

- 1979, 101, 5569.
12. (a) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. *Pure Appl. Chem.* 1975, 41, 671. (b) Whetten, R. L.; Fu, K. -J.; Grant, E. R. *J. Am. Chem. Soc.* 1982, 104, 4270.
13. Waller, I. M.; Hepburn, J. W. *J. Chem. Phys.* 1988, 88, 6658.
14. The research facilities of Korea Basic Science Institute, Taegu Branch (Kyungpook National University).
15. Chang, R. *Physical Chemistry with Applications to Biological Systems*; Macmillan: New York, 1981; p 63.
16. Dean, J. A. *Lange's Handbook of Chemistry*; McGraw-Hill: New York, 1985; p 4.14.
17. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; p 1049.

## Synthesis and Characterization of Schiff Base-Cu(II) Complexes Derived from 2-Hydroxy-1-Naphthaldehyde and Aliphatic Diamines

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Tetradentate Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and aliphatic diamine have been synthesized. Cu(II) complexes of Schiff base ligands have been synthesized from the free ligands and copper acetate. The mole ratio of ligand to copper was identified to be 1:1 by the result of elemental analysis and Cu(II) complexes were in a four-coordinated configuration. The electrochemical redox process of Cu(II) complexes in a DMF solution has been investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry. The redox process of Cu(II) complexes is one electron transfer process in quasi-reversible and diffusion-controlled reaction. The electrochemical redox potentials and the kinetic parameters of Cu(II) complexes are affected by the chelate ring of Schiff base ligands.

### Introduction

The control and understanding of the reactions of transition metal complexes with dioxygen is relevant to oxygen transport in biological systems, oxygenase enzymes, and homogeneous oxygenation catalysts.<sup>1-4</sup> Complexes of Schiff base ligands have been studied for their dioxygen uptake<sup>5</sup> and oxidative catalysis.<sup>6</sup> 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.<sup>7-12</sup> Especially, Co(II) and Cu(II) complexes employing tetradentate Schiff base 2N2O donor ligands which coordinate through donor atoms have been studied as oxygen-carriers.<sup>13,14</sup> Although the preparation, structure, spectral characterization, and the coordination chemistry of Schiff base complexes have been studied extensively,<sup>15-20</sup> yet little is reported on the electrochemical studies.

In this study, we synthesized several Cu(II) complexes of tetradentate Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with aliphatic diamines. The ligands and their Cu(II) complexes were characterized by elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-vis spectra, molar conductance, and thermogravimetric analysis. The electrochemical redox process of the ligands and their Cu(II) complexes in N,N-dimethylformamide (DMF) solutions was

investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, controlled potential coulometry. In this paper, syntheses and the electrochemical behavior of the Cu(II) complexes are reported.

### Experimental

**Materials.** Ethanol, sodium hydroxide, copper(II) acetate monohydrate, 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 was dried by a standard procedure<sup>21</sup> before use. TEAP was recrystallized twice from distilled water and dried at 70 °C *in vacuo*.

**Preparation of ligands.** A typical procedure for the synthesis of tetradentate Schiff base is as follows. A solution of 0.1 mole diamine in 50 mL ethanol was slowly added to a solution of 0.2 mole 2-hydroxy-1-naphthaldehyde in 50 mL ethanol under nitrogen atmosphere. After stirring reaction mixture for 2 hrs, the precipitate was collected by filtration. The products were recrystallized from ethanol and dried under reduced pressure at 60 °C.

**1,2-bis(naphthylideneimino)ethane; H<sub>2</sub>NAPET.** 97 % yield; mp 215-217 °C; Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.24; H, 5.47; N, 7.60; Found: C, 78.13; H, 5.55; N, 7.73; IR (KBr pellet, cm<sup>-1</sup>): 3420 (O-H), 3057 (ArC-H), 2932 (C-H), 1642 (C=N), 1541 (C=C), 1452 (C=C), 1254 (C-O); UV-vis (DMF,

$\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 272 (1.86), 308 (1.99), 404 (1.15), 424 (1.14);  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 3.84-3.78 (4H, N-(CH<sub>2</sub>)<sub>2</sub>-), 8.09-6.73 (12H, ArH), 9.16 (2H, CH=N), 14.20 (2H, C<sub>10</sub>H<sub>6</sub>OH);  $^{13}\text{C NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 50.6 (N-(CH<sub>2</sub>)<sub>2</sub>-), 106.0-137.1 (Ar), 159.7 ((C-2)OH), 177.6 (CH=N).

**1,3-bis(naphthylideneimino)propane; H<sub>2</sub>NAPPR.**

97% yield; mp. 225-227 °C; Anal. Calcd for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.51; H, 5.80; N, 7.32; Found: C, 78.50; H, 5.94; N, 7.43; IR (KBr pellet, cm<sup>-1</sup>): 3408 (O-H), 3051 (ArC-H), 2931 (C-H), 1634 (C=N), 1543 (C=C), 1462 (C=C), 1210 (C-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 272 (1.57), 308 (1.83), 404 (1.40), 424 (1.50);  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 2.15-2.10 and 3.80-3.74 (6H, N-(CH<sub>2</sub>)<sub>3</sub>-), 8.09-6.73 (12H, ArH), 9.15 (2H, CH=N), 14.20 (2H, C<sub>10</sub>H<sub>6</sub>OH);  $^{13}\text{C NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 31.8 and 48.9 (N-(CH<sub>2</sub>)<sub>3</sub>-), 106.1-137.1 (Ar), 159.7 ((C-2)OH), 176.6 (CH=N).

**1,4-bis(naphthylideneimino)butane; H<sub>2</sub>NAPBU.**

98 % yield; mp 234-236 °C; Anal. Calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.76; H, 6.10; N, 7.07; Found: C, 78.58; H, 6.28; N, 7.28; IR (KBr pellet, cm<sup>-1</sup>): 3466 (O-H), 3062 (ArC-H), 2935 (C-H), 1631 (C=N), 1534 (C=C), 1442 (C=C), 1259 (C-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 272 (2.06), 308 (2.36), 402 (1.88), 422 (1.93);  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 3.86-3.73 and 1.81-1.74 (8H, N-(CH<sub>2</sub>)<sub>4</sub>-), 8.08-6.69 (12H, ArH), 9.13 (2H, CH=N), 14.13 (2H, C<sub>10</sub>H<sub>6</sub>OH);  $^{13}\text{C NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 28.4 and 50.8 (N-(CH<sub>2</sub>)<sub>4</sub>-), 105.9-137.2 (Ar), 159.3 ((C-2)OH), 177.5 (CH=N).

**1,5-bis(naphthylideneimino)pentane; H<sub>2</sub>NAPPE.**

95 % yield; mp 265-267 °C; Anal. Calcd for C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: C, 80.00; H, 6.38; N, 6.82; Found: C, 79.84; H, 6.49; N, 7.17; IR (KBr pellet, cm<sup>-1</sup>): 3438 (O-H), 3053 (ArC-H), 2929 (C-H), 1634 (C=N), 1543 (C=C), 1463 (C=C), 1260 (C-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 272 (2.10), 306 (2.40), 402 (1.98), 422 (2.03);  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 3.69-3.63, 1.77-1.68, and 1.49-1.38 (10H, N-(CH<sub>2</sub>)<sub>5</sub>-), 7.75-6.68 (12H, Aromatic), 9.12 (2H, CH=N), 14.14 (2H, C<sub>10</sub>H<sub>6</sub>OH);  $^{13}\text{C NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 23.5, 30.0, and 50.6 (N-(CH<sub>2</sub>)<sub>5</sub>-), 105.8-137.2 (Ar), 159.2 ((C-2)OH), 177.7 (CH=N).

**Preparation of Cu(II) complexes.** Cu(II) complexes were obtained by addition of a mixture of ligand (0.01 mol) and NaOH (0.02 mol) in hot ethanol (100 mL) into an aqueous solution of copper(II) acetate monohydrate (0.01 mol) under a nitrogen atmosphere. After stirring the reaction mixture for 2 hrs, the resulting precipitates were filtered. The products were dried at 80 °C under reduced pressure.

**N,N'-ethylenebis(naphthaldiminato) copper(II); [Cu(II)(NAPET)].** 87% yield; mp 287-289 °C; Anal. Calcd for C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 67.04; H, 4.22; N, 6.52; Cu, 14.78; Found: C, 67.28; H, 4.31; N, 6.25; Cu, 14.62; IR (KBr pellet, cm<sup>-1</sup>): 3059 (ArC-H), 2945 (C-H), 1622 (C=N), 1541 (C=C), 1456 (C=C), 1252 (C-O), 742 (Cu-N), 575 (Cu-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 320 (1.53), 380 (0.98), 402 (0.87), 536 (0.33); Molar conductance (DMF,  $\Lambda_M$ , ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup>): 1.81; TGA (weight loss, %): 0.83 at 90-207 °C, 53.74 at 207-538 °C, 22.41 at 538-574 °C, 23.02 at 574 °C~.

**N,N'-propylenebis(naphthaldiminato) copper(II); [Cu(II)(NAPPR)].** 83% yield; mp 295-297 °C; Anal. Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 67.63; H, 4.54; N, 6.31; Cu, 14.31; Found: C, 67.89; H, 4.73; N, 6.48; Cu, 14.29; IR (KBr pellet, cm<sup>-1</sup>): 3059 (ArC-H), 2936 (C-H), 1629 (vC=N), 1586 (C=C), 1461 (C=C), 1193 (C-O), 747 (Cu-N), 592 (Cu-O); UV-vis

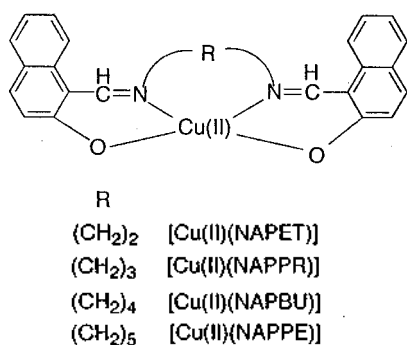
(DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 386 (0.94), 402 (0.43), 538 (0.28); Molar conductance (DMF,  $\Lambda_M$ , ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup>): 1.83; TGA (weight loss, %): 1.01 at 90-196 °C, 49.29 at 196-497 °C, 27.06 at 497-593 °C, 22.64 at 593 °C~.

**N,N'-butylenebis(naphthaldiminato) copper(II); [Cu(II)(NAPBU)].** 89% yield; mp 306-308 °C; Anal. Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 68.18; H, 4.84; N, 6.12; Cu, 13.87; Found: C, 67.96; H, 5.03; N, 6.11; Cu, 13.73; IR (KBr pellet, cm<sup>-1</sup>): 3053 (ArC-H), 2924 (C-H), 1617 (C=N), 1540 (C=C), 1458 (C=C), 1253 (C-O), 746 (Cu-N), 584 (Cu-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 336 (2.22), 382 (1.06), 544 (0.36); Molar conductance (DMF,  $\Lambda_M$ , ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup>): 1.29; TGA (weight loss, %): 0.95 at 90-188 °C, 52.47 at 188-470 °C, 25.63 at 470-542 °C, 20.95 at 542 °C~.

**N,N'-pentylenebis(naphthaldiminato) copper(II); [Cu(II)(NAPPE)].** 86% yield; mp 297-299 °C; Anal. Calcd for C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 68.70; H, 5.12; N, 5.93; Cu, 13.46; Found: C, 68.74; H, 5.37; N, 5.77; Cu, 12.98; IR (KBr pellet, cm<sup>-1</sup>): 3055 (ArC-H), 2930 (C-H), 1614 (C=N), 1542 (C=C), 1458 (C=C), 1191 (C-O), 749 (Cu-N), 594 (Cu-O); UV-vis (DMF,  $\lambda_{max}$ ,  $\epsilon \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ): 308 (0.86), 380 (0.42), 570 (0.34); Molar conductance (DMF,  $\Lambda_M$ , ohm<sup>-1</sup> cm<sup>-2</sup> mol<sup>-1</sup>): 2.18; TGA (weight loss, %): 0.76 at 90-205 °C, 51.33 at 205-591 °C, 27.44 at 591-696 °C, 20.47 at 696 °C~.

**Physical Measurements.** The elemental analysis (carbon, hydrogen, and nitrogen) was performed on a Foss Heraeus CHN Rapid (Analysentechnik GmbH) Elemental Analyzer and the copper content was determined by a Perkin-Elmer model 603 atomic absorption (AA) spectrometer. Infra-red and UV-vis spectra were recorded on Perkin-Elmer Model 1620 FT-IR and Hewlett Packard 8452A Diode Array spectrophotometer.  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra in DMSO- $d_6$  were recorded by a Bruker AMX-300 spectrometer. Melting point was measured by a Mel-Temp apparatus. Thermogravimetric analysis was carried out using a Perkin-Elmer model 2 series thermogravimetric analyzer (TGA) under N<sub>2</sub>. The molar conductance was measured in DMF solution at 25 °C by DKK model AO-6 Digital conductometer.

**Electrochemistry.** Electrochemical measurements of the Cu(II) complexes were carried out by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry in DMF solutions containing 0.1 M TEAP. Single electrochemical compartment cell in which a glassy carbon working electrode (0.071 cm<sup>2</sup>), a platinum wire counter electrode, and a Ag/AgCl reference electrode were housed, was used for electrochemical measurement. The glassy carbon electrode was polished to become a mirror-image with 1  $\mu\text{m}$  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. Controlled potential electrolysis was performed using a platinum gauze working electrode, with a platinum counter electrode separated from the solution to be electrolyzed by a compartment containing a vycor frit. All electrochemical measurements were conducted under a nitrogen atmosphere. A Princeton Applied Research (PAR) 273 potentiostat/galvanostat interfaced by 486-DX2 microcomputer through an IEEE-488 bus was used for electrochemical experiments.



Scheme 1.

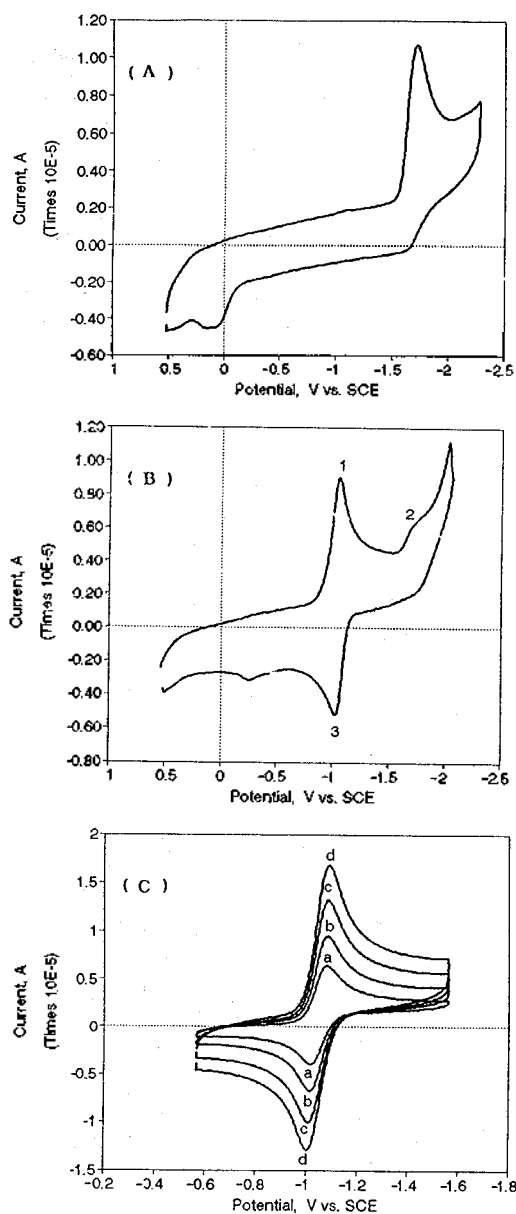
## Results and Discussion

Tetradentate Schiff base ligands with 2N2O donor sets were formed by the reactions of 2-hydroxy-1-naphthaldehyde and various linear diamines which differ in the number of carbon atoms. Cu(II) complexes were synthesized from the free ligands and copper acetate. The free ligands and their Cu(II) complexes were characterized by UV-vis, IR, TGA, NMR, AA, and elemental analysis. Elemental analysis and spectral data show the formation of the tetradentate Schiff base ligand. The results of elemental analysis agree well with the composition of the proposed complexes and support the fact that the mole ratio of Schiff base to the Cu(II) complexes is 1:1 as shown in Scheme 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 Cu(II) complexes are nonionic compounds.

**Infrared and UV-vis spectra.** The IR spectra of the free ligands show weak  $\nu(\text{OH})$  bands around  $3400\text{ cm}^{-1}$ , which indicating that there is a hydrogen bonding in the compounds. On the contrary, the complexes show no  $\nu(\text{OH})$  bands in their IR spectra. The IR spectra of the free ligands show typical bands for Schiff-base. The strong peaks observed in the  $1631\text{--}1642\text{ cm}^{-1}$  region are assignable to  $\nu(\text{C}=\text{N})$  bands.<sup>22</sup> We can see that  $\nu(\text{C}=\text{N})$  bands in the complexes are shifted to the lower energy regions about  $10\text{--}20\text{ cm}^{-1}$  relative to those of the corresponding free ligands. These observation for the  $\nu(\text{C}=\text{N})$  bands in the complexes are indicative of the coordination of the azomethine nitrogens to the copper ion. Two absorption bands at  $742\text{--}749\text{ cm}^{-1}$  and  $575\text{--}594\text{ cm}^{-1}$  in complexes are allotted to Cu(II)-N and Cu(II)-O bands, respectively.<sup>23-25</sup> The UV-vis spectra of the Cu(II) complexes obtained in DMF solution show a  $\pi\text{--}\pi^*$  ligand field absorption band at  $300\text{--}340\text{ nm}$ , a  $d\text{--}\pi^*$  charge transfer band at  $380\text{--}400\text{ nm}$ , and a  $d\text{--}d$  transition at  $540\text{--}570\text{ nm}$ .<sup>26,27</sup>

**NMR spectra.** The tetradentate Schiff base ligands of 2N2O donor sets possess two OH groups on the naphthalene and azomethine groups. <sup>1</sup>H NMR spectra of the free ligands show peaks *ca.* at 9.1 ppm and 14.1 ppm assignable to the azomethine protons and O-H protons of the two naphthalene. The aromatic and methylene protons appear at 6.71-8.08 and 1.38-1.49 ( $=\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N=}$ ), 1.68-1.77 ( $=\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N=}$ ), and 3.63-3.69 ( $=\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N=}$ ), respectively. <sup>13</sup>C NMR spectra of the free ligands show the peaks of the aliphatic carbons at 23.5, 30.0,



**Figure 1.** Cyclic voltammograms of 1 mM H<sub>2</sub>NAPPR free ligand (A) and [Cu(II)(NAPPR)] complex (B and C) containing 0.1 M TEAP as a supporting electrolyte in DMF solution. Scan rates were 100 mV/sec (A and B) and a) 50, b) 100, c) 200, and d) 300 mV/sec, respectively (C).

and 50.6 ppm and the aromatic carbons in the range of 105.8-137.2 ppm. The peaks of the azomethine carbon and C-2 carbon on the naphthalene appear at 177.7 ppm and 159.2 ppm, respectively.

**Thermogravimetric analysis.** All the Cu(II) complexes show TGA curves decreasing in weight at  $190\text{--}210\text{ }^\circ\text{C}$  and subsequently decomposing. Thermal gravimetric analysis data support that the Cu(II) complexes do not contain water molecules.

**Cyclic voltammetric studies.** The electrochemical behaviors of the tetradentate Schiff base ligands and their Cu(II) complexes in DMF solution were investigated by cyclic voltammetry, chronoamperometry, and differential pulse vol-

**Table 1.** Cyclic voltammetric data of 1 mM Cu(II) complexes in DMF

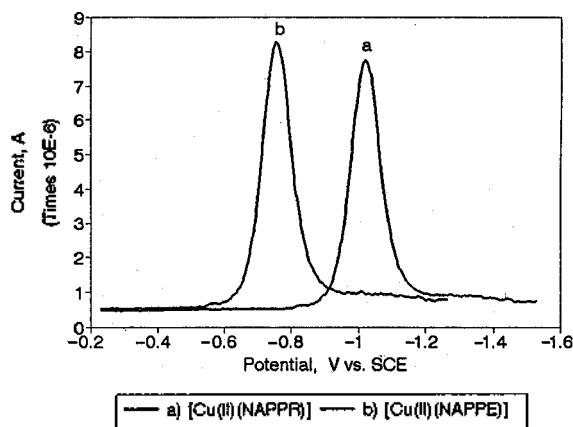
Complexes	<sup>a</sup> scan rate	<sup>b</sup> E <sub>pc</sub>	<sup>c</sup> E <sub>pa</sub>	<sup>d</sup> ΔE <sub>p</sub>	<sup>e</sup> E <sub>1/2</sub>	<sup>f</sup> i <sub>pa</sub> /i <sub>pc</sub>	<sup>f</sup> i <sub>pc</sub> /v <sup>1/2</sup>
[Cu(II)(NAPET)]	0.05	-1.186	-1.123	0.063	-1.155	0.93	23.51
	0.1	-1.188	-1.121	0.067	-1.155	0.95	23.13
	0.2	-1.190	-1.120	0.070	-1.155	0.95	22.16
	0.3	-1.192	-1.118	0.074	-1.155	0.94	23.59
[Cu(II)(NAPPR)]	0.05	-1.056	-0.982	0.074	-1.019	0.92	31.35
	0.1	-1.058	-0.980	0.078	-1.019	0.93	31.34
	0.2	-1.059	-0.976	0.083	-1.018	0.93	30.68
	0.3	-1.060	-0.974	0.086	-1.017	0.94	30.27
[Cu(II)(NAPBU)]	0.05	-0.922	-0.847	0.075	-0.885	0.84	22.81
	0.1	-0.924	-0.844	0.080	-0.884	0.84	22.94
	0.2	-0.926	-0.842	0.084	-0.884	0.85	22.03
	0.3	-0.928	-0.840	0.088	-0.884	0.83	22.44
[Cu(II)(NAPPE)]	0.05	-0.793	-0.716	0.077	-0.755	0.73	27.48
	0.1	-0.799	-0.711	0.087	-0.755	0.72	26.74
	0.2	-0.803	-0.709	0.094	-0.756	0.74	27.70
	0.3	-0.806	-0.707	0.099	-0.756	0.72	28.81

<sup>a</sup>Scan rate, V/s. <sup>b</sup>Cathodic peak potential, V vs. SCE. <sup>c</sup>Anodic peak potential, V vs. SCE. <sup>d</sup>Peak potential separation (E<sub>pa</sub>-E<sub>pc</sub>), V. <sup>e</sup>Half wave potential, V vs. SCE. <sup>f</sup>Cathodic peak current per square root of scan rate, μAs<sup>1/2</sup>V<sup>-1/2</sup>.

tammetry with a glassy carbon electrode, and controlled potential coulometry at platinum gauze electrode. A knowledge of electrochemical redox processes of the free ligand is important in properly assigning the electron transfer processes of the Cu(II) complexes with Schiff base ligands. Therefore, we investigated the electrochemical processes of the free ligands.

Figure 1 shows the cyclic voltammograms of 1 mM H<sub>2</sub>NA-PPR (A) and [Cu(II)(NAPPR)] (B and C) in DMF solution. The free ligand shows an irreversible reaction at -1.7 V. On the other hand, the copper complex undergoes a reversible reduction at -1.1 V and an irreversible reduction at ~-1.8 V; the former is assigned to be a Cu(II)/Cu(I) couple and the latter is a ligand reduction.

The scan rate dependence of the Cu(II)/Cu(I) couple for the copper complexes in DMF solution is shown in Figure 1C and a summary of the redox processes is listed in Table 1. The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the separation between the peak potentials. At slower scan rate, the peak separation (ΔE<sub>p</sub>) for the cathodic and anodic cyclic voltammetric peak potentials is close to 60 mV, indicating that the number of electrons transferred should be n=1. As shown in Table 1, the peak separation for [Cu(II)(NAPPE)] complex with a larger chelate ring is larger than that of [Cu(II)(NAPET)] complex with the smaller chelate ring. Also the reduction potential for [Cu(II)(NAPET)] complex shows more negative value than that of [Cu(II)(NAPPE)] complex. This indicates that the reduction of Cu(II) complexes with the smaller chelate ring is more difficult than that of the larger chelate ring. Therefore, we concluded that reduction potentials of Cu(II) complexes are affected by a chelate ring of ligands and [Cu(II)(NAPET)] complex is the most stable in DMF solution. Also, the ratio of the anodic to cathodic peak currents approaches to 1 when the chelate ring size decreases. From these results, we conclude that



**Figure 2.** Differential pulse voltammograms of 1 mM a) [Cu(II)(NAPPR)] and b) [Cu(II)(NAPPE)] complexes containing 0.1 M TEAP as a supporting electrolyte in DMF solution at modulation time 20 mV.

the electrochemical redox processes of the Cu(II) complexes are as follows



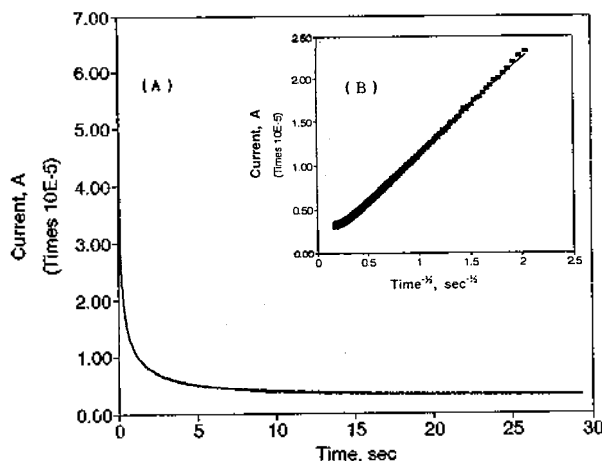
Because plots of peak current vs. square root of scan rate from cyclic voltammetric results of the Cu(II) complexes show a good linear relationship (not shown), the redox process is diffusion-controlled and the adsorption of Cu(II) complexes on the electrode is not involved.<sup>28</sup>

**Differential pulse voltammetric studies.** To establish whether the number of electrons transferred is close to n=1, we carried out differential pulse voltammetry. Figure 2 shows the differential pulse voltammograms of [Cu(II)(NAPPR)] and [Cu(II)(NAPPE)] complexes containing 0.1 M TEAP as a supporting electrolyte in DMF solution. As shown in Figure 2, the half wave potentials of the Cu(II)

**Table 2.** The kinetic parameters of Cu(II) complexes

Complexes	<sup>a</sup> E <sub>p</sub>	<sup>b</sup> n	<sup>c</sup> D <sub>0</sub>	<sup>d</sup> k <sup>0</sup>
[Cu(II)(NAPET)]	-1.350	1.01 ± 0.05	7.6 × 10 <sup>-6</sup>	8.4 × 10 <sup>-2</sup>
[Cu(II)(NAPPR)]	-1.200	0.99 ± 0.03	6.4 × 10 <sup>-6</sup>	6.8 × 10 <sup>-2</sup>
[Cu(II)(NAPBU)]	-1.075	0.93 ± 0.05	5.5 × 10 <sup>-6</sup>	5.1 × 10 <sup>-2</sup>
[Cu(II)(NAPPE)]	-0.950	0.97 ± 0.04	4.3 × 10 <sup>-6</sup>	3.2 × 10 <sup>-2</sup>

<sup>a</sup>Reduction potential applied for the controlled potential coulometry, V vs. SCE. <sup>b</sup>Number of electrons per molecule obtained from controlled potential coulometry. <sup>c</sup>Diffusion coefficients obtained from chronoamperometry, cm<sup>2</sup>/sec. <sup>d</sup>Exchange rate constants obtained from cyclic voltammetry, cm/sec.

**Figure 3.** Chronoamperometric curve (A) and Cottrell plot (B) for 1 mM [Cu(II)(NAPPR)] complex in DMF solution.

complexes affected by the chelate ring size of Schiff base ligands. All of  $W_{1/2}$  (limiting peak width at half-height) observed for Cu(II) complexes used in this study are observed to be 92-100 mV, consistent with one electron transfer processes that occur with moderate rate of heterogeneous charge transfer.<sup>28</sup>

**Controlled potential coulometric studies.** In order to confirm in details, and to further show that the number of electrons transferred is close to  $n=1$ , we carried out controlled potential coulometry in DMF solution at platinum gauze electrode. The values of  $n$  for the reduction process of Cu(II) complexes are determined and listed in Table 2. As can be seen in Table 2, controlled potential reduction is reduced by one electron transfer to what is assumed to be Cu(I) species. The number of electrons obtained from controlled potential coulometry is consistent with those determined from cyclic voltammetry and differential pulse voltammetry.

**Chronoamperometric studies.** We also carried out chronoamperometric experiments for Cu(II) complexes in a DMF solution in order to estimate the diffusion coefficient. Figure 3A shows chronoamperometric curve of 1 mM [Cu(II)(NAPPR)] complex containing 0.1 M TEAP in DMF solution. Figure 3B shows the result obtained from Cottrell equation,<sup>28</sup> i.e.,

$$i(t) = \frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}} \quad (1)$$

Here  $i(t)$ ,  $t$ ,  $n$ ,  $A$ ,  $D$ , and  $C^*$  are the current at time  $t$ , time, number of electrons transferred, electrode area, diffusion coefficient, and bulk concentration, respectively. Equation (1) predicts that the plot of  $i(t)$  vs.  $t^{-1/2}$  should be linear with a slope of  $nFAD^{1/2}C^*/\pi^{1/2}$ . The values of diffusion coefficient calculated from these plots are listed in Table 2. As can be seen in Table 2, diffusion coefficients are determined to be  $4.3-7.6 \times 10^{-6}$  cm<sup>2</sup>/sec and affected by the chelate ring size of Schiff base ligands.

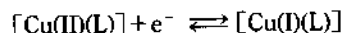
**Electro-kinetic studies.** We can also estimate the exchange rate constant for a quasi-reversible electrochemical reaction from the variations of a peak separation ( $\Delta E_p$ ). Nicholson<sup>28</sup> has  $\Psi$ -values for various  $\Delta E_p$ -values; the empirical parameter,  $\Psi$ , obtained from the  $\Delta E_p$ , is now related to the exchange rate constant  $k^0$  by an equation,

$$\Psi = \frac{\gamma k^0}{(\pi a D_0)^{1/2}} \quad (2)$$

where  $\gamma = (D_0/D_R)^{1/2}$  and  $a = nFv/(RT)$  with  $v$  = scan rate and subscripts denoting oxidant (O) or reductant (R). Assuming that  $\gamma$  is approximately 1, the exchange rate constant can be calculated from the slope of  $\Psi$  vs.  $v^{1/2}$  plot according to equation 2. The values of exchange rate constant obtained from these slopes are listed in Table 2. As can be seen in Table 2, the exchange rate constants are determined to be  $3.2-8.4 \times 10^{-2}$  cm/sec.

## Conclusions

The structure of Schiff base Cu(II) complexes was characterized as monomeric four-coordinated compounds by the results of elemental analysis, IR, NMR, UV-Visible spectra, molar conductivity, and thermogravimetric analysis. The mole ratio of ligand to copper metal was found to be 1:1. The redox process of Cu(II) complexes are quasi-reversible reactions in a DMF solution containing 0.1 M TEAP. Because the reduction potential of Cu(II) complexes with the smaller chelate ring has more negative potential than that of Cu(II) complexes with larger chelate ring, the reduction potentials of Cu(II) complexes are affected by chelate ring of Schiff base ligands. Furthermore, the redox processes of Cu(II) complexes by cyclic voltammetry, the controlled potential coulometry, and the differential pulse voltammetry were observed to be one electron charge transfer processes and diffusion-controlled reactions. From these results, we conclude that the redox process of Schiff base Cu(II) complexes used in this study is as follows:



The electrochemical redox potentials and the kinetic parameters of Cu(II) complexes were affected by chelate ring of Schiff base ligands.

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## References

- Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
- Martell, A. E.; Sawyer, D. T. *Oxygen Complexes and Oxygen Activation by Transition Metals*; Plenum: New York, 1988.
- Chen, D.; Martell, A. E.; Sun, Y. *Inorg. Chem.* **1989**, *28*, 2647.
- Kipke, C. A.; Scott, M. J.; Gohdes, J. W.; Armstrong, W. H. *Inorg. Chem.* **1990**, *29*, 2193.
- Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.
- Dixit, P. S.; Srinivasan, K. *Inorg. Chem.* **1988**, *27*, 4507.
- Nishinaga, A.; Tojo, T.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1974**, 896.
- Lloret, F.; Julve, M.; Mollar, M.; Castro, I.; Latorre, J.; Faus, J.; Solans, X.; Morgenstern-Badaran, I. *J. Chem. Soc., Dalton Trans.* **1989**, 729.
- Calligaris, M.; Manzini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1972**, 5430.
- Cummins, D.; McKenzie, E. D.; Milburn, H. *J. Chem. Soc., Dalton Trans.* **1976**, 130.
- Bailey, N. A.; Higson, B. M.; Mckenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1972**, 503.
- Kessel, S. L.; Emberson, R. M.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 1170.
- Valko, M.; Klement, R.; Pelikan, P.; Boca, R.; Dihan, L.; Böttcher, A.; Elias, H.; Müller, L. *J. Phys. Chem.* **1995**, *99*, 137.
- McAuliffe, C. A.; Parish, R. V.; Ashmayr, F. M.; Issa, R. M.; Amer, S. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2009.
- Bassek, U.; Weghermüller, T.; Wiegardt, K.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1990**, *112*, 6387.
- Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810.
- Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 7809.
- Gohdes, J. W.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 368.
- Larson, E. J.; Lah, M. S.; Li, X.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 373.
- Horwitz, C. P.; Winslow, P. J.; Warden, J. T.; Lisek, C. A. *Inorg. Chem.* **1993**, *32*, 82.
- Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U. K., 1988.
- Boucher, L. J. *Inorg. Chem.* **1976**, *15*, 1334.
- Ueno, K.; Martell, A. E. *J. Phys. Chem.* **1956**, *27*, 2544.
- Nakamoto, K.; Martell, A. E. *J. Chem. Phys.* **1960**, *32*, 588.
- Coleman, W. M.; Boggess, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2195.
- Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1966**, *88*, 5180.
- Sarama, B. D.; Ray, K. R.; Sievers, R. E.; Bailar, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 14.
- Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980.

Steric Effect on the Molecular Hyperpolarizabilities of  $\beta$ -Nitrostyrene Derivatives

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The steric effect on the first order hyperpolarizability of the  $\beta$ -nitrostyrene derivatives has been investigated by comparing the  $\beta$  values and the dihedral angles between the aryl and nitroalkenyl groups. In general the  $\beta$  value increased with the electron-donating ability of the substituent. The larger  $\beta$  value for 3,4-dimethoxy- $\beta$ -nitrostyrene than that for *p*-methoxy- $\beta$ -nitrostyrene has been attributed to the lower charge transfer energy for the former. The most striking substituent effect was observed in the  $\beta$ -methyl- $\beta$ -nitrostyrene derivatives. Thus the  $\beta$  values for 3,4-dimethoxy- and *p*-methoxy derivatives of the latter decreased to near zero, probably because of the large distortion from planarity caused by the steric repulsion between the  $\beta$ -methyl and the aryl groups. The larger  $\beta$  value for *p*-dimethylamino- $\beta$ -methyl- $\beta$ -nitrostyrene has been interpreted with an increased electron-donating ability of the substituent and increased co-planarity.

## Introduction

There are considerable research efforts in the field of

nonlinear optics to find high performance materials for second harmonic generations or electro-optic applications.<sup>1</sup> A large number of organic compounds have been examined