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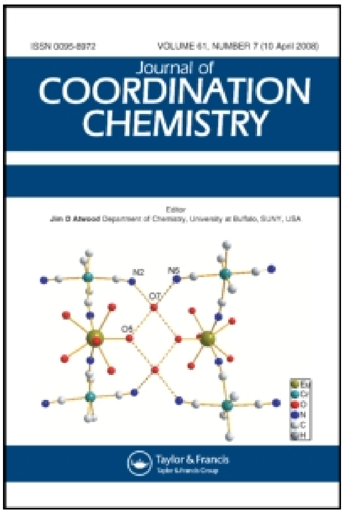

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Note: Electrochemical Behaviour of a Series of Ni(II) Complexes with Tetradentate Schiff Base Ligands

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NOTE

ELECTROCHEMICAL BEHAVIOUR OF A SERIES OF Ni(II) COMPLEXES WITH TETRADENTATE SCHIFF BASE LIGANDS

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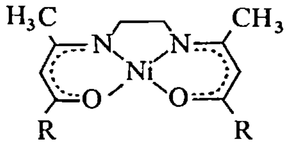
The electrochemical oxidation of Ni(II) complexes of a series of substituted *N,N′*-ethylenebis(mono-R-acetonimines), where R = ØOCH$_3$, ØCH$_3$, Ø, CH$_3$, ØCl and ØBr, was investigated by cyclic voltammetry in methanol solution at a platinum electrode. A good linear relationship was found between the anodic peak potential, E$_{pa}$, and the Taft substituent constant. The one-electron oxidation is coupled with a subsequent chemical reaction. Triphenylphosphine has a catalytic effect.

Keywords: Nickel, electrochemistry, tetradentate Schiff bases, substituents

INTRODUCTION

We have published some material on the relationship between redox potentials and electronic parameters of ligand substituents for metal complexes of Schiff base ligands.[1–3] In this work we have measured oxidation potentials of a number of Ni(II) complexes of the type (further on denoted as $NiN_2O_2R_2$), and examined the relationship between the data obtained and Taft substituent parameters. The study apart from being an investigation of the electrode process, deals mainly with redox properties of the complexes as affected by equatorial modification of the tetradentate ligand with substituents of differing electronic properties.



R = ØOCH$_3$, ØCH$_3$, Ø,
CH$_3$, ØCl, ØBr

EXPERIMENTAL

The ligands $H_2N_2O_2R_2$, where R = ØOCH$_3$, ØCH$_3$, Ø, CH$_3$, ØCl, ØBr and ØNO$_2$, were prepared according to a literature method.[4] The complexes $NiN_2O_2R_2$ were prepared by reaction of Ni(II) acetate with the corresponding ligand directly in an

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electrolysis cell at room temperature. $NiN_2O_2(ØNO_2)_2$ could not be prepared in this way. Commercially available triphenylphosphine (TPP) was purified by threefold recrystallization from ethanol. Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Methanol was purified using standard procedures.

Electrochemical measurements were carried out using a PA 3 polarographic analyzer (Laboratory Instruments, Prague), utilizing three-electrode geometry consisting of a platinum wire working electrode, a platinum-foil auxiliary electrode and an aqueous, saturated calomel, reference electrode (SCE). The SCE was separated from the test solution by a bridge filled with the solvent and supporting electrolyte. Voltammograms of the complexes were recorded with methanol solutions ($0.05\,\mathrm{mol\,dm^{-3}}$ TBAP) at room temperature with scan rates of 20, 50, 100, and $500\,\mathrm{mV\,s^{-1}}$. The triphenylphosphine content in the solution did not exceed three times that of the complex.

RESULTS AND DISCUSSION

In methanol, all the Ni(II) complexes undergo, at a platinum electrode, a one-electron anodic process which gives cyclic voltammetric responses consisting of a single anodic peak without any associated cathodic response. The significant features of the cyclic voltammetric responses have been analyzed as a function of the scan rate[6] at 20, 50, 100 and $200\,\mathrm{mV\,s^{-1}}$ (the use of fast potential scan rates was limited by the instrument) and results showed a progressive decrease of the $i_{pa}/v^{1/2}$ ratio and an anodic shift of E_{pa} with increasing potential sweep rates. Results of this analysis indicate that the anodic oxidation of the $NiN_2O_2R_2$ complexes involves a one-electron transfer, where the electrode process is complicated by a following chemical reaction. Table I summarizes the anodic peak potentials and the differences between E_{pa} and $E_{pa/2}$, the anodic half-peak potential, at a scan rate of $100\,\mathrm{mV\,s^{-1}}$.

TABLE I
Redox data for the $NiN_2O_2R_2$ complexes.

R	E_{pa}(V)	$E_{pa} - E_{pa/2}$(mV)	σ_R^{o} [a]
$ØØCH_3$	0.62(5)	57	−0.38
$ØCH_3$	0.64(8)	60	−0.28
Ø	0.67	65	−0.11
CH_3	0.67(5)	55	−0.11
ØCl	0.62	55	0.12
ØBr	0.70(2)	55	0.12

[a] Taft constants.[5]

The anodic peak potentials are sensitive to the nature of the substituent R, and may be quantified by the Hammett linear free energy relationship (*1*), where

$$E_{pa} = \rho\Sigma\sigma_R^{o} \qquad (1)$$

$\Sigma\sigma_R^{o}$ is the total of substituent constants characteristic of the electronic properties of the substituent R ($\Sigma\sigma_R^{o} = 2\,\sigma_R^{o}$ and ρ is the reaction constant, characteristic of the reaction centre as well as expressing the reaction sensitivity to substituent influence.

According to (*1*), a close relation was found (r = 0.97) with a ρ value of 0.11 V. When the Ni(II) complex with R = Cl was not considered, a better correlation was found (r = 0.99) with a reaction constant value ρ = 0.30 V. The linear relationship E_{pa} *versus* $\Sigma\sigma_R^\circ$ confirms an identical mechanism for the electrode process in the investigated series of complexes. This behaviour is rather similar to anodic oxidations of $CuN_2O_2R_2$ complexes.[3] The value of the reaction constant, ρ = 0.11 V, indicates that the oxidation of the nickel(II) complexes is not so sensitive to electronic effects as the corresponding copper(II) complexes (r = 0.98; ρ = 0.34 V). It further shows that the orbital from which the electron is extracted has in both types of complexes the same symmetry (the d_{xy} orbital).[7]

The presence of TPP caused an increase of anodic peak current (Table II). These data are quantitative proof of a catalytic chemical reaction following oxidation of the complexes.[6] The change in the anodic peak potential of the nickel complexes in the presence of TPP, E_{pa}^{TPP}, with a change of potential scan rate (anodic shift, Table II) confirms the catalytic effect of TPP in the system.

TABLE II
Dependence of the anodic peak potential of the $NiN_2O_2(CH_3)_2$ complex, E_{pa}^{TPP}, and the current ratio $i_{pa}^{TPP}(i_{pa})^{-1}$ on the polarization scan rate in the presence of TPP.

v ($mV\,s^{-1}$)	E_{pa} (V)	$i_{pa}^{TPP}(i_{pa})^{-1}$
20	0.72(5)	2.84
50	0.74	2.56
100	0.75	2.24
200	0.76(5)	2.06

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