

Synthesis and Electrochemical Studies of Ni(II) Complexes with Tetradentate Schiff Base Ligands

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A series of tetradentate Schiff base ligands; [1,2-bis(naphthylideneimino)ethane, 1,3-bis(naphthylideneimino)propane, 1,4-bis(naphthylideneimino)butane, and 1,5-bis(naphthylideneimino)pentane] and their Ni(II) complexes have been synthesized. The properties of these ligands and their Ni(II) complexes have been characterized by elemental analysis, IR, NMR, UV-vis spectra, molar conductance, and thermogravimetric analysis. The mole ratio of Schiff base to Ni(II) metal was found to be 1:1. The electrochemical redox process of the ligands and their Ni(II) complexes in DMF and DMSO solution containing 0.1 M tetraethyl ammonium perchlorate (TEAP) as a supporting electrolyte have been investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry at glassy carbon electrode. The redox process of the ligands was highly irreversible, whereas redox process of Ni(II) complexes were observed as one electron transfer process in quasi-reversible and diffusion-controlled reaction. The electrochemical redox potentials of the Ni(II) complexes were affected by the chelate ring size of ligands. The diffusion coefficients of Ni(II) complexes containing 0.1 M TEAP in DMSO solution were determined to be $5.7\text{--}6.9 \times 10^{-6}$ cm²/sec. Also the exchange rate constants were determined to be $1.8\text{--}9.5 \times 10^{-2}$ cm/sec. These values were affected by the chelate ring size of ligands.

Introduction

Several model metal complexes containing Porphyrin and Schiff base ligands have been synthesized and studied for their dioxygen uptake¹⁻⁴ and oxidative catalysis.⁵⁻¹² Also complexes of transition metal(II) involving derivatives of salicylaldehyde and aliphatic amines have gotten considerable attention because of their similarity to the biological dioxygen carriers, as well as their potential as catalysts for the insertion of oxygen into organic substrates.¹³⁻²¹ Flexibility of the ethylenediamine backbone in 1,2-bis(salicylideneimino)ethane, as observed in a number of transition-metal complexes with bidentate oxygen ligands, is responsible for its complexes to mimic the biological activity of proteins. The Schiff bases used in metal complexes are generally tetradentate ligands, but some are tridentate or pentadentate ligands. The tetradentate Schiff base ligands enforce a high degree of planarity to the metal chelates. Therefore, Co(II) and Ni(II) complexes employing tetradentate Schiff base 2N2O donor ligands which coordinate through donor atoms have been extensively studied as oxygen-carriers.²²⁻²³

In this study, we synthesized the Ni(II) complexes of new tetradentate Schiff base derived from 2-hydroxy-1-naphthaldehyde with aliphatic diamines. These ligands and their Ni(II) complexes were characterized by elemental analysis, IR, UV-vis spectra, molar conductance, NMR, and thermogravimetric analysis. The electrochemical redox process of the ligands and their Ni(II) complexes in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solutions containing 0.1 M tetraethyl ammonium perchlorate (TEAP) as a supporting electrolyte was investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry with glassy carbon electrode. From the electrochemical data, we report the effect of chelate ring size of Ni(II) complexes.

Experimental

Materials. Nickel(II) acetate tetrahydrate, sodium hydroxide, ethanol, 2-hydroxy-1-naphthaldehyde, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, and 1,5-diaminopentane were obtained from Aldrich Chemical Co. and used without further purification. DMF and DMSO were dried by standard procedures²⁴ before use. TEAP was recrystallized twice from distilled water and dried at 70 °C under vacuum.

Preparation of ligands. Typical procedures for ligand synthesis are as follows. A solution of 0.1 mole ethylenediamine in 50 mL ethanol was slowly added to 0.2 mole (34.40 g) of 2-hydroxy-1-naphthaldehyde in 50 mL ethanol under the nitrogen atmosphere. After 2 hrs at room temperature, the precipitates were collected by filtration. The products were recrystallized from ethanol and dried under the reduced pressure at 60 °C.

1,2-bis(naphthylideneimino)ethane; H₂NAPET. 97% yield; mp 215-217 °C; Anal. Calcd for C₂₄H₂₀N₂O₂: C, 78.24; H, 5.47; N, 7.60; Found: C, 78.13; H, 5.55; N, 7.73; IR (KBr pellet, cm⁻¹): 3420 (O-H), 3057 (C-H), 2932 (C-H), 1642 (C=N), 1452 (C=C), 1254 (C-O); UV-vis (DMF, λ_{max}, ε × 10⁴ cm⁻¹M⁻¹): 272 (1.86), 308 (1.99), 404 (1.15), 424 (1.14); ¹H NMR (DMSO-d₆, δ): 3.36-2.04 (4H, C₂H₄), 7.80-6.73 (12H, ArH), 8.14 (2H, CH=N), 9.20 (2H, HOC₁₀H₆).

1,3-bis(naphthylideneimino)propane; H₂NAPPR. 97% yield; mp 225-227 °C; Anal. Calcd for C₂₅H₂₂N₂O₂: C, 78.51; H, 5.80; N, 7.32; Found: C, 78.50; H, 5.94; N, 7.43; IR (KBr pellet, cm⁻¹): 3408 (O-H), 3051 (C-H), 2931 (C-H), 1634 (C=N), 1462 (C=C), 1210 (C-O); UV-vis (DMF, λ_{max}, ε × 10⁴ cm⁻¹M⁻¹): 272 (1.57), 308 (1.83), 404 (1.40), 424 (1.50); ¹H NMR (DMSO-d₆, δ): 3.32-2.00 (6H, C₃H₆), 7.79-6.83 (12H, ArH), 8.14 (2H, CH=N), 9.20 (2H, HOC₁₀H₆).

1,4-bis(naphthylideneimino)butane; H₂NAPBU. 98

% yield; mp 234-236 °C; Anal. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07; Found: C, 78.58; H, 6.28; N, 7.28; IR (KBr pellet, cm^{-1}): 3466 (O-H), 3062 (C-H), 2935 (C-H), 1631 (C=N), 1442 (C=C), 1259 (C-O); UV-vis (DMF, λ_{max} , $\epsilon \times 10^4$ $cm^{-1}M^{-1}$): 272 (2.06), 308 (2.36), 402 (1.88), 422 (1.93); 1H NMR (DMSO- d_6 , δ): 3.34-2.00 (8H, C_4H_8), 7.75-6.68 (12H, ArH), 8.12 (2H, CH=N), 9.14 (2H, $HOC_{10}H_6$).

1,5-bis(naphthylideneimino)pentane; H₂NAPPE. 95% yield; mp 265-267 °C; Anal. Calcd for $C_{27}H_{26}N_2O_2$: C, 80.00; H, 6.38; N, 6.82; Found: C, 79.40; H, 6.49; N, 7.17; IR (KBr pellet, cm^{-1}): 3438 (O-H), 3053 (C-H), 2929 (C-H), 1634 (C=N), 1463 (C=C), 1260 (C-O); UV-vis (DMF, λ_{max} , ($\epsilon \times 10^4$ $cm^{-1}M^{-1}$)): 272 (2.10), 306 (2.40), 402 (1.98), 422 (2.03); 1H NMR (DMSO- d_6 , δ): 3.34-2.00 (10H, C_5H_{10}), 7.75-6.68 (12H, ArH), 8.12 (2H, CH=N), 9.16 (2H, $HOC_{10}H_6$).

Preparation of Ni(II) complexes. Ni(II) complexes were prepared by the addition of 0.01 mole of ligands and 0.02 mole NaOH in hot ethanol (100 mL) to the same volume of 0.01 mole (2.0 g) nickel(II) acetate tetrahydrate in water (50 mL) under the nitrogen atmosphere, respectively. After 2hrs stirring, the precipitates were obtained. The products obtained were then recrystallized from ethanol and dried at 80 °C under the reduced pressure.

N,N-ethylenebis(naphthalidiiminato) nickel(II); [Ni(II)(NAPET)]. 84% yield; mp 295-297 °C; Anal. Calcd for $C_{24}H_{18}N_2O_2Ni$: C, 67.83; H, 4.24; N, 6.59; Ni, 13.8; Found: C, 67.84; H, 4.23; N, 6.57; Ni, 13.78; IR (KBr pellet, cm^{-1}): 3047 (C-H), 2932 (C-H), 1622 (C=N), 1453 (C=C), 1253 (C-O), 744 (Ni-N), 474 (Ni-O); UV-vis (DMF, λ_{max} , ($\epsilon \times 10^4$ $cm^{-1}M^{-1}$)): 316 (1.37), 425 (0.64); Molar conductance (DMF, Λ , $ohm^{-1}cm^{-2}mol^{-1}$): 1.62; 1H NMR (DMSO- d_6 , δ): 7.80-6.73 (12H, ArH), 3.36-2.04 (4H, C_2H_4), 8.36 (2H, CH=N); TGA (weight loss, %): 0.91 at 90-253 °C, 27.01 at 253-386 °C, 56.82 at 386-665 °C, 15.27 at 665 °C~.

N,N-propylenebis(naphthalidiiminato) nickel(II); [Ni(II)(NAPPR)]. 89% yield; mp 305-307 °C; Anal. Calcd for $C_{25}H_{20}N_2O_2Ni$: C, 68.40; H, 4.56; N, 6.38; Ni, 13.37; Found: C, 68.38; H, 4.58; N, 6.35; Ni, 13.39. IR (KBr pellet, cm^{-1}): 3058 (C-H), 2930 (C-H), 1615 (C=N), 1458 (C=C), 1194 (C-O), 748 (Ni-N), 475 (Ni-O); UV-vis (DMF, λ_{max} , ($\epsilon \times 10^4$ $cm^{-1}M^{-1}$)): 316 (0.45), 422 (0.18); Molar conductance (DMF, Λ , $ohm^{-1}cm^{-2}mol^{-1}$): 1.49; 1H NMR (DMSO- d_6 , δ): 7.79-6.83 (12H, ArH) 3.32-2.00 (6H, C_3H_6), 8.36 (2H, CH=N); TGA (weight loss, %): 0.88 at 90-217 °C, 26.04 at 217-423 °C, 49.05 at 423-596 °C, 24.03 at 596 °C~.

N,N-butylenebis(naphthalidiiminato) nickel(II); [Ni(II)(NAPBU)]. 86% yield; mp 344-346 °C; Anal. Calcd for $C_{26}H_{22}N_2O_2Ni$: C, 68.94; H, 4.86; N, 6.18; Ni, 12.96; Found: C, 68.92; H, 4.88; N, 6.15; Ni, 12.98; IR (KBr pellet, cm^{-1}): 3054 (C-H), 2937 (C-H), 1621 (C=N), 1439 (C=C), 1195 (C-O), 749 (Ni-N), 462 (Ni-O); UV-vis (DMF, λ_{max} , ($\epsilon \times 10^4$ $cm^{-1}M^{-1}$)): 308 (0.77), 422 (0.58); Molar conductance (DMF, Λ , $ohm^{-1}cm^{-2}mol^{-1}$): 1.31; 1H NMR (DMSO- d_6 , δ): 7.75-6.68 (12H, ArH), 3.34-2.00 (8H, C_4H_8), 8.34 (2H, CH=N); TGA (weight loss, %): 0.93 at 90-187 °C, 24.64 at 187-394 °C, 51.27 at 394-573 °C, 23.16 at 573 °C~.

N,N-pentylenebis(naphthalidiiminato) nickel(II); [Ni(II)(NAPPE)]. 90% yield; mp 283-285 °C; Anal. Calcd for $C_{27}H_{24}N_2O_2Ni$: C, 69.44; H, 5.14; N, 6.00; Ni, 12.57; Found: C, 69.41; H, 5.13; N, 5.98; Ni, 12.59; IR (KBr pellet, cm^{-1}): 3056 (C-H), 2931 (C-H), 1613 (C=N), 1438 (C=C), 1194 (C-

O), 746 (Ni-N), 464 (Ni-O); UV-vis (DMF, λ_{max} , ($\epsilon \times 10^4$ $cm^{-1}M^{-1}$)): 315 (1.63), 418 (0.55); Molar conductance (DMF, Λ , $ohm^{-1}cm^{-2}mol^{-1}$): 1.93; 1H NMR (DMSO- d_6 , δ): 7.75-6.68 (12H, ArH), 3.34-2.00 (10H, C_5H_{10}), 8.34 (2H, CH=N); TGA (weight loss, %): 0.89 at 90-214 °C, 24.46 at 214-406 °C, 50.43 at 406-587 °C, 24.22 at 587 °C~.

Physical Measurements. Melting points were measured by a Mel-Temp apparatus. The elemental analysis (carbon, hydrogen, and nitrogen) was performed on a Foss Heraeus CHN Rapid (Analysentechnik GmbH) Elemental Analyzer and the nickel content was determined by a Perkin-Elmer model 603 atomic absorption (AA) spectrometer. 1H NMR spectra in DMSO- d_6 were recorded by a Bruker AMX-300 spectrometer. Chemical shifts are reported as δ values in ppm relative to an internal standard tetramethylsilane. Infrared and UV-vis spectra were recorded on Perkin-Elmer Model 1620 FT-IR and Hewlett Packard 8452A Diode Array spectrophotometer. Thermogravimetric analysis was carried out using a Perkin-Elmer model 2 series thermogravimetric analyzer (TGA) under N_2 gas atmosphere. The molar conductance was measured in DMF solution at 25 °C by DKK model AO-6 Digital conductometer.

Electrochemistry. Electrochemical measurements of free base ligands and their Ni(II) complexes were carried out by cyclic voltammetry, chronoamperometry, controlled potential coulometry, and differential pulse voltammetry in DMF and DMSO solutions containing 0.1 M TEAP as a supporting electrolyte. Single electrochemical compartment cell in which a glassy carbon (0.071 cm^2), a platinum wire counter, and a Ag/AgCl reference electrode were housed, was used for electrochemical measurement. A glassy carbon electrode was polished to become a mirror-image with 1 μm alumina powder, subsequently cleaned in an ultrasonic cleaning bath for the removal of solid particles, and finally rinsed several times with doubly distilled deionized water before use. All electrochemical measurements were conducted under the nitrogen gas atmosphere. A Princeton Applied Research 273 potentiostat/galvanostat interfaced by 486 DX2 microcomputer through an IEEE-488 bus was used for electrochemical experiments.

Results and Discussion

Tetradentate Schiff base nickel(II) complexes have been synthesized and characterized by UV-vis, IR, TGA, NMR, AA, and elemental analysis. The nickel(II) complexes employing Schiff base ligands with the 2N2O donor sets were formed by the reaction of 2-hydroxy-1-naphthaldehyde and various linear diamines which differ in the number of carbon atoms. Elemental analysis and spectral data show the formation of the tetradentate Schiff base ligand. The results of elemental analysis of the Schiff base ligand and their Ni(II) complexes agree well with the composition of the proposed complexes and support the fact that the mole ratio of Schiff base ligand to the Ni(II) metal is 1:1 as shown in Figure 1. All complexes are highly soluble in DMF, DMSO, and pyridine but insoluble in water. The conductivity data in 1 mM DMF solution indicate that the Ni(II) complexes are nonionic compounds.

1H NMR spectra. The tetradentate Schiff base ligands of 2N2O donor sets possess two phenolic groups and azome-

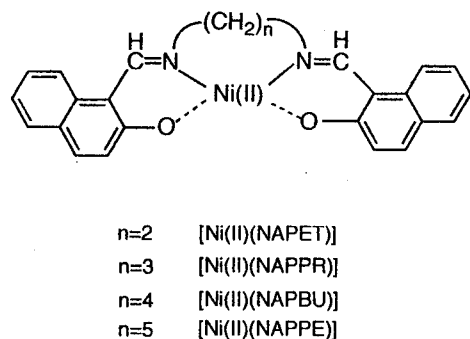


Figure 1. The proposed structure of Ni(II) complexes.

thine groups. ^1H NMR spectra of Schiff base ligands in DMSO-d_6 show the aromatic protons as multiplet in the range of 6.68-7.80 ppm and O-H protons of the two phenolic groups in the range of 9.14-9.20 ppm. The azomethine protons in free ligands appear at 8.12-8.14 ppm. But ^1H NMR spectra of the azomethine protons in Ni(II) complexes are shifted to the down field about 8.24-8.32 ppm in the corresponding free ligands and the phenolic O-H proton disappears. These observations suggest that the dianionic tetradentate Schiff base ligands coordinate to the Ni(II) atom through the charged phenolic oxygen atoms and nitrogen atoms of azomethine groups.

Infrared and UV-vis spectra. All of the IR spectra of Ni(II) complexes show typical bands of Schiff-base, with strong peaks assigned to $\nu(\text{C}=\text{N})$ in the 1610-1642 cm^{-1} region.²⁵ We can see that $\nu(\text{C}=\text{N})$ bands in the complexes are shifted about 15-20 cm^{-1} to the lower energy regions in the corresponding free ligands. These phenomena appear due to the coordination of the azomethine nitrogens to the metal ion.^{22,23,26} According to Ueno and Martell,^{27,28} characteristic absorption bands for M(II)-N and M(II)-O bonds in complexes appear in the spectral region of 650-850 cm^{-1} and 400-600 cm^{-1} , respectively. In our study, two absorption bands at 740-750 cm^{-1} and 420-470 cm^{-1} are allotted to be Ni(II)-N and Ni(II)-O bands. Also, broad $\nu(\text{OH})$ band of the free ligands about 3400 cm^{-1} disappears on complexes. These results are in accordance with the assignments for the Ni(II) complex of the salicylideneimine ligands reported previously.²⁹ The UV-vis spectra of the Ni(II) complexes obtained in DMF solution show a $\pi-\pi^*$ ligand field absorption band at 308-316 nm and a d- π^* charge transfer band at 418-425 nm.^{30,31}

Thermogravimetric analysis. An interesting observation in the TGA experiment of the complexes is that weight loss is a three step process. All Ni(II) complexes show the TGA curve decreasing in weight at 200-225 $^\circ\text{C}$ and subsequently decomposing. Thermal gravimetric analysis data support that the Ni(II) complexes do not contain the water molecules.

Electrochemical studies. The electrochemical behaviors of tetradentate Schiff base ligands and their Ni(II) complexes in DMSO and DMF solutions were investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry with a glassy carbon electrode. A knowledge of electrochemical redox processes of the free ligand is important in properly assigning the electron transfer processes of the Ni(II) complexes

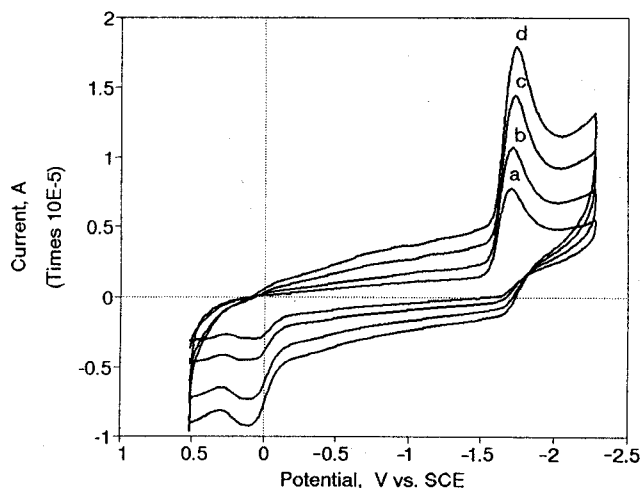


Figure 2. Cyclic voltammograms of 1 mM H_2NAPPR containing 0.1 M TEAP as a supporting electrolyte in DMSO solution. Scan rates were a) 50, b) 100, c) 200, and d) 300 mV/sec, respectively.

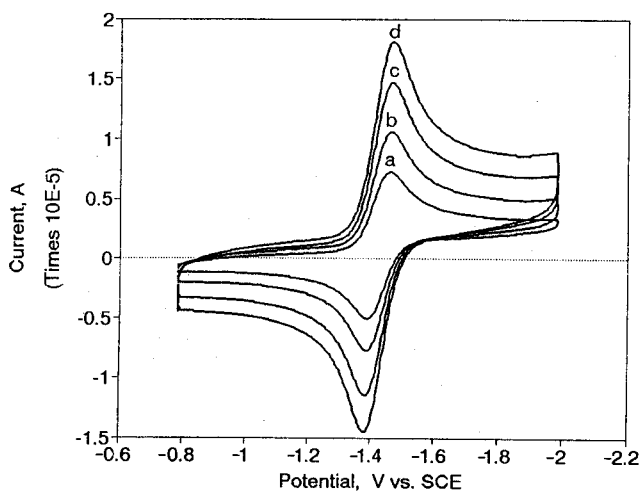


Figure 3. Cyclic voltammograms of 1 mM $[\text{Ni(II)(NAPPR)}]$ containing 0.1 M TEAP as a supporting electrolyte in DMSO solution. Scan rates were a) 50, b) 100, c) 200, and d) 300 mV/sec, respectively.

with Schiff base ligands. Therefore, we investigated the electrochemical processes of the free ligands. Figure 2 shows typical cyclic voltammograms of 1 mM H_2NAPPR free ligand in DMSO solution according to the scan rates. As shown in Figure 2, the cathodic peak currents were increased and the cathodic peak potentials shifted to more negative direction with the increase of the scan rate. The redox processes of ligands are highly irreversible.

Figure 3 shows the cyclic voltammograms of 1 mM $[\text{Ni(II)(NAPPR)}]$ complex in DMSO solution. In the Figure 3, the cathodic reduction peak at $-1.458 \sim -1.466$ V is coupled to an oxidation peak at $-1.391 \sim -1.395$ V corresponding to the Ni(II)/Ni(I) redox process. There Ni(II) complexes are reduced at much more positive potential than that of the cathodic peak for the free base ligand shown in Figure 2. Therefore, the cyclic voltammetry was carried out according

Table 1. Cyclic voltammetric data of 1 mM Ni(II) complexes in DMF solution

Complexes	scan rate	E_{pc}	E_{pa}	ΔE_p	$E_{1/2}$	i_{pa}/i_{pc}	$i_{pc}/\nu^{1/2}$
	(V/s)	(-V)	(-V)	(-V)	(-V)		($\mu\text{As}^{1/2}\text{V}^{-1/2}$)
[Ni(II)(NAPET)]	0.05	1.604	1.543	0.061	1.573	0.99	36.85
	0.1	1.605	1.542	0.063	1.574	0.96	36.24
	0.2	1.607	1.540	0.067	1.573	0.96	35.37
	0.3	1.609	1.538	0.071	1.574	0.98	36.41
[Ni(II)(NAPPR)]	0.05	1.419	1.358	0.061	1.389	1.01	38.32
	0.1	1.420	1.356	0.064	1.388	0.98	38.74
	0.2	1.422	1.354	0.068	1.388	1.00	38.35
	0.3	1.424	1.352	0.072	1.388	0.99	38.27
[Ni(II)(NAPBU)]	0.05	1.360	1.297	0.063	1.329	0.88	33.38
	0.1	1.362	1.294	0.068	1.328	0.86	33.87
	0.2	1.364	1.291	0.073	1.328	0.87	34.14
	0.3	1.366	1.288	0.078	1.327	0.88	33.37
[Ni(II)(NAPPE)]	0.05	1.357	1.292	0.065	1.325	0.73	29.78
	0.1	1.361	1.290	0.071	1.326	0.72	29.79
	0.2	1.364	1.288	0.076	1.326	0.75	29.67
	0.3	1.367	1.286	0.081	1.327	0.74	29.72

Table 2. Cyclic voltammetric data of 1 mM Ni(II) complexes in DMSO solution

Complexes	scan rate	E_{pc}	E_{pa}	ΔE_p	$E_{1/2}$	i_{pa}/i_{pc}	$i_{pc}/\nu^{1/2}$
	(V/s)	(-V)	(-V)	(-V)	(-V)		($\mu\text{As}^{1/2}\text{V}^{-1/2}$)
[Ni(II)(NAPET)]	0.05	1.638	1.580	0.060	1.610	0.94	26.25
	0.1	1.640	1.578	0.062	1.610	0.98	26.49
	0.2	1.642	1.577	0.065	1.610	0.91	26.30
	0.3	1.644	1.575	0.069	1.610	0.91	26.13
[Ni(II)(NAPPR)]	0.05	1.458	1.395	0.063	1.427	0.99	28.37
	0.1	1.460	1.394	0.066	1.427	1.00	28.75
	0.2	1.463	1.393	0.070	1.428	0.99	27.93
	0.3	1.466	1.391	0.075	1.427	0.97	28.88
[Ni(II)(NAPBU)]	0.05	1.384	1.319	0.065	1.352	0.85	20.56
	0.1	1.386	1.318	0.068	1.352	0.84	21.30
	0.2	1.389	1.316	0.073	1.352	0.83	21.06
	0.3	1.391	1.314	0.077	1.353	0.85	20.92
[Ni(II)(NAPPE)]	0.05	1.386	1.320	0.066	1.353	0.84	20.93
	0.1	1.389	1.319	0.070	1.354	0.87	19.98
	0.2	1.392	1.317	0.075	1.355	0.83	20.90
	0.3	1.395	1.315	0.080	1.355	0.85	20.19

to the scan rates at $-0.8 \sim -2.2$ V potential range. A summary of the redox processes measured for the Ni(II) complexes in DMSO and DMF solutions is listed in Table 1 and 2. As can be seen in Table 1 and 2, reduction and oxidation peaks are observed at $-1.64 \sim -1.40$ and $-1.59 \sim -1.32$ V vs. SCE, respectively.

The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the separation between the peak potentials,

$$\Delta E_p = E_{pa} - E_{pc} = 0.0591/n \quad (1)$$

where E_{pa} , E_{pc} , and n are anodic peak potential, cathodic peak potential, and the number of electrons transferred, res-

pectively. Thus one-electron process exhibits a ΔE_p of approximately 0.059 V. At slower scan rate, the peak separation, ΔE_p , for the cathodic and anodic cyclic voltammetric peak potentials is very close to 60 mV, indicating that the number of electrons transferred should be 1.0. The peak separation, ΔE_p , for the [Ni(II)(NAPPE)] complex with long chelate ring size is larger than that of the [Ni(II)(NAPET)] complex with the short chelate ring size. These results show that the electrochemical redox processes of Ni(II) complexes with long chelate ring size are quasi-reversible charge transfer.³² Also the reduction potential for the [Ni(II)(NAPET)] complex shows more negative value than that of the [Ni(II)(NAPPE)] complex. This indicates that the reduction of the Ni(II) com-

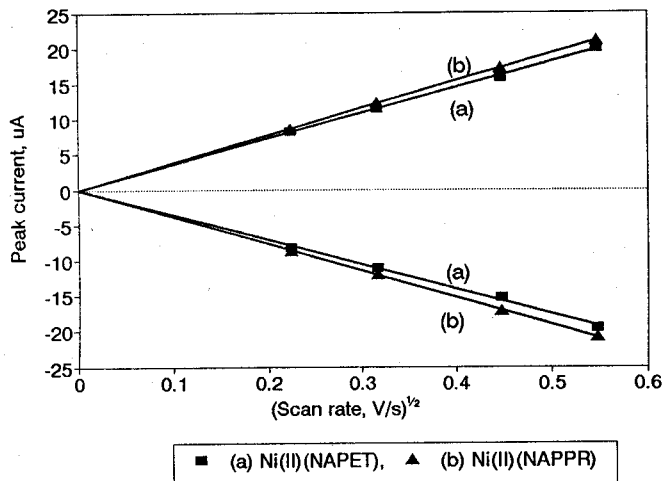


Figure 4. Plots of i_{pc} vs. $v^{1/2}$ for a) [Ni(II)(NAPET)] and b) [Ni(II)(NAPPR)] complexes in DMSO solution containing 0.1 M TEAP as a supporting electrolyte.

Table 3. The kinetic parameters of Ni(II) complexes

Complexes	$^a E_p$	$^b n$	$^c D_o$	$^d k_o$
[Ni(II)(NAPET)]	-1.80	1.0 ± 0.04	5.7×10^{-6}	9.5×10^{-2}
[Ni(II)(NAPPR)]	-1.60	0.97 ± 0.05	6.2×10^{-6}	8.7×10^{-2}
[Ni(II)(NAPBU)]	-1.54	0.95 ± 0.04	5.9×10^{-6}	3.6×10^{-2}
[Ni(II)(NAPPE)]	-1.54	0.98 ± 0.03	6.9×10^{-6}	1.8×10^{-2}

^aReduction potential for the controlled potential coulometry.

^bNumber of electrons per molecule obtained by controlled potential coulometry. ^cDiffusion coefficients obtained by chronoamperometric data, cm^2/sec . ^dExchange rate constants obtained by cyclic voltammetric data, cm/sec .

plexes with the short chelate ring size is more difficult than that of the long chelate ring size. Therefore, we concluded that reduction potentials of the Ni(II) complexes are affected by chelate ring size of ligands and [Ni(II)(NAPET)] complex is the most stable. Also, the ratio of the anodic to cathodic peak current approaches to 1 according to the decrease in the chelate ring size. These phenomena appear to have the same results in DMF and DMSO solvent as shown in Table 1 and 2. From the results, the suggested mechanism for electrochemical redox processes of Ni(II) complexes corresponds to the following reaction



Figure 4 shows plots of peak current vs. (scan rate)^{1/2} from cyclic voltammetric results of [Ni(II)(NAPET)] and [Ni(II)(NAPPR)] complexes in DMSO solution at glassy carbon electrode. These plots show a good linear relationship indicating that the process is diffusion-controlled and the adsorption of the Ni(II) complexes on the electrode surface is not involved.³³ To establish whether the number of electrons transferred is close to 1.0, we carried out controlled potential coulometry in DMSO solution at glassy carbon electrode. A summary of the number of electron is listed in Table 3. As can be seen in Table 3, controlled potential reduction

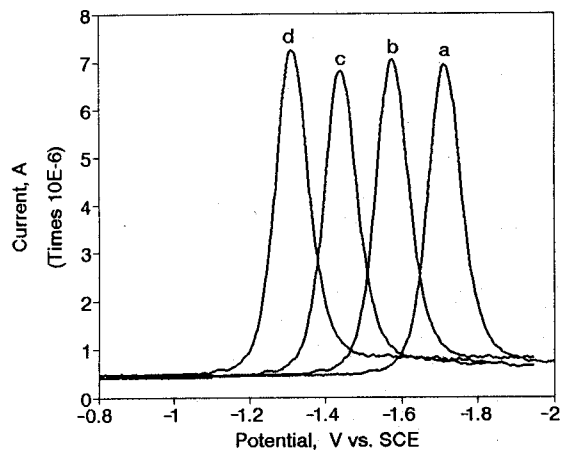


Figure 5. Differential pulse voltammograms of 1 mM a) [Ni(II)(NAPET)], b) [Ni(II)(NAPPR)], c) [Ni(II)(NAPBU)], and d) [Ni(II)(NAPPE)] complexes in DMSO solution containing 0.1 M TEAP as a supporting electrolyte.

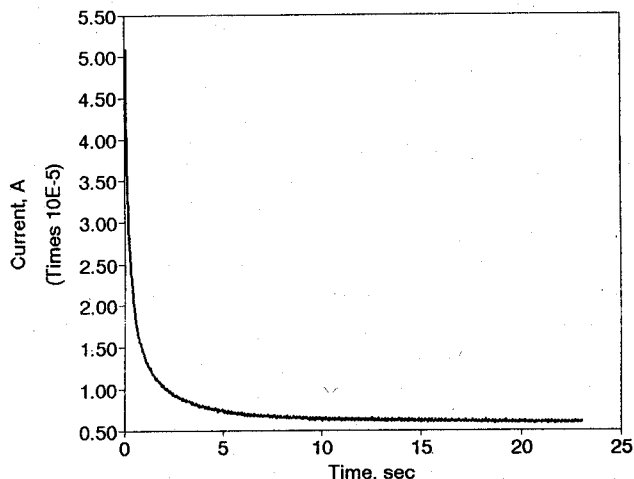


Figure 6. Chronoamperometric curves at the glassy carbon electrode for 1 mM [Ni(II)(NAPPR)] complex in DMSO solution.

at a potential corresponding to the reduction peak of the cyclic voltammograms is reduced in one electron step to what is assumed to be Ni(I) species. The low values of n for some of the complexes are due to their slow reaction with traces of H_2O or impurities in the solvent during the course of the coulometric determination. However the values of number of electron obtained from controlled potential coulometry are consistent with the values observed from cyclic voltammetry.

In order to confirm in details, and to further show that the number of electrons transferred is close to 1.0, we carried out differential pulse voltammetry. Figure 5 shows the differential pulse voltammograms of Ni(II) complexes in DMSO solution containing 0.1 M TEAP as a supporting electrolyte. For reversible charge-transfer processes, the limiting peak width at half-height ($W_{1/2}$) is given by Eq. (2)³³

$$W_{1/2} = 3.52RT/nF = 90.4 \text{ mV}/n \quad (T = 25^\circ \text{C}) \quad (2)$$

The values of $W_{1/2}$ observed for Ni(II) complexes are obser-

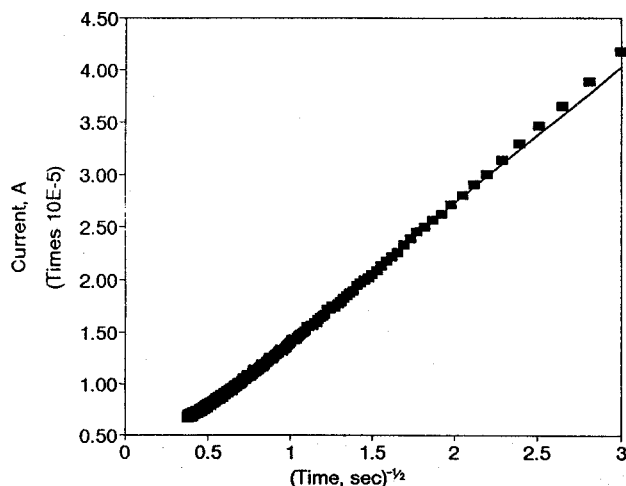


Figure 7. Cottrell plot for chronoamperometric result shown in Figure 6.

ved to be 92-100 mV, consistent with one electron transfer processes that occur with moderate rates of heterogeneous charge transfer.

We also carried out chronoamperometric experiments for the Ni(II) complexes in DMSO solution in order to estimate the diffusion coefficient. Figure 6 shows chronoamperometric result of 1 mM [Ni(II)(NAPPR)] complex in DMSO solution containing 0.1 M TEAP. Figure 7 shows the result plotted according to Cottrell equation.³³ Cottrell equation predicts that the plot of $i(t)$ vs. $t^{-1/2}$ should be linear with a slope of $nFAD_0^{1/2}C^*/\pi^{1/2}$. The values of diffusion coefficient calculated from these plots are listed in Table 3. As can be seen in Table 3, diffusion coefficients are determined to be $5.7\text{--}6.9 \times 10^{-6}$ cm²/sec. Finally, one can also estimate the exchange rate constant for a quasireversible electrochemical reaction from the variations of a peak separation, ΔE_p , upon changing scan rates. Nicholson³³ has Ψ -values for various ΔE_p -values; the empirical parameter, Ψ , obtained from the ΔE_p , is now related to the exchange rate constant k^0 by an equation,

$$\Psi = \frac{\gamma k^0}{(a n D_0)} \quad (3)$$

where $\gamma = (D_O/D_R)^{1/2}$ and $a = nFv/(RT)$ with v = scan rate and subscripts denoting oxidant (O) or reductant (R). Assuming that γ is approximately 1, the exchange rate constant can be calculated from the slope of Ψ vs. $v^{1/2}$ plot according to equation (3). The values of exchange rate constant obtained from these slopes are listed in Table 3. As can be seen in Table 3, the exchange rate constants are determined to be $1.8\text{--}9.5 \times 10^{-2}$ cm/sec. These values are affected by chelate ring size of ligands.

Conclusions

The Ni(II) complexes of tetradentate Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and aliphatic diamine have been synthesized. All Ni(II) complexes have been identified as monomeric four-coordinated non-ionic compounds by the results of elemental analysis, IR, UV-visible spectra, molar conductivity, and thermogravimetric analysis. The

mole ratio of Schiff base to the Ni(II) complexes was found to be 1 : 1. The redox process of the free ligands is irreversible reaction, whereas the redox process of the Ni(II) complexes is quasi-reversible in DMSO and DMF solutions containing 0.1 M TEAP as a supporting electrolyte. The reduction of Ni(II) complexes with the short chelate ring size is occurred to be more negative potential than that of complexes with long chelate ring size. These results indicate that the reduction potentials of the Ni(II) complexes are affected by chelate ring size of ligands. Furthermore, the redox processes of Ni(II) complexes by cyclic voltammetry, controlled potential coulometry, and differential pulse voltammetry were observed as one electron charge transferred process and diffusion-controlled reaction. From these results, we conclude that the redox process of all Schiff base Ni(II) complexes used in this study is the following reaction



The diffusion coefficients of Ni(II) complexes containing 0.1 M TEAP as a supporting electrolyte in DMSO solution were determined to be $5.7\text{--}6.9 \times 10^{-6}$ cm²/sec. Also the exchange rate constants were determined to be $1.8\text{--}9.5 \times 10^{-2}$ cm/sec. These values were affected by chelate ring size of ligands.

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Hydrodediazoni-ation of Arenediazonium Tetrafluoroborate with Triethylamine

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Hydrodediazoni-ation product (**3a-d**) was found to be the major product in the reaction of arenediazonium tetrafluoroborate (**1a-d**) with triethylamine (**2**) in methanol under nitrogen at room temperature. A quantitative study on the title reaction was investigated in detail and two remarks were noteworthy. One was the linear increase in the yield of **3a-d** by increasing the molar concentration of **2** until equimolar concentration was reached between **1a-d** and **2**. The other was the suppression of the formation of **3a-d** in the presence of oxygen. Based on these results, the title reaction was better understood by 1:1 electron transfer reaction between reactants (**1a-d** and **2**) rather than by radical chain mechanism proposed in the reaction of arenediazonium tetrafluoroborate and triphenylphosphine.

Introduction

Hydrodediazoni-ation of arenediazonium salt is chiefly achieved by using various inorganic and organic reductants¹ such as hypophosphorous acid,² hot ethanol,^{2,3} triphenylphosphine,⁴ *N,N*-dimethylformamide,^{5,6} *N*-benzylpiperidine,⁷ and ferrocene⁸ etc.. In spite of many dediazoni-ation methods, there are problems in each method. For instances, a substrate bearing electron-donating substituent in the para position, such as methoxy and methyl as in *p*-anisidine and *p*-toluidine does not give the expected arene but tarry materials.⁵ On the other hand, some inorganic reductants are not effective in organic solvent.⁸ Herein, we report that triethylamine, a common and cheap compound, is an efficient reductant in reaction with arenediazonium tetrafluoroborate under nitrogen atmosphere to give corresponding arene. To the best of our knowledge, this quantitative study on the reaction of arenediazonium tetrafluoroborate with triethylamine is a first report⁹ though derivatives of piperidine and pyrrolidine are documented in the literature.⁷

Experimental

Synthesis of Diazonium Tetrafluoroborates. Nine substrates (**1a-d**) were prepared according to the known procedure.¹⁰ The diazonium salt was dried overnight in a vacuum dessicator. IR spectrum showed the complete removal of water in the starting diazonium salt which was used directly for the reaction.

Quantitative Determination of Reaction Products (Standard Procedure). For the nine substrates employed in this work, similar procedure was followed for the determination of the reaction products. The typical procedure in the case of *m*-nitrobenzenediazonium tetrafluoroborate (**1a_m**) is as follows; In a two-necked round bottomed flask was introduced a solution of methanol (10 mL) containing tridecane (20 mM) as an internal standard. To this solution was added **1a_m** (1 mmol) and nitrogen was passed through the solution for 10 min. After then appropriate amount of triethylamine (0.5-1.5 eq) in methanol (3 mL) kept in addition funnel was run in dropwise. Immediately reaction took place