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Spectrochimica Acta Part A 57 (2001) 2337–2344

SPECTROCHIMICA
ACTA
PART A

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Preparation, spectral behaviour and oxidation of some new zinc(II) salicylaldimines containing sterically hindered phenol

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Received 17 November 2000; accepted 5 December 2000

Abstract

A series of new bis[*N*-(2,6-di-*tert*-butyl-1-hyxyphenyl)salicylideneminato]zinc(II) complexes bearing one or two HO- and CH_3O-substituents on the salicylaldehyde moiety were prepared, and their spectroscopic properties (IR, electronic, ^1H NMR) as well as the ESR spectra of the one-electron oxidation products were examined. The ^1H NMR examination of $Zn(L_x)_2$ indicates that, contrary to expectations, the proton resonances of the complexes are shifted to the high-field side compared with those of the free ligands. Oxidation of these compounds with PbO_2 results in the formation of mono- and biradical types Zn(II)-stabilized phenoxyls in which there are both anisotropic and alternating line-width trends. Some spectral patterns are typical for weak interacting ($J \ll A$) or the case of $J \sim A$ biradicals, in which ESR signal appeared as superimposition of two non-interacting monoradical centers with $S = 1/2$. ESR studies on biradicals type of $Zn(L^{\bullet}{}_x)_2$ at 300 and 77 K did not show any evidence of strong exchange coupling in these systems. All radical species were characterized by the ESR parameters. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bis(salicylaldiminato)Zn(II) complexes; Coordinated phenoxyl radicals; ESR; ^1H NMR; Optical spectra

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1. Introduction

The oxidation of phenol compounds catalyzed by transition-metal complexes often involves electron transfer reactions from the substrates to the metal centers [1–4]. Specific questions concern the nature of the organic radical species, which is often the initial product of an electron transfer process [1]. The fact that sterically hindered phenol and its derivatives can readily undergo one or two-electron oxidation to the phenoxyl or *p*-quinone [5,6], respectively, offers the possibility of preparing chelates with unusual oxidation states of ligands. In particular, it is interesting to know in what ways the redox reactivities of the sterically hindered phenol systems change upon coordination. The character of the coupling between the two radical centers in the oxidized bis(ligand) metal complexes is also considered another interesting aspect of these radical systems.

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PII: S1386-1425(01)00430-9

Previously we reported the results of synthesis, X-ray, spectroscopic (UV/Vis, IR, ^{1}H NMR ESR) investigation and redox reactivity of Cu(II), VO(II), Co(II), Ni(II) and Pd(II) complexes with bi-, tri- and tetradentate salicylideneiminate, β-ketoiminate and azo-ligands containing sterically hindered phenol fragment [7–13]. All these complexes, except Cu(II) and VO(II), readily undergo one- or two-electron transfer oxidation with PbO_2 resulting in the formation of the stable metal-containing phenoxyl or secondary phenoxyl radical species.

Although a series of radical containing complexes with sterically hindered bidentate salicylaldimines bearing some electron-withdrawing substituents (Cl, Br, NO_2) on salicylic moiety have been prepared and studied [7–15], the complexation capability of these ligands and the redox behavior of their complexes are not completely clear.

The present paper is devoted to the synthesis and spectroscopic characterization of new salicylideneiminate Zn(II) complexes containing peripheral sterically hindered phenol fragment and electron-donating OH and CH_3O substituents, attached to the salicylaldehyde moiety. The radical intermediates generated by the oxidation of the synthesized complexes with PbO_2 also were examined.

We report the synthesis, spectroscopic behaviours and oxidation with PbO_2 of the zinc (II) complexes [$Zn(L_x)_2$] prepared from Schiff bases (L_xH) formed from 2,6-di-*tert*-butyl-1-hydroxyaniline and HO-, CH_3O-substituted salicylaldehyde derivatives as shown in Scheme 1.

2. Experimental

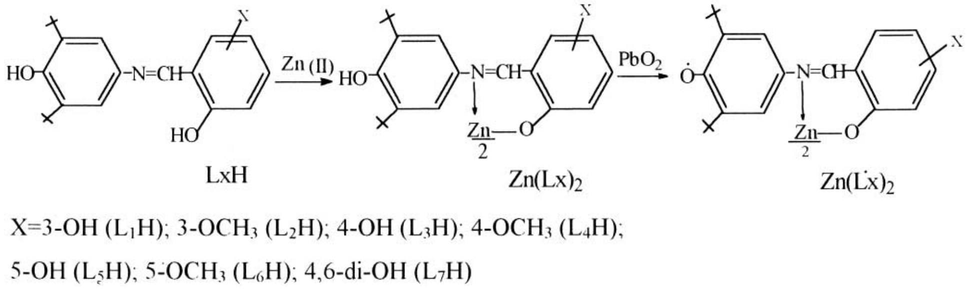
Salicylaldehyde, its hydroxy- and methoxy-substituted derivatives, zinc(II) acetate dihydrate and all solvents were commercial (Merck, Fluka, Sigma) products and were used without further purification. 1-Hydroxy-2,6-di-*tert*-butyl-aniline and ligands (L_xH) were prepared by a previously described procedure [7–9,14,15]. The analytical and spectroscopic data of L_xH and their oxidation with PbO_2 were reported [14,15].

2.1. Preparation of $Zn(L_x)_2$ complexes

A hot methanol solution (10 cm^3) of zinc(II) acetate dihydrate (0.2 g, 1 mmol) was added to a stirred and heated methanol solution (70–80 cm^3) of the appropriate ligand (2.1 mmol). The stirred mixture was heated at reflux (60–65°C) for 1–1.5 h and then allowed to cool to room temperature. After standing for 2–3 h, the solution was evaporated to c. 10–15 ml, and the precipitated yellow product was filtered off, washed with n-hexane, recrystallized from $CHCl_3$-n-hexane and dried in a vacuum at 50°C. The analytical and spectral data of the complexes are presented in Tables 1 and 2.

3. Spectra

Elemental analyses were performed by the Science and Technology Research Council of Turkey (TÜBITAK) in Gebze. The infrared spectra were taken in KBr discs with a MATTSON 1000 FT-IR spectrophotometer in the 400–4000 cm^{-1} region. The electronic absorption spectra were



Scheme 1. The structure of L_xH, $Zn(L_x)_2$ and generation of the radical ligand $Zn(L_x)_2$ complexes.

Table 1
Melting point and analytical data for $Zn(L_x)_2$ complexes

Compound	M.p. (°C) (dec.)	Yields (%)	Empirical formula	Elemental analysis, found/calculated (%)		
				C	H	N
$Zn(L_1)_2$	270	86.8	$C_{42}H_{52}N_2O_6Zn$	67.63/68.25	7.04/7.28	2.98/3.61
$Zn(L_2)_2$	280	90.5	$C_{44}H_{58}N_2O_6Zn$	67.16/67.60	6.55/7.02	3.10/3.75
$Zn(L_3)_2$	275	84.8	$C_{42}H_{52}N_2O_6Zn$	68.80/68.25	7.15/7.28	3.28/3.61
$Zn(L_4)_2$	290	83.6	$C_{44}H_{58}N_2O_6Zn$	66.72/67.60	6.66/7.02	2.97/3.75
$Zn(L_5)_2$	285	86.3	$C_{42}H_{52}N_2O_6Zn$	69.26/68.25	6.84/7.28	3.67/3.61
$Zn(L_6)_2$	(310)	90.4	$C_{44}H_{58}N_2O_6Zn$	63.30/64.82	7.02/6.73	3.49/3.59
$Zn(L_7)_2$	295	79.8	$C_{42}H_{52}N_2O_{10}Zn$	67.87/68.93	6.96/7.16	3.57/3.82

measured on a Shimadzu UV 160 A spectrophotometer in the 200–1100 nm region in various solvents. ^1H NMR was recorded on a BRUKER AC 200 spectrometer using TMS as an internal reference in $CDCl_3$ solutions. 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 DPPH sample. The errors for the g- and A-parameters of radicals are ± 0.0005 and ± 0.005 G, respectively. Oxidation of $Zn(L_x)_2$ compounds was carried out with lead dioxide in a sealed, degassed system at room temperature under vacuum. The compound dissolved in 4–5 ml toluene and PbO_2 were transferred into separate glass tubes on a vacuum line. Solution was deoxygenated under vacuum (10^{-3} mmHg) by repeated freeze–pump–thaw cycles. Then, 90–110 mg of PbO_2 were suspended in the solution of sample and shaken for 30 s at room temperature under vacuum. After the sedimentation of the heterogeneous phase, 1 ml of the solution was taken for ESR measurements. All ESR spectra of the reaction mixtures were immediately recorded at room temperature under a vacuum as oxidation proceeded.

4. Results and discussion

The data of the elemental analyses are consistent with the bis(chelate) structure of $Zn(L_x)_2$ complexes. As supported by the ESR examination, the products did not show any evidence of the formation of radical species during complexation.

4.1. IR and electronic spectra

The characteristic infrared group frequencies and electronic spectral absorption data are given in Table 2. The observed low-frequency shift of νC=N stretching in the IR spectra of $Zn(L_x)_2$ complexes (1594–1616 cm^{-1}) relative to free L_xH ligands (1608–1649 cm^{-1}) indicates the participation of the azomethine nitrogen atom of the ligands in coordination with the zinc(II) ion. Although the νOH stretching frequency of the sterically hindered phenol usually appeared at ca. 3600 cm^{-1}, in the spectra of $Zn(L_1)_2$, $Zn(L_2)_2$, $Pd(L_5)_2$ and $Pd(L_6)_2$ complexes showed two bands in the 3441–3570 cm^{-1} range. The broad medium bands within the range 3441–3485 cm^{-1} can be attributed to stretching vibrations of the associated sterically hindered phenol νOH or νN–H (ketoamine tautomer forms of L_xH in the solid state). This assignment was made on the basis that the low-energy stretching bands (~ 3400 cm^{-1}) also appeared for methoxy-bearing $Zn(L_2)_2$ and $Zn(L_6)_2$ complexes. In addition, these complexes, like others, were readily oxidized by PbO_2 with the formation of phenoxyl radicals. Note that the similar low-frequency shifts in the νOH were also observed for some free L_xH ligands bearing OH and OCH_3 [14,15]. It is interesting to note that the IR spectra of the sterically hindered phenol containing salicylaldimines with X=H, Cl, Br and NO_2 substituents on the salicylaldehyde moiety and their metal complexes did not exhibit any lower-frequency absorption bands in the range 3100–3600 cm^{-1} [8].

On the basis of the recorded electronic spectra of $Zn(L_x)_2$ and L_xH in dioxane as shown in Table 2, it is clear that the absorption bands except the bands within the range 242–254 nm of all complexes investigated are substantially different from those for the corresponding free ligands. A comparison of the electronic spectra of the L_xH and their $Zn(L_x)_2$ complexes (Table 2) measured in dioxane solution indicates that some bands in the ultraviolet region and all bands in the 400–460 nm range of the L_xH disappeared in the spectra of complexes. The bands observed in the 242–270 nm range can be assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic rings. The absorptions appeared in the range 400–590 nm, presumably due to intraligand or metal-to-ligand charge-transfer transitions in the $Zn(L_x)_2$.

The absorption bands centered at 480–590 more likely arise from the intraligand $\pi \rightarrow \pi^*$ transitions in the quinonoid type structure in solutions. It is known that the appearance of the absorption bands in this range is not characteristic for bis(salicylaldiminato)Zn(II) chelates [16]. The examination revealed that the electronic spectral behaviors of the free and coordinated salicylaldimines are significantly different.

4.2. ^{1}H NMR spectra

The ^{1}H NMR spectral results obtained for some L_xH and their $Zn(L_x)_2$ complexes in $CDCl_3$, together with the assignments, are given in Table 3. The proton resonance appears as a broad, low-intensity singlet at δ 11.45–14.86 ppm in the spectra L_xH attributable to the exchangeable salicylic OH and NH ketoamine tautomer form of L_xH protons (hydrogen-bonded OH/NH) and is absent in the spectra of $Zn(L_x)_2$ (Table 3). The absence of this signal in the spectra of $Zn(L_x)_2$ suggests the coordination of the salicylaldehyde through deprotonated oxygen atom. Another difference in the spectral feature is high-field shifts of all proton signals of $Zn(L_x)_2$ relative to the resonances found for uncoordinated free ligands due to the shelding upon complexation (Table 3). The CH=N, OH and OCH_3 signals appear as a singlet in the range 7.75–8.37, 4.45–5.23 and 3.78–3.83 ppm, correspondingly, which was slightly shifted to higher fields compared with those for the free ligand. Interestingly, the similar high-field shift in the protons resonances was also observed in

Table 2
IR and electronic spectral data for $Zn(L_x)_2$ and L_xH in dioxane

Compound	IR spectra cm^{-1}		Electronic spectra, λ_{max} (log ε), nm
	$\nu_{C=N}$	ν_{OH}	
$Zn(L_1)_2$	1614	3570, 3441	245, 290, 338, 410
L_1H	1649	3635, 3437	244(4.26), 330^a, 358(4.21), 375^a, 480^a
$Zn(L_2)_2$	1610	3456, 3444	246, 290, 336, 353^a, 376^a, 405^a
L_2H	1614	3440	240 (4.2), 254(4.1), 276(4.2), 338(4.4), 380(3.3), 420(2.4)
$Zn(L_3)_2$	1616	3620	254, 290^a, 324, 387, 590^a
L_3H	1620	3631, 3304	242(4.1), 254(4.0), 275(4.0), 340(4.3), 380(3.6), 460 (.9)
$Zn(L_4)_2$	1610	3610	254, 294^a, 326, 385
L_4H	1620	3580	243 (4.3), 279 (4.2), 349 (4.3), 430 (3.5)
$Zn(L_5)_2$	1606	3629, 3562	244, 270^a, 335^a, 342, 372, 435
L_5H	1618	3618, 3443	245 (4.37), 282 (4.22), 351 (4.48), 420^a
$Zn(L_6)_2$	1594	3531, 3485	245, 270^a, 336^a, 340, 371, 431
L_6H	1608	4490	244 (4.5), 271 (4.2), 344 (4.3), 368 (4.3)
$Zn(L_7)_2$	1609	3643	242, 258^a, 288^a, 381, 400^a, 450^a, 480^a
L_7H	1618	3632	243(4.5), 272(4.1), 320(4.2), 343(4.3), 368(4.3), 395(3.5), 480^a

[a] Shoulder.

Table 3
^{1}H NMR chemical shifts (δ in ppm) of L_xH and $Zn(L_x)_2$ complexes in $CDCl_3$[a]

Compound	OH/NH	CH(N	OH	OCH_3	Sal. (H)	Phen (H)	t-Butyl (H)
L_1H	14.25	8.55	5.32	–	6.55–6.60	7.15s	1.49s
$Zn(L_1)_2$	–	7.75, 8.14	4.75, 3.32	–	6.19–6.29	6.50–6.59	0.91, 1.25, 1.47
L_2H	14.18	8.60	5.29	3.93	6.88–6.99m	7.03–7.15s	1.47s
$Zn(L_2)_2$	–	8.32	5.18	3.83	6.65–7.00	7.15, 7.25	1.27, 1.47
L_3H	11.45	8.41	5.26	–	6.46m	7.05m	1.26, 1.47m
$Zn(L_3)_2$	–	8.23, 8.37	5.1, 5.23	–	6.15–6.35	6.96, 7.12	1.28, 1.46
L_4H	14.15	8.48	5.29	3.84	6.49d	7.10s, 7.25d	1.47–1.56
$Zn(L_4)_2$	–	8.29	5.12	3.78	6.37–6.38	7.03–7.11	1.30
L_5H	13.15	8.50	5.28	–	6.89s	7.13s, 7.26s	1.42s, 1.59s
L_6H	13.11	8.55	5.27	3.81	6.95m	7.14m	1.32
$Zn(L_6)_2$	–	8.29	5.15	3.78	6.64, 6.86	7.05, 7.14	1.29, 1.48

[a] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.

NMR spectra of Pd(II) complexes with the same L_xH salicylaldimines [17]. Note that the high-field shift of the proton resonances on the complexation has been reported previously by G. Schetty and E. Steiner for some diamagnetic Co(III) complexes with tridentate salicylaldimine and *o,o′*-dihydroxy-arylazo ligands [18]. The possible reason for the observed high-field shift may be due to the structural changes of the coordinated ligands, which can form *o*-quinonoid type structures in the solution. It is well known that, usually, the proton signals must be shifted down-fields side upon complexation ligand molecule as a result of the deshielding effect of the diamagnetic metal ions, which is in accordance with the decreased electron density on the ligand. The protons of the *tert*-butyl groups of all complexes except $Zn(L_4)_2$ exhibit two or three sharp singlet peaks at δ 0.91–1.48 ppm indicating that the *tert*-butyl protons of these compounds are magnetically non-equivalent. The ring protons of salicylaldehyde and phenol moieties of L_xH and $Zn(L_x)_2$ display multiplets within 6.46–7.26 and 6.15–7.25 ppm ranges, respectively, and many resonance of complexes compared with those of the free ligands are shifted to a high field c. 0.02–0.65 ppm. In some cases, the singlet lines due to the aromatic protons of L_xH appeared as multiplets in the corresponding $Zn(L_x)_2$ ^{1}H NMR spectra (Table 3). Thus, the ^{1}H NMR examination of $Zn(L_x)_2$ indicates that in spite of the expected low-field shifts in the proton resonances of the complexes, the high-field shifts were observed. The reason for the observed shielding effect is not apparent. However, it is thought that one alternative reason for this may be the deviation of the planarity of free ligand because of the unfavorable steric hindrance in the coordinated salicylaldimines.

4.3. ESR spectra

The oxidation of $Zn(L_x)_2$ was carried out with PbO_2 in a toluene/$CHCl_3$ mixture at room temperature under a vacuum. The ESR spectrum of the reaction mixture was simultaneously recorded as oxidation of the complex progressed. All of these radicals are more stable than the phenoxyls generated from uncomplexed free ligands. No additional splittings were observed from the *tert*-butyl protons in any of these radical spectra. The radicals generated from complexes were stable at room temperature for at least 2–3 days, as shown by the ESR spectra, but the intensity of radical signals formed from the ligands decreased slowly even under a vacuum. Although, in principle, in the examined $Zn(L_x)_2$-PbO_2 systems, the formation of biradicals is expected, the oxidized complexes did not show any evidence of ESR, indicating the existence of strongly interacting radical centers ($J \gg A$) attributable to the typical half-field line ($\Delta m = \pm 2$, $g = 4$) of triplet state biradical species. Some of the observed spectra are similar to those found for weak interacting ($J \ll A$) or the case of $J \sim A$ biradicals, in which

ESR spectra appeared as a superimposition of two non-interacting monoradical centers with S = 1/2 [19–21]. For some biradicals, anisotropic spectra with an alternating line width were observed.

X-band ESR spectra of the lead dioxide generated radical complexes are shown in Fig. 1. The one-electron oxidation of $\mathrm{Zn(L_1)_2}$, $\mathrm{Zn(L_3)_2}$ and $\mathrm{Zn(L_4)_2}$ with $\mathrm{PbO_2}$ in $\mathrm{CHCl_3}$/toluene solutions leads to the formation of the Zn(II)-containing phenoxyl radicals, which are rather more stable than those obtained from corresponding free uncomplexed ligands. The relatively broadening (presumably due to intramolecular dipolar exchange interactions) spectral features observed for these radicals are similar to each other and consist of less-resolved (in some case very poor resolved) nine lines with a relative intensity distribution close to 1:2:3:4:4:4:3:2:1 and ESR parameters such as $A^{\mathrm{H}}_{\mathrm{m}} = 1.063$ G, $g = 2.0038$ [$\mathrm{Zn(L_1^{\bullet})_2}$], $A^{\mathrm{H}}_{\mathrm{m}} = 1.033$, $g = 2.0039$ [$\mathrm{Zn(L_3^{\bullet})_2}$] and $A^{\mathrm{H}}_{\mathrm{m}} = 1.325$ G, $g = 2.0045$ [$\mathrm{Zn(L_4^{\bullet})_2}$]. The number of hyperfine lines of the ESR spectra of these radicals suggests that the unpaired electron interacts with one nitrogen $^{14}\mathrm{N}(\mathrm{I} = 1)$ nucleus and two sets of three hydrogens (one hydrogen atom of the CH group and two equivalent protons of the phenoxyl fragment) with the values hfsc related as $A^{\mathrm{N}} = A^{\mathrm{CH}}_{\mathrm{H}} = 2A^{\mathrm{H}}_{\mathrm{m}}$. Note that a more accurate determination of the splitting constants is difficult, because of overlapping and broadening some lines of these spectra. It is interesting that the spectral patterns of the radicals generated from $\mathrm{Zn(L_2)_2}$, $\mathrm{Zn(L_5)_2}$ and $\mathrm{Zn(L_6)_2}$ are quite different from the abovementioned radical species (Fig. 1b, c, d). That ESR spectrum of the radical $\mathrm{Zn(L_2^{\bullet})_2}$ consists of 14 equidistant well-resolved lines (Fig. 1b). The ESR spectrum of this radical ($A^{\mathrm{H}} = 1$ G, $g = 2.0043$) was analyzed in terms of the interaction of the unpaired electron spin density with two magnetically equivalent nitrogen ($A^{\mathrm{N}} = 4$ G) and two sets of four protons [$A^{\mathrm{C1H}} = 2$ G (1H), $A^{\mathrm{C2H}} = 2$ G (1H) and $A^{\mathrm{H}}_{\mathrm{m}} = 1$G (2H)]. At the same time, the ESR spectrum of $\mathrm{Zn(L_5^{\bullet})_2}$ is considerably different from those of all other $\mathrm{Zn(L_x^{\bullet})_2}$ in toluene solution at room temperature (Fig. 1c). For this radical, a quartet signal centered at $g = 2.0047$ and spacing of 1.75 G with relative intensity ratios of 1:2:2:1 were observed, which shows no evidence of any additional hfsc from the m-protons of the phenoxyl rings. This four-line pattern probably arises from splitting one nitrogen ($A^{\mathrm{N}} = 1.75$ G) and one proton of CH ($A^{\mathrm{H}}_{\mathrm{CH}} = 3.8$ G). The absence of an additional hyperfine structure from the meta-protons of phenoxyl rings may be caused by a broadening from anisotropic dipolar interactions between radical centers and a broadening from the modulation of isotropic hfsc due to the rotation of the phenoxyl group [22]. The spectrum of oxidized $\mathrm{Zn(L_6)_2}$ also differs from all of other $\mathrm{Zn(L_x^{\bullet})_2}$. This signal centered at $g = 2.0045$ consists of 11 well-resolved hyperfine lines with a spacing of 1.1 G between central lines and an intensity distribution of 1:2:4:6:7:8:7:6:4:2:1 (Fig. 1d). This spectrum was analyzed in terms of an interaction of the unpaired with one nitrogen

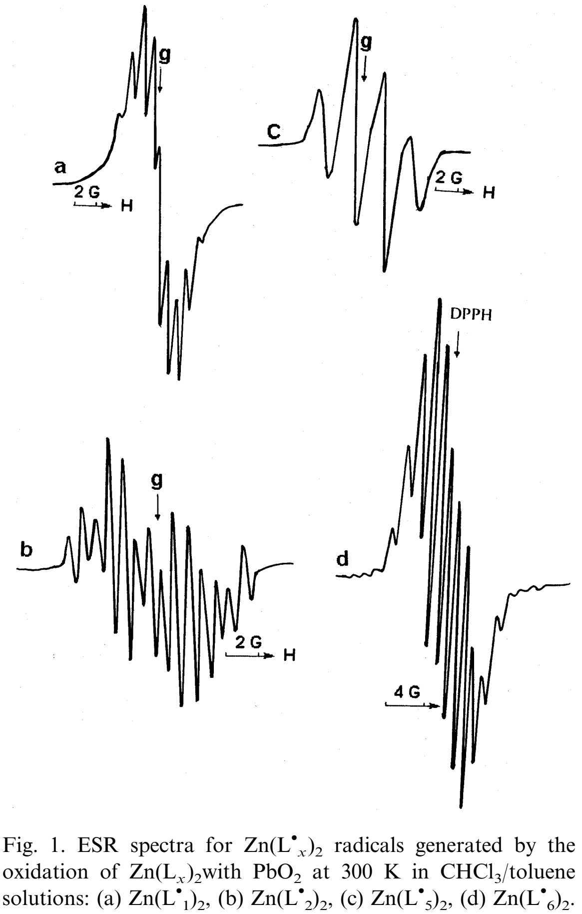


Fig. 1. ESR spectra for $\mathrm{Zn(L^{\bullet}_x)_2}$ radicals generated by the oxidation of $\mathrm{Zn(L_x)_2}$with $\mathrm{PbO_2}$ at 300 K in $\mathrm{CHCl_3}$/toluene solutions: (a) $\mathrm{Zn(L^{\bullet}_1)_2}$, (b) $\mathrm{Zn(L^{\bullet}_2)_2}$, (c) $\mathrm{Zn(L^{\bullet}_5)_2}$, (d) $\mathrm{Zn(L^{\bullet}_6)_2}$.

($A^{N} = 2.22$ G) and two sets of two hydrogens [$A^{H}_{CH} = 2.22$ G(2H) and $A^{H}_{m} = 1.11$ G] assuming hfsc related as $A^{N} = A^{H}_{CH} = 2A^{H}_{m}$. Additional, equally spaced very-low-intensity four lines, are also observed at both ends of the central multiplet. We assigned these peaks to the satellite lines arising from ^{13}C isotopes in natural abundance. It should be noted that similar splitting patterns were also observed in the ESR spectra of some oxidized free ligand and complexes [14,15,23,24]. Thus, all of the observed spectra except $Zn(L^{\bullet}_{5})_2$ and $Zn(L^{\bullet}_{6})_2$ are typical for weak interacting ($J \ll A$) or the case of $J \sim A$ biradicals, in which the ESR signal appeared as a superimposition of two non-interacting monoradical centers with $S = 1/2$.

It is interesting that in the oxidation of bis(*N*-2,6-di-*tert*-butyl-1-hydroxyphenyl-5-chloro-salicylaldiminato)zinc(II) [$Zn(L_8)_2$] and bis(*N*-2,6-di-*tert*-butyl-1-hydroxyphenyl-3-nitro-5-bromo-salicylaldiminato)zinc(II) [$Zn(L_9)_2$] complexes, slightly different anisotropic spectral patterns are observed (Fig. 2). These spectral features can be considered as two superimposed signals. The central lines of the spectrum ($g = 2.0034$) generated from [$Zn(L_8)_2$] in benzene under vacuum are narrowed and split into doublets (c. 0.75 G), and their intensity is decreased with respect to the low- and high-field doublets (Fig. 2b). The unusual asymmetric distribution of the intensity and alternating line-width trends of these spectra are typical for weakly interacting biradicals [19–23]. However, the ESR spectrum of the oxidized sample of [$Zn(L_9)_2$] shows a relatively intense and broadened central line ($g = 2.0029$) (Fig. 2b). The temperature dependence of this spectrum exhibited a change in the intensity and resolution of the ESR signal (Fig. 3). When the temperature of the benzene solution is decreased from 283 to 253 K, the intensity of the spectrum of $Zn(L^{\bullet}{}_9)_2$ is decreased without a significant change in the values of hfsc and remained low intensity slightly broad 9 lined equidistantly separated ($A^{H} = 1.094$ G) spectral pattern. Upon warming the solution over the temperature range of 283–303 K, the original 17 lined spectrum returned, but in the range of 303–333 K, the resolution of the spectrum improved, and the intensity distributions as well as the linewidth of some lines at its wings were significantly changed (Fig. 3b, c, d). Similar behavior was observed reversibly by either warming or cooling the solution in this range. The intensity of the spectrum dramatically decreased again and the spectral features were changed over $T > 340$ K. The temperature-dependence studies of this spectrum indicate that a change of intensity of the central lines in Fig. 3 did not follow Curie law behavior ($I \propto 1/T$), so this spectrum cannot be assigned to uncoupled monoradical species.

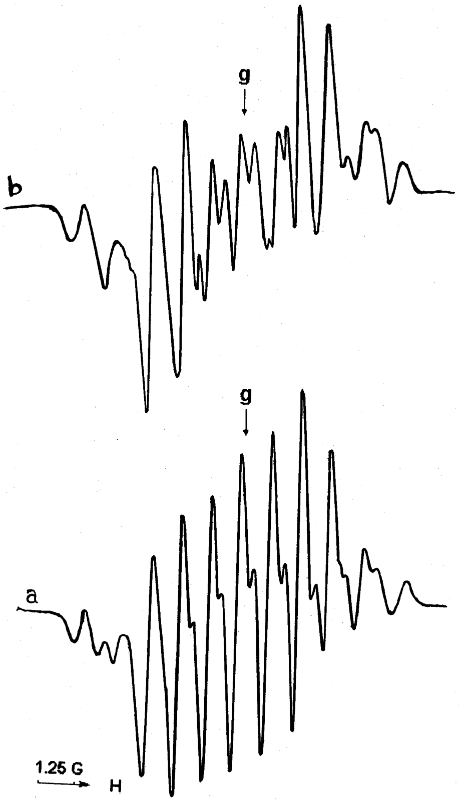


Fig. 2. ESR spectra of the radicals obtained by the oxidation of $Zn(L_9)_2$ (a) and (b) $Zn(L_8)_2$ at 300 K in benzene.

Summarizing, it can be said that the IR and electronic spectral behaviors of $Zn(L_x)_2$ complexes are significantly different from those observed for similar complexes bearing electron-withdrawing substituents on salicyladehyde moiety. The ESR examinations performed indicate that the spectral features of the radicals generated from bis[N(1-OH-2,6-di-*tert*-

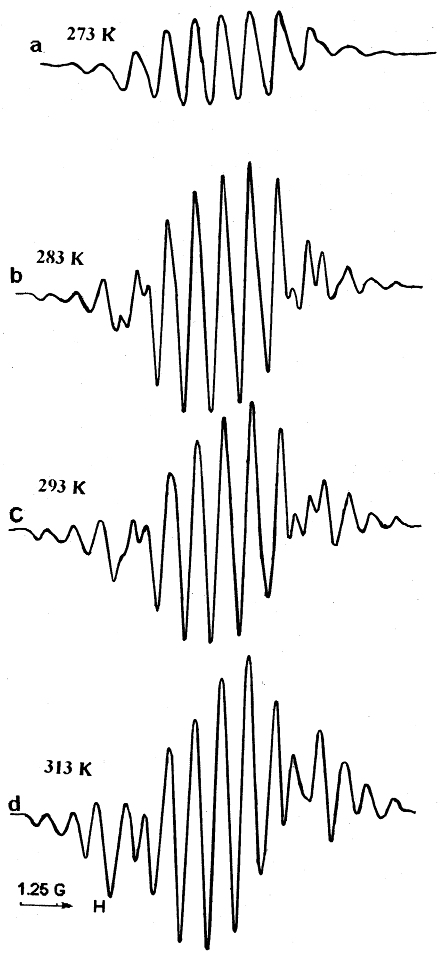


Fig. 3. Temperature dependence of the ESR spectra of benzene solution samples of $Zn(L^{\bullet}_9)_2$.

butylphenyl)salicylaldiminato)]Zn(II) are different from those for free ligand and other metal-stabilized phenoxyl radicals. The generated Zn(II)-stabilized phenoxyl radicals are more stable than the corresponding phenoxyl obtained from uncomplexed free ligands. The fact that the values of the g-factors and hfsc are close to each other and slightly different from those for the free ligand radicals undoubtedly indicates that the unpaired electron spin density is localized mainly on the ligand moiety. ESR studies on the biradical type of $Zn(L^{\bullet}_x)_2$ did not show any evidence of strong exchange coupling in these systems.

Acknowledgements

The author would like to thank the Science and Technology Research Council of Turkey (TÜBITAK) for financial support of this research (Grant TBAG-1424) and Dr I. Kartal for recording the ^1H NMR spectra.

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