.22
Co(L'_3)$_2$	48.6	Brown	>250	58.45/57.97	5.85/6.26	4.15/3.96
Ni(L'_1)$_2$	65.8	Green	>250	70.98/70.87	7.68/7.93	4.15/3.94
Ni(L'_2)$_2$	63.4	Green	>250	65.38/64.61	6.76/6.98	3.89/3.59
Ni(L'_3)$_2$	71.6	Dark green	>250	49.56/58.05	6.12/6.27	3.32/3.22
Pd(L'_1)$_2$	48.7	Brown	>250	67.12/66.42	7.16/7.44	3.34/3.68
Pd(L'_2)$_2$	52.9	Brown	>250	60.68/60.88	6.49/6.57	3.56/3.38
Pd(L'_3)$_2$	56.4	Brown	>250	54.78/54.98	6.19/5.94	3.56/3.05
VO(L'_1)$_2$	44.67	Green	>250	69.85/70.06	7.47/7.56	4.18/3.89
VO(L'_2)$_2$	56.5	Green	>250	63.67/63.91	6.67/6.91	3,66/3.55
VO(L'_3)$_2$	59.4	Green	>250	58.02/57.45	6.52/6.21	3.34/3.19

uum and recrystallized from hexane-acetone, yielded 85–93%.

The complexes of $M(L_x)_2$ [M = Co(II), Ni(11), VO(II)] were prepared by the following general method. Metal(II) acetate (2 mmol) was dissolved in the minimum volume of methanol (10–15 ml) and added to an equivalent amount L'_xH (4 mmol) in warm methanol (40–50 ml). Soon green or brown crystals were precipitated. After the mixture was warmed at 50–60°C with stirring for 50–60 min and left to cool. The precipitated crystals were by suction filtration, washed with methanol and diethyl ether, and then dried in the open air and recrystallized from methanol–acetone mixture. Pd(L'_x)$_2$ complexes were prepared according to previously reported procedure [6a] using Pd(II) acetate and L'_xH in glacial acetic acid (20–25 ml). Analytical and spectroscopic data of the compounds synthesized are given in the Tables 1–3.

3.1. Generation of radicals

L'_xH and $M(L'_x)_2$ compounds were oxidized as follows. The compound, dissolved in 5 ml toluene or chloroform and PbO_2 (70–90 mg), were transferred into separate glass tubes on vacuum line. Solution was degassed under vacuum (10^{-3}–10^{-4} mmHg) by four to five freeze–pump–thaw cycles. Then degassed solution was mixed with PbO_2 (70–80 mg) and shaken for 30 s at room temperature. After the sedimentation of heterogeneous phase, 1 ml of the solution was introduced into an ESR sample tube for monitoring the spectrum. The ESR spectra taken rapidly after the sedimentation of reaction mixture. Reduction of Pd(L'_x)$_2$ complexes with an excess of PPh_3 was carried out by mixing their degassed $CHCl_3$ solutions at room temperature under vacuum.

4. Results and discussion

The analytical data of the complexes (Table 1) indicate 2:1 (ligand/metal) stoichiometry and hence the figands are behaving as bidentate monobasic anions in the $M(L'_x)_2$ complexes. The examination show a higher complexation ability of hydrogenated L'_xH ligands than that of corresponding salicylaldimines precursors. This behavior is undoubtedly caused by the higher basicity of the nitrogen atom in hydrogenated benzylamine ligands than in their salicylaldimine analogous. Additionally, the Ni(L'_x)$_2$ and VO(L'_x)$_2$ complexes, unlike their salicylaidiminate precursors, were readily oxidized by PbO_2 giving very stable secondary radical. Note that the nonhindered bis(benzylaminato) complexes reported by West [8], does not undergo any oxidative conversion in the interaction with PbO_2. The prepared ligands, except L'_1H, are sensitive to air oxidation even in the solid state. However, the bis(benzylaminato) complexes ($M(L'_x)_2$, are quite stable in air.

5. Infrared spectra

The IR spectra of the complexes provide direct information about the coordination of the ligand via NH nitrogen atom and deprotonated oxygen of the OH group (Table 2). The L_xH spectra exhibit broad medium bands at 3320–3345 cm^{-1} and a sharp strong band at 3610–3640 cm^{-1} due to the ν(NH) and sterically hindered phenolic ν(OH) stretching vibrations, respectively. A strong band in the salicylaldimines in the 1615–1635 cm^{-1} region due to the $\nu(C=N)$ stretch disappeared in the spectra of hydrogenated L'_xH and $M(L'_x)_2$ compounds. A strong band appeared in the IR spectra of L'_xH at 1280–1310 cm^{-1} which was attributed to the hydrogen bond in-plane bending mode, and very weak broad absorption near 2700 cm^{-1} assignable to the intramolecular hydrogen bonding of O–H stretching vibration were not observed in the complexes as a result of the displacement of the acidic proton by the metal ions. The $\nu(V=O)$ frequencies of the $VO(L_x)_2$ complexes occur in the range 910–960 cm^{-1} and this is in the usual range (960 ± 50 cm^{-1}) observed for the majority of VO(11) complexes [9].

6. L_xH benzylamines

The electronic spectra of L'_xH (Table 2) exhibit bands at about 230 and 250–289 nm attributable to the $\pi \rightarrow \pi^*$ transition of benzene rings. The bands in the range 308–314 and 362–365 nm may assigned to $n \rightarrow \pi^*$ charge transfer transition. These CT seems to originate from the OH and NH groups to a phenyl rings of the ligand. The low intensity broad band appeared at 446–454 nm which can be attributed to the bipolar ions formed as a result of the intramolecular proton transfer from OH to NH group, disappeared in the spectra of $M(L'_x)_2$ complexes. In all complexes the intraligand $\pi \rightarrow \pi^*$ band at 230 nm is red shifted and appeared at 248–254 nm (Table 2).

Table 2
Spectroscopic and magnetic data of ligands and their metal complexes

Compound	μ_{ef} M.B.	IR spectra (cm^{-1})		Electronic spectra, λ/nm (εl mol^{-1} cm^{-1})
		ν_{NH}	ν_{OH}	
L'_1H	–	3325	3630	230,289,308,362,454
L'_2H	–	3320	3620	232,250,289,308,365,454
L'_3H	–	3345	3630	230,289,311,364,446
$VO(L'_1)_2$	1.75	3380	3628	255,260,275,288,338,365,485,666,890
$VO(L'_2)_2$	1.78	3398	3640	256,267, 320, 336, 365, 382, 490, 625, 790
$VO(L'_3)_2$	1.73	3385	3615	260,278,289,315,340,365,385,490,665,725
$Co(L'_1)_2$	5.16	3395	3610	3 12, 328, 373, 431, 556 (102)
$Co(L'_2)_2$	4.49	3382	3615	287, 318, 335, 364, 382, 406, 510, 602(124)
$Co(L'_3)_2$	4,46	3379	3625	276,288,335,346,385,417, 500, 610(614)
$Ni(L'_1)_2$	3.36	3388	3620	273, 286, 370, 382, 458, 588, 790 (320)
$Ni(L'_2)_2$	3.32	3390	3649	256,270,322,335,365,381, 515,685(450)
$Ni(L'_3)_2$	3.38	3385	3620	251, 287, 335, 364, 386, 521, 685 (380)
$Pd(L'_1)_2$	Dia.	3395	3620	253,285,317,334,350,362, 373,485,526
$Pd(L'_2)_2$	–	3388	3645	285,317,333,362,382,434, 524
$Pd(L'_3)_2$	–	3395	3620	253,285,317,334,350,362, 373,485,526

Table 3
ESR parameters of $VO(L'_x)_2$ complexes

Compound	g_{iso}	$g_{//}$	$g_{\perp}$	$*A_{iso}$	$*A_{//}$	$*A_{\perp}$	Oxidized complex	
							g	A^{Ha}
$VO(L'_1)_2$	1.996	1.963	2.013	96.3	188.2	50.4	2.0031	1.129
$VO(L'_2)_2$	1.993	1.950	2.003	94.5	182.3	52.3	2.0041	1.129
$VO(L'_3)_2$	1.992	1.950	2.013	94.5	182.8	50.4	2.0034	1.129

[a] In Causs.

In the oxidation of L'_xH with PbO_2 at 300 K in toluene, THF and $CHCl_3$ solutions, the formation of less resolved asymmetric ESR spectra with similar magnetic resonance parameters have been observed. For oxidized L'_1H and L'_2H in $CHCl_3$ or toluene, at room temperature, 7 line ($g = 2.0044$, $A^{\mathrm{H}}_{\mathrm{NH}} = 1.85$ G, $A^{\mathrm{N}} = 3.8$ G) and 5 line ($g = 20046$, $A^{\mathrm{N}} = A^{\mathrm{NH}}_{\mathrm{H}} = 3.82$ G) asymmetric spectral patterns, respectively, were observed. These spectra are quite different from those of the corresponding salicylaldimine ligands [4a,10]. Note that generation of the aminyl radicals in these systems can not be ruled out and it is seems that the observed less resolved unusual spectral features are originated from the aminyl radicals [11]. Aminyl radicals might be formed by removing of the –N–H hydrogen atom by oxidation with PbO_2. On the other hand, relatively less resolved 9-line isotropic spectrum ($g = 2.0049$, $A^{\mathrm{H}}_{\mathrm{m}} = 1.23$ G, $A^{\mathrm{NH}}_{\mathrm{H}} = A^{\mathrm{N}} = 2.46$ G) generated from L'_3H under similar conditions, can be considered as phenoxyl radicals.

7. Bis chelates of VO(11)

On mixing hot methanolic solutions equivmolar amount of L'_xH and $VO(acet)_2$ in a 2:1 ratio, the dark green complex precipitated simultaneously. Upon complexation of L'_xH as evidenced by ESR, unlike parent salicylaldimine analogous, the formation of the radical species were not observed.

The oxovanadium(IV) complexes belong to $S = 1/2$ system and it is expected that the magnetic moments of magnetically dilute oxovanadium(IV) complexes would be very close to the spin-only magnetic moment, as the spin-orbit coupling constant is positive and the orbital contribution is almost completely quenched in oxovanadium(IV) complexes [10a]. The room temperature effective magnetic moments of the $VO(L'_x)_2$ (1.72–1.74 B.M.) are close to that expected [10b], spin-only values of 1.73 B.M. and indicate the magnetically diluted nature and absence of antiferromagnetic exchange interaction in these complexes at room temperature.

The electronic spectra of the $VO(L'_x)_2$ complexes in chloroform (Table 2) exhibit three absorption bands in the range 485–490, 625–666 and 790–890 nm. These bands, according to Ballhausen and Gray molecular orbital scheme [12], are assigned to the $d_{xy} \rightarrow d_{z^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{xz,yz}$ transitions, respectively. This assignment also is agreement with our ESR data. Some charge-transfer bands are also observed at 365–385 mm.

The ESR parameters of $VO(L'_x)_2$ determined direct from the spectra recorded at room temperature (77 K) are presented in Table 3. The room temperature isotropic ESR spectra of $VO(L'_x)_2$ in chloroform consist of the usual eight-line hyperfine pattern resulting from coupling of the unpaired electron to the $^{51}V(I = 7/2)$ nucleus (Fig. 1(a)). There was no observed additional splitting from $^{14}N(I = 1)$ nucleus. The isotropic vanadium electron spin–nuclear spin hyperfine coupling constants (A_{iso}), were obtained by averaging the separation of the $-m_I$ to m_I transitions. The anisotropic spectra of these complexes at 77 K exhibit axial rather than rhombic symmetry (Fig. 1(c)) with the values of $A_z > A_x = A_y$ and $g_z < g_x = g_y$. The following expressions can be used as good approximations for the estimation of g values

$$g_{x,y} = g_{e} - 2\alpha^{2}\gamma^{2}\lambda / E_{xy} \rightarrow E_{xz,yz} \quad (1)$$

$$g_{z} = g_{e} - 8\alpha^{2}\beta^{2}\lambda / E_{xy} \rightarrow E_{x^{2}-y^{2}} \quad (2)$$

where α, β and γ are modified molecular orbital coefficients of the d_{xy}, $d_{x^{2}-y^{2}}$, and d_{xz}, d_{yz} orbitals, respectively, and λ is the spin-orbit coupling constant of the vanadium ion in the complex [13]. The absence of hyperfine splitting from nitrogen nucleus in the ESR spectra, in agreement with Ballhausen and Gray, indicate that the unpaired electron occupies an essentially non-bonding vanadium d_{xy} orbital which is largely metal in character and thus independent of the covalent character of the bonding orbitals.

The one-electron oxidation of $VO(L'_x)_2$ with PbO_2 in $CHCl_3$ at room temperature, unlike their salicylaldiminate VO(II), readily leads to the formation of stable phenoxyl radicals and gradually disappearance of VO(II) signals. These spectral patterns are similar to each other and have quite close g-factors and hfsc values (Table 3), but quite different from those of the radicals generated from L'_xH and parent salicylaldimine ligands. The spectra of all of the radicals generated from $VO(L'_x)_2$ exhibit well resolved equidistant nine-line pattern spacing of 1.129 G with an intensity distribution of 1:4:7:8:9:7:4:1 (Fig. 1(b)). These spectra can be analyzed in terms of an interaction of the unpaired electron spin density with one

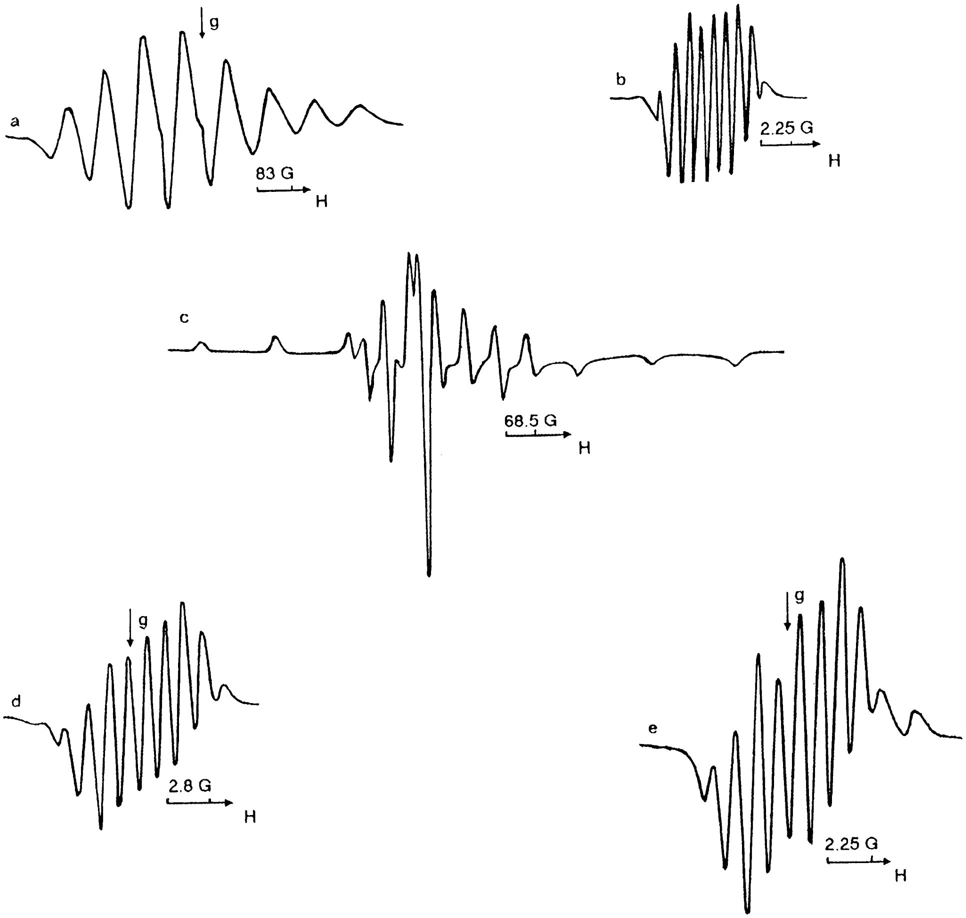


Fig. 1. ESR spectra of $VO(L'_1)_2$. (a) at 300 and (c) 77 K; (b) oxidized sample of $VO(L'_1)_2$ at 300 K, spectra detected for the oxidized samples of $Ni(L'_x)_2$ at 300 K: (d) $Ni(L'_2)_2$, (e) $NI(L'_3)_2$. All spectra recorded in $CHCl_3$.

nitrogen ($A^{N} = 2.22$ G) and two sets of three protons [($A^{H}_{m} = 1.11$ G (2H) and $A^{H}_{NH} = 2.22$ G (1H)] assuming that $A^{N} = A^{H}_{NH} = 2A^{H}_{m}$. It is interesting to note that in the oxidation of parent bis(salicylaidiminato)VO(II) chelates, only for X = H complex the formation of low intensity radical was observed. At the same time, our attempts to oxidize X = Cl, Br, NO_2 bearing bis(salicylaldiminato)VO(II) complexes in various solvents were unsuccessful [4c]. Thus, the hydrogenated $VO(L'_x)_2$ complexes, unlike their salicylaldimine precursors, are readily oxidized with PbO_2 with the formation of the stable phenoxyl radicals.

8. Bis chelates of Ni(II)

All $Ni(L'_x)_2$ complexes are paramagnetic in the solid state with magnetic moments in the range 3.32–3.38 B.M. (Table 1), which are close to those found for tetrahedral Ni(II) complexes [14]. Electronic spectra of $NI(L'_x)_2$ in $CHCl_3$ in the visible region show absorption bands in the range 458–590 and 685–790 nm and according to the values of coefficient extinction ($\varepsilon = 320$–450) can be assigned to $^3T_1 \rightarrow {}^3A_2$ and $^3T_1 \rightarrow {}^3T(P)$ in tetrahedral symmetry [14]. The bands appeared at 364–385 nm, and can be attributed to the ligand-to-metal charge-transfer transitions.

These complexes, unlike their salicylaldimine analogous, rather readily oxidized with PbO_2 in $CHCl_3$ at room temperature giving corresponding radical species. In the oxidation of $Ni(L'_x)_2$ low intensity unresolved signal centered at $g = 2.0038$ was observed. However, under the same conditions, oxidation of $Ni(L'_2)_2$ and $Ni(L'_3)_2$ results in an ESR spectra which consist of equidistant nine- and ten-line patterns (Fig. 1(d) and (e)) with the parameters such as $g = 2.0041$, $A^{H} = 1.013$ G and $g = 2.0038$, $A^{H} = 1.127$ G, respectively. The nine-line spectrum, according to line shapes, number of lines, intensity ratios and the values of g-factors and hfsc (within experimental error) are very similar to those of the oxidized $VO(L_x)_2$ and Pd(II) samples spectra. The highest field component of the spectrum in Fig. 1(e) most probably has another origin and equal spacing nine-line part of this signal is similar to that of the oxidized $NI(L'_2)_2$ sample. Note that essentially similar ESR spectra were also observed in the oxidation of Cu(II) [15] complexes with the same ligands. These experimental observations allow us to conclude that, the observed ESR spectra originated from secondary radical species.

9. Bis chelates of Pd(II)

All the $Pd(L_x)_2$ complexes are diamagnetic, suggesting a square planar geometry for these compounds. The electronic spectra of these compounds are different from those of the parent salicylaldimine Pd(II) chelates. In the electronic spectra of the $Pd(L'_x)_2$ complexes together intraligand absorptions in the UV region, the new bands at 378–385, 434–485 and 515–526 nm were also observed. The bands in the regions of 434–485 and 515–526 nm may be assigned to the $^1A_g \rightarrow {}^1A_{2g}$ and $^1A_g \rightarrow {}^1B_{1g}$ transitions, respectively [16]. The other intense band observed in the UV region at 378–385 nm, probably has metal to ligand charge transfer character.

Upon treatment of $Pd(L'_1)_2$ and $Pd(L'_3)_2$ complexes with PbO_2 in $CHCl_3$ solution under the above mentioned conditions, well resolved ESR spectral patterns having quite close magnetic resonance parameters were observed. In all cases during oxidation the gradually precipitation of the metallic Pd occurred. Upon oxidation of $Pd(L'_1)_2$ and $Pd(L'_3)_2$ complexes, relatively stable radical species exhibiting nine line hyperfine splitting spectral features with an intensity distribution of 1:4:7:8:8:8:7:4:1 and ESR parameters such as $g = 2.0062$, $A^{H} = 1.25$ G and $g = 2.0045$, $A^{H} = 1.223$ G, respectively, were observed (Fig. 2(e)). In the case of oxidized $Pd(L'_2)_2$ sample in $CHCl_3$, at 300 K, the unusual spectrum having unresolved low field wing and a well resolved nine-line pattern on the high field side ($g = 2.0053$, $A^{H} = 1.166$ G) was detected (Fig. 2(g)). This spectral pattern remains unchanged on varying in concentration of complex over range of 10^{-4}–10^{-3} M as well as with changes in gain and modulation amplitude from 0.05 to 2 G. The unusual broadness and the asymmetry of the overall pattern was probably

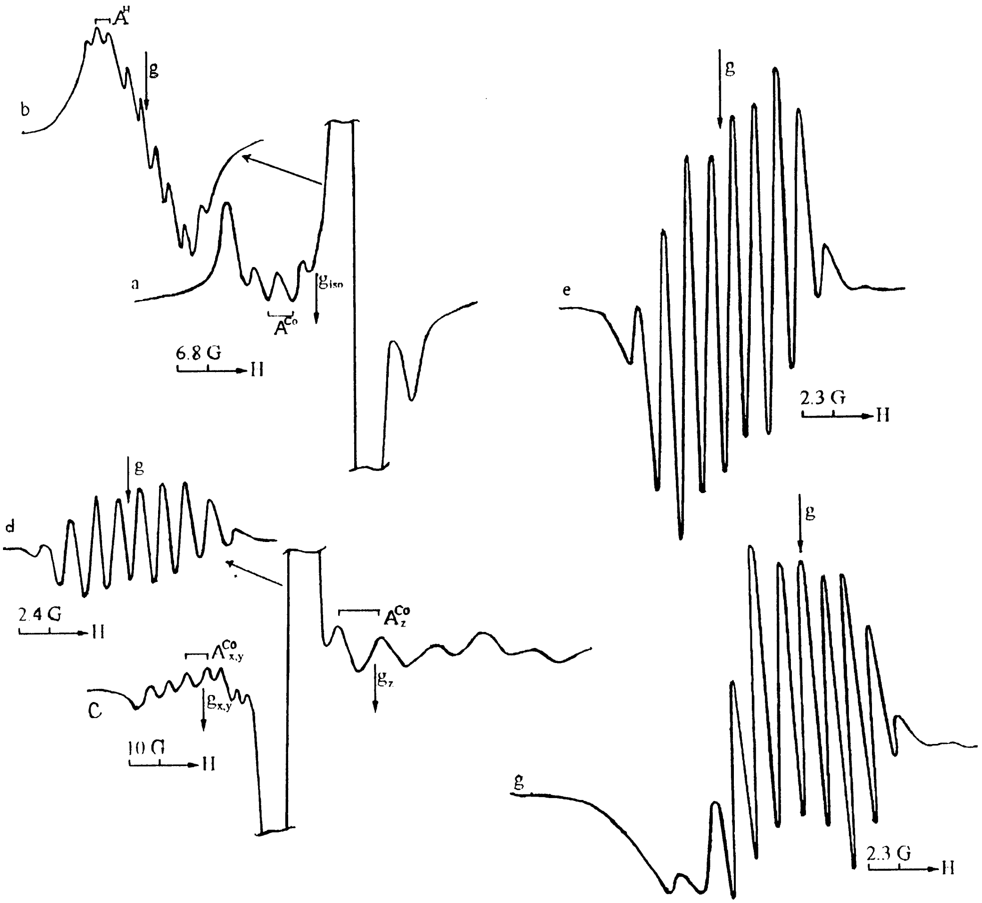


Fig. 2. ESR spectra of the oxidation products of $Co(L'_x)_2$ and $Pd(L'_x)_2$ in $CHCl_3$ at 300 K. (a, b): $Co(L'_1)_2$, (c, d): $Co(L'_2)_2$, (e): $Pd(L'_1)_2$ and (g): $Pd(L'_3)_2$. The central multiplets (b) and (d) were recorded at scan range of 50 G and modulation amplitude of 0.2 G.

due to the anisotropy of the hyperfine coupling tensors and that of the g-tensor [17]. At 77 K, for this sample, unresolved symmetric singlet centered at $g = 2.005$ was detected.

Interaction of $Pd(L'_x)_2$ with an excess of PPh_3 in $CHCl_3$ solutions at 300 K under vacuum, by analogy with those which were observed for corresponding bis(salicylaldiminato) palladium(II) [6a], results in reduction of the complexes accompanied by the precipitation of the metallic Pd. Upon reduction of $Pd(L'_1)_2$ with PPh_3 in $CHCl_3$ the complicated ESR spectrum $g = 2.0045$, $A^H = 1.42$ G was detected. But in the cases of $Pd(L'_2)_2$ and $Pd(L'_3)_2$, under similar conditions, along with immediate precipitation of Pd, a very weak intensity hardly detectable spectral patterns centered at $g = 2$ were observed.

10. Bis chelates of Co(II)

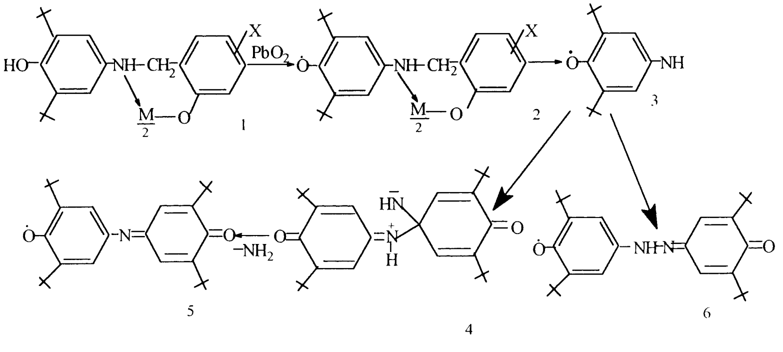
The values of the effective magnetic moments of these complexes ranging between 4.46 and 5.16 B.M. suggest a spin quartet state $S = 3/2$, and electronic spectra in $CHCl_3$ ($\varepsilon = 102$–614 l $mol^{-1}cm^{-1}$) in the visible region (Table 2) are indicative of tetrahedral coordinate Co(II) (d^7) complexes [18]. The absorption band in the region of 556–610 nm may be assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition in tetrahedral symmetry.

Oxidation of $Co(L'_x)_2$ complexes in the toluene and $CHC1_3$ solutions under the above mentioned conditions resulted in ESR spectra which were quite different from those of the oxidized $Ni(L'_x)_2$, $Pd(L'_x)_2$ and $Co(L'_x)_2$ (Fig. 2(a), (c)). For instance, on treatment with PbO_2, toluene solution of $Co(L'_1)_2$ gives a spectrum consisting of superimposition of less resolved very intense radical signal ($g = 2.0035$, $A^H = 1.11$ G) and low intensity octet pattern spacing of 6.2 G ($g = 2.01$) due to interaction of the unpaired electron to the $^{59}Co(I = 7/2)$ nucleus (Fig. 2(a)) was observed. A frozen solution (77 K) anisotropic spectrum of this sample shows resolved g_{xy} and g_z components with the parameters such as $g_{x,y} = 2.276$, $g_z = 1.998$, $A_{x,y}(^{59}Co) = 122.7$ G, and $A_z(^{59}Co) = 150$ G clearly indicate a (d_{z^2}) ground configuration characteristic of the low-spin Co(II) complexes [19]. In the presence of atmospheric oxygen the radical part of this spectrum was disappeared. ESR spectrum of oxidized of $Co(L'_2)_2$ in toluene at room temperature, also consists of overlapped radical signal ($g = 2.0054$, $A^H = 1.18$ G) and anisotropic eight-line pattern typical of the paramagnetic Co(III) with parameters as $g_{x,y} = 2.015$, $A_{x,y} = 4.66$ G, $g_z = 1.989$, $A_z = 10$ G (Fig. 2(c)). On the other hand, the spectrum generated from the complex of $Co(L'_3)_2$ under the similar conditions, exhibit six line pattern centered at $g = 2.0037$ and has an hfsc of 4.09 G with an intensity distribution of 1:2:3:3:2:1. At 77 K this spectrum transformed into two different signals centered at $g = 2.009$ ($\Delta H = 16.5$ G) and $g = 2.0012$ ($\Delta H = 3.3$ G), respectively, However, exact analysis of this spectrum is not easy, the observed frozen solution signal undoubtedly indicate that the room temperature six-line pattern of the oxidized $Co(L'_1)_2$ sample, can be attributed to superimposed two signals.

The performed studies indicate that except $Co(L_x)_2$ complexes practically all of the oxidized complexes independently of the ligand and metal nature display nearly identical ESR spectral feature. The ESR parameters and intensity distribution of 1:4:7:8:8:8:7:4:1 of the detected spectra are similar of those reported by Coppinger [20] indophenoxyl type radical 5 in Scheme 2.

According to Scheme 2, the indirectly generated unstable radical 2 immediately distorted 3 and this radical product may result from disproportion of the aminophenoxyl-aminophenoxyl ligand can be to give quinine-phenoxyl type stable radicals such as 5 or 6. It is necessary to note that the nine line spectral pattern with similar intensity ratios were also observed in the oxidation of some salicylaldimines and their complexes [4a,10].

Finally, this work clearly demonstrates the replacement of the –C = N– group by the $–CH_2–NH–$ linkage in bis[*N*-(2,6-di-tert-butyl-l-hydroxyphenyl)salicylaldimine] metal(II) complexes significantly increases their oxidative reactivity towards lead dioxide. ESR studies indicate that bis(benzylaminato) complexes of Ni(II) and VO(II) containing peripheral sterically hindered phenol fragment, in opposite to their salicylaldimine precursors are more readily oxidized



Scheme 2.

with lead dioxide and results to the formation of secondary phenoxyl radicals. On the other hand in the cases of Pd(II) and Co(II) the radical intermediates generated from salicylaldiminate and benzylaminate are significantly different from each other. In the oxidation of benzylaminate, unlike their salicylaldiminate precursors, the detection of primery radical species In generally, ESR spectra of the generated radical species according to their *g*-factors and hyperfine coupling constants are very similar each other and essentially different from those of the salicylaldimine analogous and free benzylamine ligands. In addition, the complexation ability of the hydrogenated benzylamine ligands was found rather higher than that of the parent salicylaldinine precursors.

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