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Polyhedron 24 (2005) 1821–1828
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Electrochemistry of nickel(II) complexes with *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)polymethylenediamines

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Received 18 January 2005; accepted 27 May 2005
Available online 3 August 2005

Abstract

The electrochemical oxidation of several *N*,*N*′-polymethylenebis(3,5-di-*tert*- butylsalicylaldiminato)nickel(II) complexes, Ni(L_x), has been studied by cyclic voltammetry and in situ UV–Vis spectroscopy in DMF. Cyclic voltammograms of Ni(L_x) ($x = 1$–4) complexes displayed two-step oxidation processes under nitrogen gas atmosphere. The first oxidation peak potentials of all the Ni(II) complexes corresponds to the reversible one-electron oxidation process of the metal center, yielding Ni(III) species. EPR spectrum of the electrolysis solution was recorded after one electron transfer at liquid nitrogen temperature also confirms the formation of $[\mathrm{Ni^{III}(L_3)}]^+$ species ($g_x > g_y > g_z$) with a $^2A_1(d_z^2)^1$ ground state. Upon addition of pyridine to one electron oxidised solutions a new penta coordinated species, $[\mathrm{Ni^{III}(L_3)Py}]^+$ ($g_\perp > g_\parallel$, $a_\parallel(^{14}N) = 8$ G), was produced. The second oxidation peak of the complexes was assigned as the ligand based oxidation, generating a coordinated phenoxy radical species.

Keywords: Spectroelectrochemistry; Ni(II) complexes; Schiff bases; Ni(III) species; EPR

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1. Introduction

The recognition of the less common oxidation states of nickel, Ni(I) and Ni(III), play a crucial role in the activity of several hydrogenase reactions [1] and several catalytic redox reactions [2]. Nickel(II) complexes with tetradentate N_2O_2–Schiff base ligands derived from salicylaldehyde and aliphatic diamines have been known for a long time [3]. Nevertheless, their redox properties still attract the interest of the scientist because these complexes provide examples of systems where the final reduction/oxidation site of the complexes can be controlled by the aromaticity of the ligand [4] and by the solvent [5]. Planar Ni(II) chelate complexes are generally known to undergo one-electron oxidation at the Ni(II) center [6–10]. The EPR spectra imply the formation of Ni(III) with a low spin $(d_{z^2})^1$ electronic configuration [6–11]. The EPR spectra of the pyridine adduct of the Ni(III) species indicate that the solvents are able to stabilise the (+3) oxidation state of the nickel in the complexes. The Ni(III) species refer to six coordination with salicylaldimine, salicylaldehyde [7,10], naphthaldehyde [9] and macrocyclic polyazacycloalkene [12] derivative ligands with two adduct solvent molecules to the axial positions, however, those with macrocyclic amide, thiolate [13] and amine [14] derivatives imply five coordination with a mono adduct of the solvent molecule.

The chemistry and reactivity of transition metal complexes involving both redox-active metal ions and redox-active salicylaldimine ligands bearing readily oxidisable phenolate pendant arms with bulky di-*tert*-butyl groups

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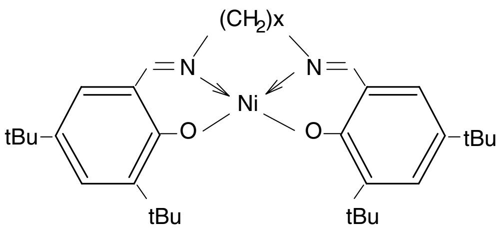
doi:10.1016/j.poly.2005.05.024



H_2L_x	$Ni(L_x)$	$(CH_2)_x$
H_2L_1	$Ni(L_1)$	$-(CH_2)_2CH(CH_3)-$
H_2L_2	$Ni(L_2)$	$-(CH_2)_2-$
H_2L_3	$Ni(L_3)$	$-(CH_2)_3-$
H_2L_4	$Ni(L_4)$	$-(CH_2)_4-$
H_2L_5	$Ni(L_5)$	$-(CH_2)_5-$
H_2L_6	$Ni(L_6)$	$-(CH_2)_6-$

Scheme 1.

on the aniline or salicylaldehyde moieties have stimulated their possible antioxidant activity and ability to form stable phenoxyl- or semiquinone type radical complexes on chemical oxidation or reduction [15]. In some cases the complexation of these ligands was accomplished by non-predictable redox-reactions depending on the nature of the ligands, solvents and oxidants [15,16]. The introduction of bulky groups in these ligands influences the redox reactivity and overall catalytic properties of the complexes [2b,15c,16]. In this study, we present the synthesis, spectroscopic and electrochemical behaviour of a new series of *N*,*N*′-polymethylenebis(3,5-di-*tert*-butylsalicylaldiminato)nickel(II) complexes, $Ni(L_x)$, [H_2L_x = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-polymethylenediamines] (Scheme 1).

2. Experimental

2.1. Preparation of the ligands and the complexes

All the ligands and their Ni(II) complexes were prepared according to the methods in the literature [17–19] and the analyses of the compounds were made by comparing the spectroscopic results with the reported ones [17,20–24].

2.2. Electrochemistry

Voltammetric recordings were made using Volta Lab PGZ 301 Dynamic Voltammetry. A platinum-bead working, platinum-coil counter electrode and saturated calomel reference electrode (SCE) were used for CV measurements. Cyclic voltammograms (CV) were recorded under N_2 gas atmosphere in DMF at room temperature. The concentration of the complexes was 0.001 M in the electrolyte solution, where commercially obtained $[n\text{-}(C_4H_9)_4N]BF_4$ was used as a supporting electrolyte. The voltage scan rate during the CV measurements was 100 mV/s. Controlled potential electrolysis at the anodic peak potential was carried out with a Ag-wire reference electrode after making a correction between the SCE and the Ag-wire (280 mV for SCE, and the oxidation potential of the ferrocene/ferrocenium couple was found to be 0.84 V versus SCE and 0.56 V versus Ag-wire, in our system). The oxidation process was followed in situ on a Hewlett Packard UV–Vis HP 8453A diode array spectrophotometer. Platinum gauze electrodes were used as the working and the counter electrodes. N_2 gas was bubbled through the electrolysis solution for stirring purposes between the scans.

2.3. Electron paramagnetic resonance spectroscopy (EPR)

The EPR spectrum of the electrochemically generated product, $Ni^{III}(L_x)$, was recorded by using a Varian E12 spectrometer in a quartz EPR cell in liquid nitrogen where diphenylpicrylhydrazyl (DPPH) was used as a reference.

3. Results and discussion

3.1. Voltammetric studies

The electrochemical data for all the Ni(II) complexes obtained in this study are presented in Table 1. The vol-

Table 1
Cyclic voltammetry data (VSR = 100 mV/s) for H_2L_x and $Ni(L_x)$ complexes in DMF

Compound	E_a (V)	E_c (V)	ΔE_p (V)
$Ni(L_1)$	0.90[a], 1.20	1.10[b]	0.062
$Ni(L_2)$	0.84[a], 1.17	1.10[b]	0.059
$Ni(L_3)$	0.74[a], 1.00	0.93[b]	0.058
$Ni(L_4)$	0.68[a], 0.96	0.80[b]	0.062
$Ni(L_5)$	0.84, 1.11		
$Ni(L_6)$	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_a represents the oxidation peak potential.
E_c represents the reduction peak potential.
ΔE_p represents the difference between the peak potentials of the reversible anodic peaks.

[a] Reversible peak potential.

[b] Dependence on the second oxidation peak potential.