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# Synthesis, spectroscopy and electrochemical behaviors of nickel(II) complexes with tetradentate shiff bases derived from $3,5-Bu_2^t$ -salicylaldehyde

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#### Abstract

Nickel(II) complexes of a series of *N*,*N*'-polymethylenebis(3,5-Bu<sub>2</sub>'-salicylaldimine) ligands containing 2,4-di-Bu<sub>2</sub>'-phenol arms, NiL<sub>x</sub>, were synthesized and their spectroscopic and redox properties were examined. The UV–vis, <sup>1</sup>H NMR spectroscopic and magnetic results indicate that complexes NiL<sub>1</sub>–NiL<sub>4</sub> unlike NiL<sub>5</sub> and NiL<sub>6</sub> have a square-planar structure in the solid state and in solution. Cyclic voltammograms of NiL<sub>x</sub> (x = 1-4) complexes displayed two-step oxidation processes. The first oxidation peak potentials of all Ni(II) complexes corresponds to the reversible one-electron oxidation process of the metal center, yielding Ni(III) species. The second oxidation peak of the complexes was assigned as the ligand based oxidation generating a coordinated phenoxyl radical species. (© 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

The coordination chemistry of transition metal complexes with salen-type ligands has achieved a special status in the last decades [1-3], because of their very interesting O<sub>2</sub>-binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as models for metalloproteins [5], as catalysts for the oxidation and epoxidation reactions [1,4,6], and as "metalloligands" for the design and the syntheses of a various heteronuclear complexes [7]. Salen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensoring applications and as sources of planar supramolecular building blocks [8,9].

Previously, one of us (V.T.K.) has reported the properties and spectroscopic characterization of some metal complexes with salen- and salan-type ligands prepared from ethylenediamine and 3,5-di-*tert*-butylsalicylaldehyde [10]. In this study, we present the synthesis, spectroscopic and electrochemical behavior of a new series of N,N'-polymethylenebis(3,5-di-*t*-butylsalicylaldiminato)nickel(II) complexes, Ni( $L_x$ ) [H<sub>2</sub> $L_x = N,N'$ -bis(3,5-Bu<sup>t</sup><sub>2</sub>-salicylidene)-polymethylenediamines] (Fig. 1).

## 2. Experimental

## 2.1. Materials and physical measurements

All chemicals and solvents were reagent grade and used without further purification. Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O, 2,4-di*tert*-butylphenol, all diamines, NH<sub>2</sub>–(CH<sub>2</sub>)<sub>n</sub>–NH<sub>2</sub>, where n=2-4, were obtained from Aldrich Chemical Co. The reagent 3,5-di-*tert*-butylsalicylaldehyde was prepared from 2,4-di-*tert*-butylphenol according to literature [4b].

IR spectra were recorded in KBr using a Perkin-Elmer spectrophotometer. Electronic absorption spectra of the complexes measured by Hewlett Packard UV-VIS HP 8453A

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Fig. 1.

Diode Array and by a Shimadzu 1601 UV-vis Spectrophotometers in several solvents. A Bruker Spectro spin Avance DPX400 Ultra Shield Model NMR was used to obtain <sup>1</sup>H NMR of the diamagnetic compounds. Room temperature solid-state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. The effective magnetic moment,  $\mu_{eff}$ , per nickel atom was calculated from the expression  $\mu_{eff} = 2.83 (\chi_M T)^{1/2}$  B.M, where  $\chi_{M}$  is the molar susceptibility corrected using Pascal's constants [11] for diamagnetism for all the atoms in the compounds. The temperature-independent paramagnetism associated with nickel ions was not included in the calculations of  $\mu_{\text{eff}}$ . Voltammetric recordings were made by using Volta Lab PGZ 301 Dynamic Voltammetry. A platinum-bead working, a platinum-coil counter electrode and saturated calomel reference electrode (SCE) were used for CV measurements. Cyclic voltammograms (CV) were recorded under N2 gas atmosphere in DMF at room temperature. Concentration of the complexes was 0.001 M in the electrolyte solution where commercially obtained [n-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]BF<sub>4</sub> was used as a supporting electrolyte. The voltage scan rate during the CV measurements was 100 mV/s.

## 2.2. Synthesis of $H_2L_x$ ligands

The tetradentate Schiff base ligands used in this work, N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane (H<sub>2</sub>L<sub>1</sub>), N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminopropane (H<sub>2</sub>L<sub>2</sub>), N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,3-diaminopropane (H<sub>2</sub>L<sub>3</sub>) and N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,4-diaminobutane (H<sub>2</sub>L<sub>4</sub>) and other ligands were prepared by refluxing 0.02 mol of 3,5-di-*tert*-butylsalicylaldehyde and 0.011 mol of the appropriate diamine in 60 ml of methanol/ethanol mixture (v/v = 3:1) for ca. 1 h. The products were recrystallised from methanol/CHCl<sub>3</sub> mixture (v/v = 5:1) and dried in air (Yield: 92–95%). The analytical and spectral data of the ligands are presented in Tables 1–3.

#### 2.3. Synthesis of $NiL_x$ complexes

# 2.3.1. Synthesis of [N,N'-bis(3,5-di-tertbutylsalicylaldiminato)-1,4-butylene]nickel(II) [Ni(L4)]

A solution of  $Ni(AcO)_2 \cdot 4H_2O$  (0.125 g, 0.5 mmol) dissolved in 5 ml warm methanol was added to the hot

solution (50–55 °C) of H<sub>2</sub>L<sub>4</sub> (0.26 g, 0.5 mmol) and Et<sub>3</sub>N (0.05 g, 0.53 mmol) dissolved in methanol/CHCl<sub>3</sub> (v/v = 3:1) mixture by stirring. A green precipitate formed immediately. After refluxing for 30 min, the volume of the solution was reduced to 20 ml by evaporation and then allowed to cool to room temperature. The precipitated green crystals were collected by filtration, then washed with methanol, CHCl<sub>3</sub> and dried at 70 °C in air for 4 h. The precipitate was recrystallised from CHCl<sub>3</sub>/methanol (v/v = 1:2).

Other NiL<sub>x</sub> complexes were prepared in a similar manner. It should be noted that the NiL<sub>5</sub> and NiL<sub>6</sub> complexes could not be prepared in the absence of Et<sub>3</sub>N. NiL<sub>1</sub> complex reported in [10], for electrochemical characterization and comparative purposes, also was prepared. The analytical and spectral data of the complexes are presented in Tables 1, 3 and 4.

## 3. Results and discussion

The analytical data of the NiL<sub>x</sub> complexes indicate 1:1 metal to ligand stoichiometry. All the isolated complexes are soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, DMSO and partially soluble in alcohols, THF, acetonitrile.

## 3.1. IR spectra

The IR spectra of the complexes were interpreted by comparing the spectra with that of the free ligands. The absence of the broad band at 2500–3100 cm<sup>-1</sup> due to  $\nu$ (OH) of the intramolecularly bonded N–HO in the spectra of the complexes indicates the deprotonation of the salicylaldimine moiety of H<sub>2</sub>L<sub>x</sub> in the complexation. The shift of the characteristic imine (>CH=N) band from 1629–1634 to 1615–1622 cm<sup>-1</sup>, demonstrates the coordination of the azomethine nitrogen to the nickel atom. Furthermore, the bands observed at 450–650 cm<sup>-1</sup> assigned to Ni–O and Ni–N bending vibrations, supporting the ligand and Ni(II) ion coordination [12].

## 3.2. <sup>1</sup>H NMR spectra

All  $H_2L_x$  tetradentate Schiff bases show a narrow intense singlet in the region of  $\delta$  13.64–13.99 ppm assigned to hydrogen bonded salicylic proton. The CH=N imine, protons except  $H_2L_2$  exhibit a singlet resonance in  $\delta$  8.16–8.37 ppm region. The presence of a doublet signal at  $\delta$  8.16 and

Table 1
The melting points, yields and analytical data for $H_2L_x$ and $NiL_x$ compounds

$H_2L_x$	Colour	$T(^{\circ}C)$	Yield (%)	Elemental analyses (%) (Found/Calcd.)		
				С	Н	Ν
H <sub>2</sub> L <sub>2</sub>	Yellow	138	95	79.12/78.20	9.86/9.94	6.34/5.53
$H_2L_3$	Yellow	144	92	79.24/78.20	9.21/9.94	6.14/5.53
$H_2L_4$	Yellow	154	92	79.18/78.42	11.45/10.06	5.78/5.37
$H_2L_5$	Yellow	134	94	78.34/78.60	9.85/10.17	5.45/5.24
$H_2L_6$	Yellow	121	95	79.34/78.78	9.89/10.28	4.92/5.10
NiL <sub>2</sub>	Green	>270	83	71.35/70.33	7.87/8.58	5.34/4.97
NiL <sub>3</sub>	Green	>270	93	71.45/70.33	9.38/8.58	5.59/4.97
NiL <sub>4</sub>	Brown green	>270	88	69.78/70.70	9.56/8.73	5.75/4.85
NiL <sub>5</sub>	Dark green	Dec > 160	60	70.16/71.06	9.12/8.86	4.68/4.73
NiL <sub>6</sub>	Dark green	236	74	71.89/71.39	8.75/8.98	4.58/4.62

Table 2

IR and electronic absorption spectral data for the  $H_2L_x$ 

Ligand	IR spectra (cm <sup>-</sup>	<sup>1</sup> ), νCH=N	Electronic spectra $\lambda_{max}$ (nm) (log $\varepsilon M^{-1} L^{-1}$ )
$H_2L_1$	1629	1595	215 (4.86), 235 <sup>a</sup> , 264 (4.22), 328 (3.81), 420 (2.29)
$H_2L_2$	1629	1594	219 (4.86), 263 (4.82), 330 (4.41), 428 (2.59)
$H_2L_3$	1633	1594	222 (4.85), 262 (4.58), 328 (4.13), 416 (2.61)
$H_2L_4$	1634	1595	218 (4.56), 240 <sup>a</sup> , 264 (4.13), 328 (4.11), 416 (2.82)
$H_2L_5$	1631	1592	219 (4.89), 235 (4.76), 264 (3.89) 331 (3.88) 416 (2.67)
$H_2L_6$	1634	1597	217 (486), 238 <sup>a</sup> , 261 (3.97), 330 (3.97), 416 (2.75)

<sup>a</sup> Shoulder.

Table 3
<sup>1</sup> H NMR spectral data for the $H_2L_x$ and $NiL_x$ ( $\delta$ ppm) compounds

Compound	δОН	δCH=N	δSal.H	Others	δC(CH <sub>3</sub> ) <sub>3</sub>
$H_2L_1$	13.70	8.16 s, 1 H; 8.37 s, 1 H	7.05 d, $J = 2.1$ Hz; 7.35 d, $J = 2.4$ Hz	3.34 t, N-CH <sub>2</sub> , 3.75 m, N-CH	1.29 s, 1.45 s
NiL <sub>1</sub>	_	7.23 s, 2 H	6.81 d, J=2.5 Hz; 7.38 d, J=2.4 Hz	2.72 d, N-CH <sub>2</sub> , 3.52 m, N-CH	1.17 s, 1.33 s
$H_2L_2$	13.64	8.38 s, 2 H	7.07 d, $J = 2.4$ Hz; 7.36 d, $J = 2.4$ Hz	3.91 t, N-CH <sub>2</sub>	1.28 s, 144 s
NiL <sub>2</sub>	-	7.42 s, 2 H	6.81  d, J = 2.3  Hz 7.23  d, J = 2.6  Hz	3.23 s, N–CH <sub>2</sub>	1.17 s, 1.33 s 1.47 s
$H_2L_3$	13.80	8.38 s, 2 H	7.07 d, $J = 1.7$ Hz 7.37 d, $J = 2.4$ Hz	2.14 qw, CH <sub>2</sub> , 3.65 t, N-CH <sub>2</sub>	1.29 s, 1.45 s
NiL <sub>3</sub>	-	7.1 s, 2 H	6.75 d, J = 2.5 Hz 7.17 d, J = 2.6 Hz	1.74 qw –CH <sub>2</sub> –, 3.47 t, N–CH <sub>2</sub>	1.17 s, 1.32 s
$H_2L_4$	13.89	8.36 s, 2 H	7.08 d, $J = 1.4$ Hz 7.37 d, $J = 2.2$ Hz	3.61 m,-CH2-,1.97 t, N-CH2	1.30 s, 1.46 s
$H_2L_6$	13.99	8.34 s, 2 H	7.07 d, J=2.2 Hz 7.36 d, J=2.4 Hz	3.57 t, 4 H, 1.72 m, -CH <sub>2</sub> -, 8 H	1.30 s, 1.45 s

Table 4

IR (cm<sup>-1</sup>), electronic absorption spectral data and magnetic moments for NiL<sub>x</sub> complexes

Compound	IR spectra, vC=N	$\mu_{\mathrm{eff}},\mathrm{BM}$	Solvent	Electronic spectra $\lambda_{max}$ (nm) (log $\varepsilon$ M <sup>-1</sup> L <sup>-1</sup> )
NiL <sub>1</sub>	1615	Diamagnetic	CHCl <sub>3</sub>	258 (4.47), 320 <sup>a</sup> , 347 (4.21), 428 (4.09), 650 <sup>a</sup> (2.33)
		•	DMF	320 <sup>a</sup> , 346 (3.93), 420 (3.82), 460 <sup>a</sup> , 570 (2.30)
			Dioxan	341, 425, 556
NiL <sub>2</sub>	1622	Diamagnetic	CHCl <sub>3</sub>	257 (4.67), 340 <sup>a</sup> , 350 (4.17), 428 (3.07), 460 <sup>a</sup> , 650 <sup>a</sup> (2.63)
		-	DMF	340 (4.04), 400 <sup>a</sup> , 419 (3.93), 466 <sup>a</sup> , 570 <sup>a</sup> (2.31)
			Dioxan	331, 425, 470 <sup>a</sup> , 570 <sup>a</sup>
NiL <sub>3</sub>	1620	Diamagnetic	CHCl <sub>3</sub>	270 (4.37), 330 (3.98), 407 (3.80), 648 (2.19)
			DMF	355 (3.35), 426 (3.28), 500 <sup>a</sup> , 600 <sup>a</sup> (2.12)
			Dioxan	358, 432, 500 <sup>a</sup> , 628
NiL <sub>4</sub>	1615	1.71	CHCl <sub>3</sub>	261 (4.41), 321 (3.99), 446 (3.87), 630 (2.02)
			DMF	372 (3.88), 437 (3.69), 500 <sup>a</sup> (2.67), 640 (1.97)
			Dioxan	364, 441, 500 <sup>a</sup> 630 <sup>a</sup>
NiL <sub>5</sub>	1622	1.56	CHCl <sub>3</sub>	260 (3.02), 331 (3.96), 399 (3.75), 510 (2.91) <sup>a</sup> , 642 (2.15)
			DMF	328 (3.93), 389 (3.82), 638 (2.19)
			Dioxan	259, 407, 633
NiL <sub>6</sub>	1621	Diamagnetic	CHCl <sub>3</sub>	267 (4.32), 360 (4.06), 433 (3.98), 510 (2.85) <sup>a</sup> , 618 (2.09)
			DMF	330 (3.50), 398 (3.84), 642 (2.18)
			Dioxan	322, 408, 456, 530 <sup>a</sup> , 647

8.37 ppm for the azomethine protons in the spectra of  $H_2L_2$ indicates, as it would be expected, the nonequivalent nature of the azomethine protons. Protons of the bridging methylene groups attached to a nitrogen atom, N–CH<sub>2-</sub>, resonances in the region of  $\delta$  3.57–3.91 ppm as a triplet pattern. Salicylic protons at 4 and 6 positions appeared as *meta*-coupled doublets from ring protons on salicylic moiety at  $\delta$  7.05–7.08 (d, 1 H, J = 1.4–2.4 Hz) and  $\delta$  7.35–7.37 (d, 1 H, J = 2.41 Hz) ppm. The spectra of H<sub>2</sub>L<sub>x</sub> contains only two a single resonances at  $\delta$  1.28–1.30 and at  $\delta$  1.44–1.46 ppm corresponding to each of the unique *t*-Bu groups. As can be examined from Table 3, along with the disappearance of NH/OH resonance, the high field shifts for all proton resonance signals in the <sup>1</sup>H NMR spectra for diamagnetic NiL<sub>1</sub>–NiL<sub>3</sub> complexes compared to those of free L<sub>1</sub>H<sub>2</sub>–L<sub>3</sub>H<sub>2</sub> ligands in CDCl<sub>3</sub> were observed.

## 3.3. Electronic spectra

Electronic absorption spectral data of  $H_2L_x$  are very similar to each other because of their structural identity (Table 2). The strong absorption band observed below 300 nm is assigned to intraligand  $\pi \rightarrow \pi^*$  transitions of the phenolic chromophores. The absorption band observed in all ligand spectra within the range of 328–331 nm is most probably due to the transition of  $n \rightarrow \pi^*$  of imine group [13]. The bands appeared in the range of 414–428 nm in ethanol solutions are attributed to  $n \rightarrow \pi^*$  transition of dipolar zwitterionic keto-amine tautomeric structures of  $H_2L_x$  [14].

Electronic absorption spectral data of  $NiL_x$  complexes in CHCl<sub>3</sub>, DMF and dioxan are presented in Table 3. The weak d-d transitions ( $\varepsilon = 50-500 \text{ M}^{-1} \text{ cm}^{-1}$ ) of square planar nickel(II) complex in D<sub>4h</sub> symmetry observed in the regions of 370-430 and 430-670 nm [15]. More intense charge transfer bands obscure the third and second d-d bands at high-energy region ( $\lambda < 450 \text{ nm}$ ) in many cases. These bands are usually assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g} {}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and  ${}^{1}A_{1g} \rightarrow {}^{1}E_{1g}$  transition [16], respectively. The bands observed in the 570–660 nm ( $\varepsilon \approx 100-420 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 460–510 nm ( $\varepsilon \approx 460-820 \text{ M}^{-1} \text{ cm}^{-1}$ ) regions (Table 4) can be assigned to the  $^1A_{1g} \rightarrow {}^1A_{2g}$  and  $^1A_{1g} \rightarrow {}^1B_{1g}$  transitions, respectively. As can be seen from Table 4, the electronic absorption bands of the presented complexes in the visible region exhibit solvent dependence behaviour. The observed red shifts in the low-energy d-d band of  $NiL_x$  complexes in DMF can be interpreted in terms of weaking of ligand field strength [17]. In a general, as the number of methylene group increased in the bridge from 2 to 4, a decrease in the ligand field energies is expected. It is interesting that the same trend is not observed in the electronic absorption spectra of our bulky *tert*-butylated Ni( $L_x$ ) complexes in CHCl<sub>3</sub> (Table 4).

#### 3.4. Magnetic moments

There is still much controversy present on the magnetism of the Ni(II) complexes with salen type ligands, containing diamine bridges, =N-(CH<sub>2</sub>)<sub>n</sub>-N= with n=3-12, in the

Table 5	
Cyclic voltammetry data (VSR = $100 \text{ mV/s}$ ) for $H_2L_x$ and $NiL_x$ in DMF	

Compound	$E_{\rm a}$ (V)	$E_{\rm c}$ (V)
NiL <sub>1</sub>	0.90 <sup>a</sup> , 1.20	1.10 <sup>b</sup>
NiL <sub>2</sub>	$0.84^{\rm a}, 0.96$	1.10 <sup>b</sup>
NiL <sub>3</sub>	$0.74^{\rm a}, 1.00$	0.93 <sup>b</sup>
NiL <sub>4</sub>	0.68 <sup>a</sup> , 0.96	0.80 <sup>b</sup>
NiL <sub>5</sub>	0.84, 1.11	_
NiL <sub>6</sub>	0.83, 1.16	-
$H_2L_1$	0.98	_
$H_2L_2$	1.10	-
$H_2L_3$	1.10	_
$H_2L_4$	1.06	_
$H_2L_5$	1.12	_
$H_2L_6$	1.17	-

 $E_{\rm a}$  represents the oxidation peak potential.  $E_{\rm c}$  represents the reduction peak potential.

<sup>a</sup> Reversible peak potential.

<sup>b</sup> Dependence on the second oxidation peak potential.

literature [16–18]. Our magnetic moment measurements (Table 4) carried out at room temperature reveals that NiL<sub>1</sub>, NiL<sub>2</sub>, NiL<sub>3</sub> and NiL<sub>6</sub> complexes are diamagnetic, indicating the low spin (S=0) square planar d<sup>8</sup>-systems, as its expected. The magnetic moments for NiL<sub>4</sub> and NiL<sub>5</sub> complexes were 1.70 and 1.56 BM, respectively. For these complexes it would be suggested that there should be two chemically unequivalent Ni<sup>+2</sup> sites: low-spin (S=0) square planar Nickel(II) and high spin (S=1) octahedral (II) in ca. 1:2 ratio.

#### 3.5. Electrochemical oxidation of $NiL_x$ complexes

The electrochemical data for all Ni(II)-complexes obtained in this study are presented in Table 5. The voltammograms of all Ni(II)-complexes show two step oxidation processes in DMF at room temperature under N<sub>2</sub>-gas atmosphere. As seen in Fig. 2 or Table 5, the first oxidation peak potential of all Ni(II)-complexes, reveals a reversible electron transfer with slight differences from 0.68 to 0.90 V versus SCE. The anodic potential of NiL<sub>2</sub> is more positive than of that for NiL<sub>1</sub> complex, most likely due to the steric effect of methyl group on the ethylene bridge, which header the axial coordination of the DMF molecules to the Ni(II) ion.



Fig. 2. Cyclic voltammogram of 0.001 M NiL<sub>3</sub> in DMF at room temperature vs. SCE (VSR = 100 mV/s).

We found one-electron transfer for the first oxidation peak by using a digital coulometer. Since the integrated area under the second oxidation peak is two times larger than the area under the fist anodic peak, 2-e<sup>-</sup> transfer was assigned for the second anodic peak, as well. This experimental fact indicates that the ligand-localized oxidation takes place in both coordinated salicylaldimine fragments. More positive potentials are obtained as the methylene group chain decreased from 4 to 2. This is in well agreement with the observed a red shift in the electronic spectra of  $NiL_x$  in DMF (Table 4). It is known that in increasing length of the bridging  $N-(CH_2)_r-N$  chain (x=2-4) is expected initially to increase steric strain in the ligand ring, resulting in distortion from planarity toward a tetrahedral geometry [7a]. For NiL<sub>x</sub>, increasing n (n = 2-4) causes a red shift in the absorption band near 600 nm, interpreted in terms of effective weakening of ligand field strength [16].

## 4. Conclusion

The reactivity and coordination modes of  $H_2L_x$  are similar to those exhibited by non-tertbutylated salen type ligands when they are treated with Ni(acet)<sub>2</sub> in the presence of Et<sub>3</sub>N. The electrochemical behaviours of NiL<sub>x</sub> are subsequently different from those reported for analogous salen type Ni(II) complexes with polymethylene bridges. This features seems to be due to the steric requirements of the tert-butyl groups on the 3,3'-positions of the salisylic fragments.

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