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

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Received May 13, 1997

A series of tetradentate Schiff-base ligands; 1,3-bis(salicylideneimino) propane, 1,4-bis(salicyli-deneimino)butane, and 1,5-bis(salicylideneimino)pentane, and their Cu(II) and Ni(II) complexes have been synthesized. The properties of ligands and complexes have been characterized by elemental analysis, IR, NMR, UV-Vis spectra, molar conductance, and thermogravimetric anaylsis. The mole ratio of Schiff base to metal at complexes was found to be 1 : 1. All complexes were four-coordinated configuration and non-ionic compound. The electrochemical redox processes of the ligands and their complexes in DMF solution containing 0.1 M TEAP as supporting electrolyte have been investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry at glassy carbon electrode, and by controlled potential coulometry at platinum gauze electrode. The redox process of the ligands was highly irreversible, whereas redox process of Cu(II) and Ni(II) complexes was observed as one electron transfer process of quasi-reversible and diffusion-controlled reaction. Also the electrochemical redox potentials of complexes were affected by chelate ring size of ligands. The diffusion coefficients of Cu(II) and Ni(II) complexes in DMF solution were determined to be $4.2\text{-}6.6\times10^{\ 6}$ cm^2/sec. Also the exchange rate constants were determined to be $3.6\text{-}9.7\times10^{\ 2}$ cm/sec.

Introduction

Investigations involving reversible dioxygen complexation to Schiff base cobalt(II) compounds employing tetradentate ligands have yielded numerous significant findings.[1] There has been considerable interest in Schiff base metal complexes because of their relationship to the natural iron-containing oxygen carriers hemoglobin and myoglobin.[2] The bis(salicylaldehyde) ethylenediimine (salcomine), abbreviated as salen, is easily prepared from the salicylaldehyde and diamine, and one of the ligands most often used in models of porphyrins. One of the best known cobalt(II) complex as model compounds of synthetic oxygen carrier is Co(salen). The salen derivatives have been investigated the first and the most extensively for their catalytic activities. Transition metal complexes involving salen derivatives have received 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.[3,4] The chemistry of transition metal (especially cobalt) complexes with the tetradentate Schiff base ligand salen and the dioxygen affinity of Co(salen) and its analogues have been extensively studied.[5,6]

Transition metal complexes play a very important role in many elecrochemical catalytic processes.[7] Although synthesis and characterization for a variety of transition metal complexes of Schiff base ligands have been investigated,[8,9] including several salen analogues, there has not yet been a sufficient study on the electrochemical properties of Schiff base complexes. Gosden,[10] Isse,[11] and Smith[12] have reported on electrochemical studies of a series of Schiff base nickel (II) complexes of Ni(salophen) [salophen=N,N'-1,2-phenylenebis(sallicylideneiminato)] family. Kotočová *et al.*[13-16] have published some materials on the relationship between redox potentials of ligand substituents for transition metal complexs of tetradentate Schiff base ligands. The works devoted to the electrochemical behaviour of Nickel(II) and Copper(II) complexes containing salen analogues are very limited.

The present paper examines the effect of chelating ring size on the non-aromatic part of the ligands of the complexes. In this study, we synthesized the Cu(II) and Ni(II) complexes of tetradentate Schiff base ligands derived from the condensation of salicylaldehyde with aliphatic diamines. The ligands and their Cu(II) and Ni(II) complexes were characterized by elemental analysis, IR, NMR, UV-vis spectra, molar conductance, and thermogravimetric analyses. The electrochemical redox process of the ligands and their Cu(II) and Ni(II) complexes in N,N-dimethylformamide (DMF) solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) as a supporting electrolyte was investigated by cyclic voltammetry, chronoamperomery, and differential pulse voltammetry at glassy carbon electrode, and by controlled potential coulometry at platinum gauze electrode. Upon the basis of results on the electrochemical data, we report the effect of chelate ring size for the redox potential of Ni(II) and Cu(II) complexes.

Experimental

Materials. Copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, salicylaldehyde, sodium hydroxide, and ethanol were obtained from Aldrich Chemical Co. and used as received. DMF was dried by standard procedures[17] before use. TEAP was recrystallized twice from distilled water and dried at 70 °C under vacuum.

Preparation of ligands. Typical procedures for tetradentate Schiff base synthesis are as followed. A soluion of 0.1 mole diamine in 50 mL ethanol was slowly added to 0.2 mole salicylaldehyde 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.

1,3-bis(salicylideneimino)propane; H_2SALPR. 98% yield; mp 94-96 °C; Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92; Found: C, 72.35; H, 6.39; N, 9.88; IR (KBr pellet, cm^{-1}): 3408 (O-H), 3051 (ArC-H), 2931 (C-H), 1636 (C=N), 1612 (C=C), 1447 (C=C), 1210 (C-O); UV-vis (DMF, λ_{max}, $\varepsilon \times 10^4$ cm^{-1} M^{-1}): 272 (1.93), 306 (2.47), 346 (2.24); ^{1}H NMR (DMSO-d_6, δ): 2.00 (quintet, 2H, =N-CH_2-$C\underline{H}_2$-), 3.66 (t, 4H, =N-$C\underline{H}_2$-CH_2-), 6.86-7.43 (m, 8H, Ar), 8.56 (s, 2H, CH=N), 13.51 (s, 2H, ArOH); ^{13}C NMR (DMSO-d_6, δ): 31.9 and 56.4 (=N-$(CH_2)_3$-), 116.8-132.6 (Ar), 161.0 ((C-2)OH), 166.6 (CH=N).

1,4-bis(salicylideneimino)butane; H_2SALBU. 98% yield; mp 92-94 °C; Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45; Found: C, 73.04; H, 6.78; N, 9.34; IR (KBr pellet, cm^{-1}): 3445 (O-H), 3049 (ArC-H), 3015 (ArC-H), 2945 (C-H), 1632 (C=N), 1609 (C=C), 1497 (C=C), 1285 (C-O); UV-vis (DMF, λ_{max}, $\varepsilon \times 10^4$ cm^{-1} M^{-1}): 272 (2.08), 308 (2.68), 346 (2.44); ^{1}H NMR (DMSO-d_6, δ): 1.68 (quintet, 4H, =N-CH_2-$C\underline{H}_2$-), 3.61 (d, 4H, =N-$C\underline{H}_2$-), 6.84-7.42 (m, 8H, Ar), 8.54 (s, 2H, CH=N), 13.61 (s, 2H, ArOH); ^{13}C NMR (DMSO-d_6, δ): 28.4 and 58.3 (N-$(CH_2)_4$-), 116.8-132.6 (Ar), 161.2 ((C-2)OH), 166.2 (CH=N).

1,5-bis(salicylideneimino)pentane; H_2SALPE. 96% yield; mp 93-95 °C; Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.02; Found: C, 73.54; H, 7.16; N, 8.97; IR (KBr pellet, cm^{-1}): 3438 (O-H), 3053 (ArC-H), 2929 (C-H), 1634 (C=N), 1609 (C=C), 1497 (C=C), 1260 (C-O); UV-vis (DMF, λ_{max}, $\varepsilon \times 10^4$ cm^{-1} M^{-1}): 274 (2.13), 308 (2.42), 348 (2.56); ^{1}H NMR (DMSO-d_6, δ): 1.35 (septet, 2H, =N-CH_2-CH_2-$C\underline{H}_2$-), 1.63 (quintet, 4H, =N-CH_2-$C\underline{H}_2$-), 3.54 (t, 4H, =N-$C\underline{H}_2$-), 6.80-7.37 (m, 8H, Ar), 8.49 (s, 2H, CH=N), 13.61 (s, 2H, ArOH); ^{13}C NMR (DMSO-d_6, δ): 24.4, 30.2, and 58.3 (N-$(CH_2)_5$-), 116.7-132.4 (Ar), 161.1 ((C-2)OH), 166.0 (CH=N).

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

N,N-propylenebis(salicylaldiminato)nickel(II); [Ni(II)(SALPR)]. 87% yield; mp 348-350 °C; Anal. Calcd for $C_{17}H_{16}N_2O_2Ni$: C, 60.23; H, 4.76; N, 8.26; Ni, 17.31; Found: C, 60.21; H, 4.74; N, 8.29; Ni, 17.29. IR (KBr pellet, cm^{-1}): 3058 (ArC-H), 2930 (C-H), 1622 (C=N), 1541 (C=C), 1475 (C=C), 1194 (C-O), 752 (Ni-N), 464 (Ni-O); UV-vis (DMF, λ_{max}, $\varepsilon \times 10^4$ cm^{-1} M^{-1}): 356 (1.41), 389 (1.35); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.79; TGA (weight loss, %): 0.70 at 90-262 °C, 44.95 at 262-428 °C, 31.87 at 428-678 °C, 22.48 at 678 °C~.

N,N-butylenebis(salicylaldiminato) nickel(II); [Ni(II)(SALBU)]. 85% yield; mp 350-352 °C; Anal. Calcd for $C_{18}H_{18}N_2O_2Ni$: C, 61.24; H, 5.14; N, 7.93; Ni, 16.63; Found: C, 61.21; H, 5.12; N, 7.95; Ni, 16.68; IR (KBr pellet, cm^{-1}): 3045 (ArC-H), 2922 (C-H), 1616 (C=N), 1541 (C=C), 1470 (C=C), 1148 (C-O), 750 (Ni-N), 463 (Ni-O); UV-vis (DMF, λ_{max}, $\varepsilon\times10^4$ cm^{-1} M^{-1}): 276 (2.36), 369 (1.69); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.46; TGA (weight loss, %): 1.33 at 90-235 °C, 39.56 at 235-437 °C, 37.60 at 437-642 °C, 21.51 at 642 °C~.

N,N-pentylenebis(salicylaldiminato) nickel(II); [Ni(II)(SALPE)]. 88% yield; mp 356-358 °C; Anal. Calcd for $C_{19}H_{20}N_2O_2Ni$: C, 62.17; H, 5.49; N, 7.63; Ni, 15.99; Found: C, 62.18; H, 5.52; N, 7.61; Ni, 15.95; IR (KBr pellet, cm^{-1}): 3056 (ArC-H), 2931 (C-H), 1614 (C=N), 1541 (C=C), 1472 (C=C), 1194 (C-O), 754 (Ni-N), 463 (Ni-O); UV-vis (DMF, λ_{max}, $\varepsilon\times10^4$ cm^{-1} M^{-1}): 287 (2.51), 372 (1.88); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.88; TGA (weight loss, %): 1.05 at 90-249 °C, 42.67 at 249-370 °C, 35.32 at 370-651 °C, 20.96 at 651 °C~.

Preparation of Cu(II) complexes. Cu(II) complexes were prepared by the addition of 0.01 mole of ligand which was mixed with 0.02 mole NaOH in hot ethanol (100 mL) to the same volume of 0.01 mole copper(II) acetate monohydrate in water (50 mL) under the nitrogen atmosphere, respectively. After 2 hrs stirring, the precipitates were obtained. The products obtained were recrystallized from ethanol and then dried at 80 °C under the reduced pressure.

N,N-propylenebis(salicylaldiminato) copper(II); [Cu(II)(SALPR)]. 84% yield; mp 324-325 °C; Anal. Calcd for $C_{17}H_{16}N_2O_2Cu$: C, 59.38; H, 4.69; N, 8.15; Cu, 18.48; Found: C, 59.35; H, 4.67; N, 8.19; Cu, 18.43; IR (KBr pellet, cm^{-1}): 3059 (ArC-H), 2936 (C-H), 1616 (C=N), 1539 (C=C), 1472 (C=C), 1193 (C-O), 773 (Cu-N), 598 (Cu-O); UV-vis (DMF, λ_{max}, $\varepsilon\times10^4$ cm^{-1} M^{-1}): 272 (1.74), 369 (0.71), 552 (0.38); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.37; TGA (weight loss, %): 1.08 at 90-213 °C, 39.64 at 213-638 °C, 36.27 at 638-692 °C, 23.01 at 692 °C~.

N,N-butylenebis(salicylaldiminato) copper(II); [Cu(II)(SALBU)]. 87% yield; mp 313-315 °C; Anal. Calcd for $C_{18}H_{18}N_2O_2Cu$: C, 60.41; H, 5.07; N, 7.83; Cu, 17.76; Found: C, 60.39; H, 5.05; N, 7.87; Cu, 17.79; IR (KBr pellet, cm^{-1}): 3042 (ArC-H), 3015 (ArC-H), 2932 (C-H), 1609 (C=N), 1533 (C=C), 1472 (C=C), 1148 (C-O), 760 (Cu-N), 598 (Cu-O); UV-vis (DMF, λ_{max}, $\varepsilon\times10^4$ cm^{-1} M^{-1}): 274 (2.23), 378 (1.02), 548 (0.35); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.84; TGA (weight loss, %): 0.86 at 90-218 °C, 39.18 at 218-576 °C, 37.33 at 576-627 °C, 22.63 at 627 °C~.

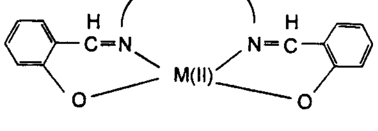
N,N-pentylenebis(salicylaldiminato) copper(II); [Cu(II)(SALPE)]. 82% yield; mp 319-320 °C; Anal. Calcd for $C_{19}H_{20}N_2O_2Cu$: C, 61.36; H, 5.42; N, 7.53; Cu, 17.08; Found: C, 61.32; H, 5.46; N, 7.50; Cu, 17.12; IR (KBr pellet, cm^{-1}): 3055 ArC-H), 2930 (C-H), 1622 (C=N), 1601 (C=C), 1470 (C=C), 1191 (C-O), 756 (Cu-N), 591 (Cu-O); UV-vis (DMF, λ_{max}, $\varepsilon\times10^4$ cm^{-1} M^{-1}): 274 (2.26), 367 (1.13), 552 (0.42); Molar conductance (DMF, Λ_M, ohm^{-1} cm^{-2} mol^{-1}): 1.95; TGA (weight loss, %): 0.94 at 90-216 °C, 40.22 at 216-542 °C, 36.96 at 542-646 °C, 21.88 at 646 °C~.

Physical Measurements. The elemental analysis (carbon, hydrogen, and nitrogen) was performed on a EA 1108 CHNS-O (FISONS) Elemental Analyzer and the metal content was determined by a Perkin-Elmer model 603 atomic absorption spectrometer. Infrared and UV-vis spectra were recorded on Perkin-Elmer Model 1620 FT-IR and Hewlett Packard 8452A Diode Array spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer model 2 series thermogravimetric analyzer under N_2 gas atomsphere. Melting points were measured by a Mel-Temp apparatus. ^1H NMR and ^{13}C 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. 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 Cu(II) and Ni(II) complexes were carried out by cyclic voltammetry, chronoamperomery, controlled potential coulometry, and differential pulse voltammetry in DMF solutions contained 0.1 M TEAP as a supporting electrolyte. Single elctrochemical compartment cell in which the 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 a removal 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 (PAR) 273 potentiostat/galvanostat interfaced by 486 DX2 microcomputer through an IEEE-488 bus was used for electrochemical experiments.

Results and Discussion

Tetradentate Schiff bases and their nickel(II) and copper (II) complexes have been synthesized and characterized by UV-vis, IR, TGA, NMR, and elemental analysis. The nickel (II) and copper(II) complexes employing Schiff base ligands with the 2N2O donor sets were formed by the reaction of salicylaldehyde 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 ligands. The results of elemental analysis of the Schiff base ligands and their nickel(II) and copper(II) complexes agree well with the expected compositon of the proposed com-



(M : Ni, Cu)

n=3 [M(II)(SALPR)(H$_2$O)$_2$]
n=4 [M(II)(SALPR)(H$_2$O)$_2$]
n=5 [M(II)(SALPR)(H$_2$O)$_2$]

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

plexes and support the fact that the mole ratio of Schiff base to the metal complexes is 1 : 1 as shown in Figure 1. Although crystral structures are not available, the proposed structures are consistent with all other evidence. All complexes are highly soluble in DMF, pyridine, and DMSO but insoluble in water. The results of conductivity measurements in 1 mM DMF solution indicate that the nickel(II) and copper(II) complexes are non-ionic compounds.[18]

Infrared and UV-vis spectra. All of the IR spectra of nickel(II) and copper(II) complexes show typical bands of Schiff-base, with strong peaks assigned to ν(C=N) in the 1609-1622 cm^{-1} region.[19] We can see that ν(C=N) bands in the complexes are shifted about 12-23 cm^{-1} to the lower energy regions in the corresponding free ligands. A shift to lower frequency of the ν(C=N) band is attributed to conjugation of the p-orbital of the double bond with the d-orbitals of the metal atom with reduction of the force constant.[20] These phenomina appear due to the coordination of the azomethine nitrogens of the Schiff base ligand to the metal ion.[8,9] As well as indicating that the imine groups of the Schiff base ligands are coordinated to metal atom, a shift to lower energy may be taken as evidence of a dianionic tetradentate Schiff base coordination.[21] According to Ueno and Martell,[22,23] characteristic absorption bands for Metal(II)-N and Metal(II)-O bonds in complexes appear in the spectral region of 650-850 cm^{-1} and 400-600 cm^{-1}, respectively. New bands are observed in the ranges 750-773 cm^{-1} and 463-598 cm^{-1}, which may be assigned to ν (Metal-N) and ν(Metal-O), respectively, and which are absent in the spectra of the corresponding free ligands. Also, broad ν(OH) band of the free ligands about 3400 cm^{-1} disappears on complexes. These results show that the Schiff base ligands of 2N2O type donor atom sets behave in a tetradentate manner binding to the metal ion through the phenoxide oxygen atoms and the azomethine nitrogen atoms. The UV-vis spectra of the Ni(II) and Cu(II) complexes obtained in DMF solution show a π-π^* ligand field absorption band at 272-287 nm and a d-π^* charge transfer band at 356-389 nm. Also, the UV-vis spectra of the Cu(II) complexes show a d-d transition at 548-552 nm.[24,25]

NMR spectra. The tetradentate Schiff base ligands of 2N2O donor sets possess two phenolic groups and azomethine groups. ^1H NMR spectra of Schiff base ligands in DMSO-d_6 show the aromatic protons as multiplet in the range 6.80-7.43 ppm and O-H protons of the two phenolic groups in the range 13.51-13.61 ppm. The azomethine protons appear at 8.49-8.56 ppm. ^{13}C NMR spectra of the free ligands show the peaks of aliphatic carbons at 24-58 ppm and the aromatic carbons in the range of 116-132 ppm. The peaks of the azomethin carbon and C-2 carbon on the benzene appear at 166 and 161 ppm, respectively.

Thermogravimetric analysis. The Ni(II) complexes show TGA curves decreasing in weight at 230-440 °C and subsequently decomposing. Also the Cu(II) complexes show decreasing in weight at 200-640 °C. Thermal gravimetric analysis data support that the metal(II) complexes do not contain the water molecules.

Electrochemical Studies. The electrochemical behaviors of free base ligands and their Cu(II) and Nil(II) complexes in DMF solutions were investigated by cyclic voltammetry, chronoamperomery, and differential pulse voltammetry at a glassy carbon electrode, and by controlled potential coulometry at platinum gauze electrode. In order to study the electron transfer processes of the Cu(II) and Ni(II) complexes with Schiff base ligands, we investigated the electrochemical redox processes of ligands. Typical cyclic voltammogram of 1 mM H_2SALPR in DMF solution is shown in Figure 2. As can be seen in Figure 2, the redox processes were highly irreversible.

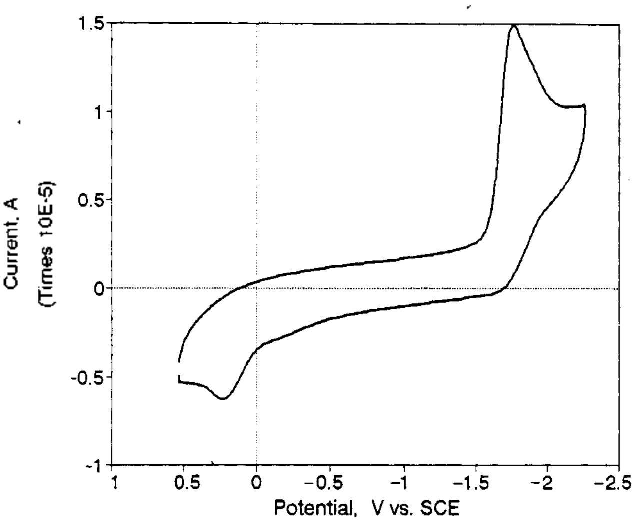


Figure 2. Cyclic voltammograms of 1 mM H_2SALPR ligand containing 0.1 M TEAP as a supporting electrolyte in DMF solution. Scan rates was 100 mV/sec.

Figure 3 shows the cyclic voltammograms of 1 mM [Ni(II)(SALPR)] complex in DMF solution at various scan rates. As can be seen in Figure 3, the cathodic peak current of the complexes was increased and the peak potentials shifted to more negative direction with the increase of the scan rate. A summary of the redox processes observed for the Ni(II) and Cu(II) complexes in DMF solution is listed in Table 1. In the Table 1, the cathodic reduction peak of

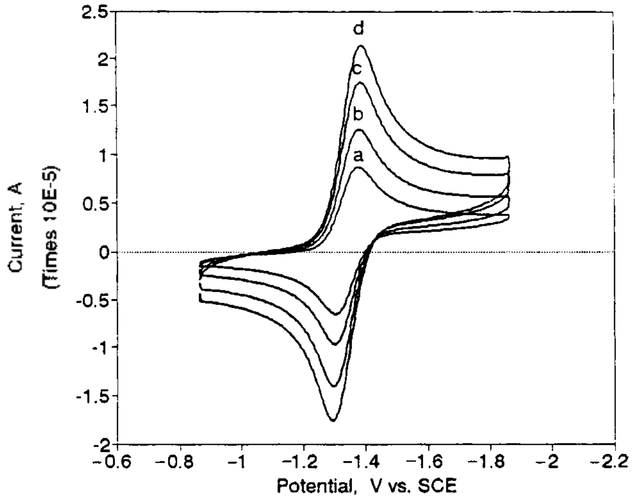


Figure 3. Cyclic voltammograms of 1 mM [Ni(II)(SALPR)] complex containing 0.1 M TEAP as a supporting electrolyte in DMF solution. Scan rates were a) 50, b) 100, c) 200, and d) 300 mV/sec, respectively.

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

Complexes	scan rate (V/s)	$-E_{pc}$ (V)	$-E_{pa}$ (V)	ΔE_p (mV)
[Ni(II)	0.05	1.391	1.323	68
	0.1	1.393	1.320	73
	0.2	1.395	1.318	77
	0.3	1.397	1.316	81
[Ni(II)	0.05	1.385	1.315	70
	0.1	1.387	1.312	75
	0.2	1.390	1.310	80
	0.3	1.392	1.307	85
[Ni(II)	0.05	1.286	1.213	73
	0.1	1.288	1.211	77
	0.2	1.291	1.208	83
	0.3	1.294	1.204	90
[Cu(II)	0.05	0.877	0.812	65
	0.1	0.878	0.810	68
	0.2	0.880	0.808	72
	0.3	0.881	0.806	75
[Cu(II)	0.05	0.866	0.799	67
	0.1	0.868	0.797	71
	0.2	0.872	0.795	77
	0.3	0.874	0.792	82
[Cu(II)	0.05	0.768	0.698	70
	0.1	0.770	0.696	74
	0.2	0.780	0.693	87
	0.3	0.785	0.691	94

Ni(II) complexes at $-1.29\sim-1.39$ V is coupled to an oxidation peaks at $-1.20\sim-1.31$ V corresponding to the Ni(II)/Ni(I) redox process. Also the reduction peak of Cu(II) complexes at $-1.00\sim-0.78$ V is coupled to an oxidation peaks at $-0.80\sim-0.70$ V corresponding to the Cu(II)/Cu(I) redox process. As can be seen in Table 1, Cu(II) complexes are reduced and oxidized at much more positive potentials than those of the Ni(II) complexes.

The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the separation between the peak potentials[27]

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

where E_{pa}, E_{pc}, and n are anodic peak potential, cathodic peak potential, and the number of electrons transferred, respectively. 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 60-70 mV, indicating that the number of electrons transferred should be 1.0. The peak separation for the [Ni(II)(SALPE)] and [Cu(II)(SALPE)] complexes with long chelate ring is larger than that of the [Ni(II)(SALPR)] and [Cu(II)(SALPR)] complex with the short chelate ring. These results show that the electrochemical redox processes of Metal(II) complexs with long chelate ring are quasi-reversible charge transfer.[26] Also the reduction potential for the [Ni(II)(SALPR)] and [Cu(II)(SALPR)] complexes show more negative value than that of the [Ni(II)(SALPE)] and [Cu(II)(SALPE)] complexes. This indicates that the reduction of the Metal(II) complexes with the short chelate ring is more difficult than that of the long chelate ring. Therefore, we concluded that reduction potentials of the Metal(II) complexes are affected by chelate ring of ligands and [Ni(II)(SALPR)] and [Cu(II)(SALPR)] complexes are the most stable. Also, the ratio of the anodic to cathodic peak current approaches to 1 according to the decrease in the chelate ring. From the results, the suggested mechanism for electrochemical redox processes of Metal(II) complexes corresponds to the following reaction

$$[M(II)(L)] + e^- \rightleftharpoons [M(I)(L)] \quad (M;\ Ni\ and\ Cu,\ L;\ ligand)$$

Table 2. The kinetic parameters of Metal(II) complexes

Complexes	^aE_p	^bn	^cD_o	^dk_o
[Ni(II)	-1.53	1.02 ± 0.03	4.2×10^{-6}	8.1×10^{-2}
[Ni(II)	-1.53	1.09 ± 0.03	4.7×10^{-6}	8.7×10^{-2}
[Ni(II)	-1.43	0.95 ± 0.05	5.9×10^{-6}	3.6×10^{-2}
[Cu(II)	-1.03	0.99 ± 0.03	6.4×10^{-6}	9.7×10^{-2}
[Cu(II)	-1.03	1.03 ± 0.04	6.2×10^{-6}	8.8×10^{-2}
[Cu(II)	-0.92	0.98 ± 0.04	6.6×10^{-6}	7.8×10^{-2}

[a] Reduction potential applided for the controlled potential coulometry. [b] Number of electrons per molecule. [c] Diffusion coefficients (cm^2/sec). [d] Exchange rate constants (cm/sec).

To establish whether the number of electrons transferred is close to 1.0, controlled potential coulometry in DMF solution at platinum gauze electrode are carried out and a summary of the number of electron is listed in Table 2. As can be seen in Table 2, controlled potential reduction at a potential corresponding to the reduction peak of the cyclic voltammograms is reduced in one electron step to what is assumed to be Metal(I) species. The somewhat-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 po-

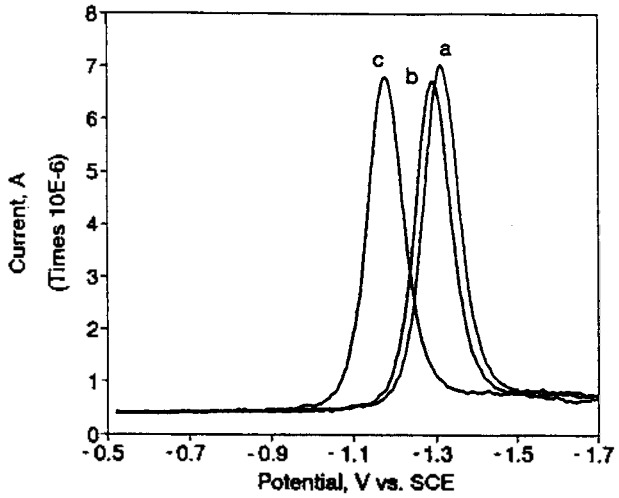


Figure 4. Differential pulse voltammograms of 1 mM a) [Ni(II)(SALPR)], b) [Ni(II)(SALPR)], and c) [Ni(II)(SALPE)] complexes containing 0.1 M TEAP as a supporting electrolyte in DMF solution at modulation time 20 mV.

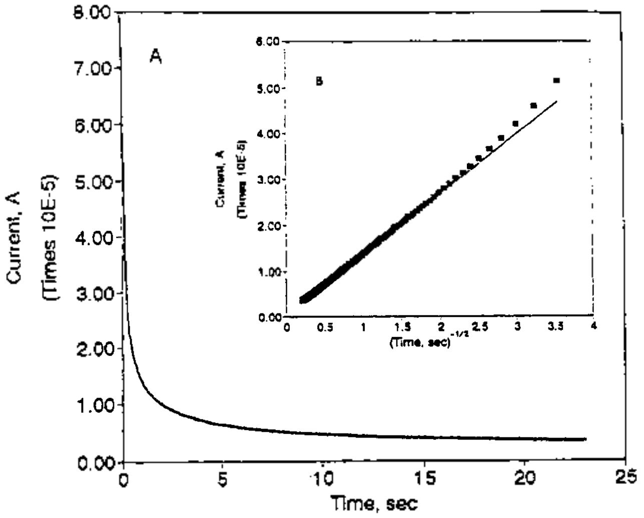


Figure 5. Chronoamperometric curve (A) and Cottrell plot (B) for 1 mM [Ni(II)(SALPR)] complex at the glassy carbon electrode in DMF solution.

tential 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 4 shows the differential pulse voltammograms of [Ni(II)(SALPR)] and [Ni(II)(SALPE)] complex in DMF solution. For reversible charge-transfer processes, the limiting peak width at half-height ($W_{1/2}$) is given by Eq. (2)

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

All of the values of $W_{1/2}$ observed for Metal(II) complexes used in this study are observed to be 92-100 mV, consistent with one electron transfer processes that occur with moderate rates of heterogeneous charge transfer.[27]

We also carried out chronoamperometric experiments for the Metal(II) complexes in DMF solution in order to estimate the diffusion coefficient. Figure 5 (A) shows chronoamperometric result of 1 mM [Cu(II)(SALPR)] complex containing 0.1 M TEAP in DMF solution and Figure 5 (B) shows the result plotted according to Cottrell equation,[27] *i.e.*,

$$i(t)=\frac{nFAD^{1/2}C^*}{\pi^{1/2}t^{1/2}} \qquad (3)$$

Eq. (3) 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 $4.2\text{-}6.6\times10^{-6}$ cm^2/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. Nicholson[27] reported 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,

$$\psi=\frac{\gamma k^o}{(\pi a D_o)^{1/2}} \qquad (4)$$

where $\gamma=(D_O/D_R)^{1/2}$ and $a=nF\nu/(RT)$ with ν=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.* $\nu^{1/2}$ plot according to eq. (4). 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 $3.6\text{-}9.7\times10^{-2}$ cm/sec.

Conclusions

The Ni(II) and Cu(II) complexes of tetradentate Schiff base ligands derived from salicylaldehyde and aliphatic diamine have been synthesized. All Metal(II) complexes have been identified monomeric four-coordinated non-ionic compounds by the results of elemental anaylsis, IR, UV-Visible spectra, molar conductivity, and thermogravimetric analysis. The mole ratio of Schiff base to the Metal(II) complexes was found to be 1 : 1. The redox process of the free ligands was totally irreversible reaction, whereas the redox process of the Cu(II) and Ni(II) complexes were quasi-reversible reaction in DMF solution containing 0.1 M TEAP as a supporting electrolyte. The reduction of the complexes with the short chelate ring occured to be more negative potential than that of complexes with long chelate ring and the reduction potentials of the Metal(II) complexes were affected by chelate ring size of ligands. The Cu(II) complex was reduced and oxidized at much more positive potential than that of the Ni(II) complex with the same ligand. Futhermore, redox processes of Cu(II) and 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 concluded that the redox process of all Schiff base Metal(II) complexes used in this study are following reaction.

$$[\text{M(II)(L)}]+e \rightleftharpoons [\text{M(I)(L)}] \quad (\text{M; Ni and Cu, L; ligand})$$

The diffusion coefficients of Metal(II) complexes in DMF solutions were determined to be $4.2\text{-}6.9\times10^{-6}$ cm^2/sec. Also the exchange rate constants were determined to be $3.6\text{-}9.7\times10^{-2}$ cm/sec.

Acknowledgment. This research was supported by the Basic Science Research Institute Program, Ministry of Education (BSRI-96-3429).

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Product Studies by HPLC on the Hydrolysis of the *anti*- and *syn*-Tetrahydrodiol Epoxides and the 1,2-Tetrahydro Epoxide of Naphthalene

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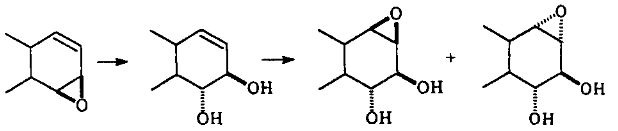
Received May 16, 1997

The arene epoxides from naphthalene, 1β,2α-dihydroxy-3α,4α-epoxy- (**1**) and 1β,2α-dihydroxy-3β,4β-epoxy-1,2,3,4-tetrahydronaphthalene (**2**) (*anti*- and *syn*-diol epoxide), 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**3**), and 1,2-epoxy-1,2-dihydronaphthalene (**4**), are model componds of the ultimate carcinogenic metabolites of polycyclic aromatic hydrocarbons, ubiquitous environmental pollutants which may be causal in several human cancers. The product distribution in the hydrolysis of **1-4** have been studied by HPLC analysis of reaction mixtures. The yields of the trans product from the hydronium-ion-catalyzed and pH-independent hydrolysis in 9 : 1 (v/v) 20 mM buffer-dioxane at 25 °C, respectively, were; **1**: 98, 100; **2**: 74, 87, **3**: 95, 97, **4**:100, 100. The results were rationalized by conformational equilibria of the epoxides and the carbocationic and zwitterionic intermediates from the epoxides.

Introduction

Polycyclic aromatic hydrocarbons (PAH's) are widespread environmental pollutants which are considered to be an important class of mutagenic and carcinogenic compounds. They are metabolized in part by the cytochrome P-450 monooxygenases to arene epoxides followed by hydrolysis to the *trans*-diols and further oxygenation at the adjacent double bond to form diol epoxides.[1-3] These diol epoxides may express their electrophilic reactivity by initiating the carcinogenic process through DNA alkylation.[4] In an effort to understand the mechanism of the initiation of the PAH carcinogenesis, *in vitro* electrophilic reactivities of several PAH diol epoxides have been studied in detail.[5,6]



The following epoxides, **1-4** are model compounds of the metabolites of carcinogenic PAH's.

To date, kinetic studies on the hydrolysis of these epoxides have been undertaken by Bruice[7,8] and by the author,[9] but no product studies on their hydrolysis have been carried