



Synthesis of 14- π nickel(II) complexes with disubstituted benzoN₄ macrocycles and electrochemical studies of 14- π nickel(II) complexes with monosubstituted benzoN₄ macrocycles

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Abstract

The template reaction of a 1:1 mixture of 4,5-disubstituted(2CH₃ or 2Cl)-1,2-phenylenediamine and alkylenediamine [NH₂(CH₂)_n-NH₂; *n* = 2 or 3] with 2,4-pentanedione in the presence of a nickel(II) salt gave a series of asymmetric 14- π nickel(II) complexes with disubstituted tetraazaannulene, [Ni(Me₄-X₂bzotetraaza[Y]ene)] (X = CH₃ and Cl, Y = 14 and 15), which were characterized by mass, infrared, ¹H and ¹³C NMR spectra. The electronic effects of the disubstituent groups on the phenyl ring significantly affected the spectral properties of the complexes. The electrochemical behaviors of the nickel(II) complexes with monosubstituted benzoN₄ macrocycles, [Ni(Me₄-Xbzotetraaza[Y]ene)] (X = H, NO₃, CH₃ and Cl, Y = 14 and 15) exhibited cyclic voltammograms characterized by, two irreversible, one electron, waves due to oxidation of the macrocycle (Mc); Mc → Mc^{•+} in the ranges of +0.06–+0.28 V for 14-X and +0.01–+0.29 V for 15-X, and Mc^{•+} → Mc²⁺ in the ranges of +0.58 to +0.81 V for 14-X and +0.36 to +0.79 V for 15-X versus Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M tetraethylammonium perchlorate (TEAP) acetonitrile solution). In the reduction area only one reversible wave Ni²⁺/Ni⁺ was detected at E_{1/2} = –1.65 to –2.65 V in DMSO. The relationships between the oxidation potentials (E_{ap}) and σ_p were linear with the slopes of 0.23 V for 14-X and 0.18 or 0.23 V for 15-X (correlation coefficients of 0.99). The catalytic reduction of dioxygen by the electropolymerized glassy carbon electrodes (GCE) occurred at about 400 mV more positive than by the bared one. The catalytic reduction using 14-X occurred at potentials somewhat more positive than using 15-X. © 2002 Published by Elsevier Science Ltd.

Keywords: Synthesis and electrochemistry; Asymmetric 14- π nickel(II) tetraazaannulene; Hammett plot; Electrocatalysis

1. Introduction

The transition metal complexes of tetraaza[14]annulene and tetraaza[15]annulene have attracted much attention for their similarity with porphyrins and corrins in biological system or their utilities as model compounds [1–4]. The potential of these macrocyclic complexes as catalysts has also fostered some interest and is efficient [5–7]. The complexes are also efficient as electrode modifiers for anodic oxidation or cathodic reduction [8,9]. Electropolymerization is an effective

way for modification of the electrode surface by deposits of redox entities such as metallic complexes. Such a modification of an electrode by symmetric nickel(II) tetraazaannulene was first investigated by Bereman and coworkers [10]. It has been shown that the electropolymerization of the nickel(II) tetraazaannulene is possible even when the ligand has a large variety of substituents on the carbon atoms of the tetraaza macrocycle as well as the two benzene rings [11]. However, most of the tetraazaannulene complexes used to study electrocatalytic reactions have a symmetric structure, such as nickel(II)-5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene which could be deposited on the electrode surface by oxidative electropolymerization. The synthesis of asymmetric complexes and their

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electrochemical studies are rarely carried out. We have synthesized several asymmetric nickel(II) complexes of tetraaza[14]annulene and tetraaza[15]annulene in previous papers [12,13]. It is expected that the electrochemical characteristics of such asymmetric complexes will be similar to those of the symmetric ones.

In this paper, we attempted to monitor the electrochemical behaviors of the asymmetric nickel(II) complexes with monosubstituted monobenzotetraazaannulene and considered the electrocatalytic properties of the glassy carbon electrodes (GCEs) electropolymerized by the complexes. The GCEs modified by such a process were applied for the electrocatalytic reduction of dioxygen. We also synthesized and characterized several asymmetric nickel(II) complexes with disubstituted monobenzotetraaza[14]annulene (or monobenzotetraaza[15]annulene) for future use in order to further understand the properties and the catalytic reactions of asymmetric tetraazaannulene macrocycles.

2. Experiments

2.1. Materials and instruments

All reagents used were of analytical grade. Dimethylsulfoxide and acetonitrile as solvents were distilled according to the published method [14]. Tetraethylammonium perchlorate (TEAP) as supporting electrolyte was prepared and purified by the method described by Kolthoff and Coetzee [15].

Elemental analyses (C, H, N) of the complexes synthesized were carried out on a Carlo-Ebra, EA 1108 analyzer. Electronic spectra were recorded in chloroform solution on a JASCO V 550 UV-Vis. spectrophotometer at r.t. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker instrument in CDCl_3 at r.t. and the chemical shifts were given in ppm relative to tetramethylsilane as an internal reference standard. EI mass spectra were measured with a JEOL MS-DX 300 gas chromatograph mass spectrometer at 70 eV using a direct inlet system. Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and C2 cell stand at 25 ± 0.2 °C. The three electrode system for the electrochemical measurements was composed of the GCE as a working electrode, Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TEAP acetonitrile solution) as a reference electrode, and platinum wire as an auxiliary electrode.

2.2. Synthesis of nickel(II) complexes with disubstituted tetraazaannulene macrocycles

2,4,9,11-Tetramethyl-15,16-dimethylbenzo-1,5,8,12-tetraaza[14]cyclotetradecinato(2-)-nickel(II) (14-2Me).

Under nitrogen atmosphere, 2,4-pentanedione (0.06 mol) was added to a methanol (80 cm^3) solution of nickel(II) acetate tetrahydrate (0.03 mol), 4,5-Dimethyl-1,2-phenylenediamine (0.03 mol) and ethylenediamine (0.03 mol) were added to the hot mixture. The solution was refluxed for about 3 h until precipitation of the product was complete. The hot solution was filtered, washed with methanol, and then air-dried. The product was recrystallized from dichloromethane-methanol (1:1). Yield: 65%. *Anal. Calc.* for $\text{NiC}_{20}\text{H}_{26}\text{N}_4$: C, 63.03; H, 6.68; N, 14.70. *Found:* C, 62.30; H, 7.23; N, 14.72%. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1,534; $\nu(\text{C}=\text{N})$, 1473 and 1410; $\nu(\text{aromatic})$, 737. UV-Vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) in CHCl_3 377 and 551, and 24030 and 2630. ^1H NMR (CDCl_3 , 300 MHz): δ 2.17 and 2.38 (s, MeH), 2.05 (s, ArMeH), 3.34 (s, ethyleneH), 4.98 (s, methineH), 6.95 (s, ArH). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 20.28 23.18, 19.75, 52.60, 103.28 (methine), 121, 127.37, 120.70, 154.61, 157.49. EI MS: m/z 380 $[\text{M}]^+$.

2,4,9,11-Tetramethyl-15,16-dichlorobenzo-1,5,8,12-tetraaza[14]cyclotetradecinato(2-)-nickel(II) (14-2Cl) was prepared from 2,4-pentanedione (0.06 mol), nickel(II) acetate tetrahydrate (0.03 mol), 4,5-dichloro-1,2-phenylenediamine (0.03 mol) and ethylenediamine (0.03 mol) according to the procedure as described above. The product of fine dark violet was obtained by recrystallizing in chloroform. Yield: 54%. *Anal. Calc.* for $\text{NiC}_{18}\text{H}_{20}\text{N}_4\text{Cl}_2$: C, 51.23; H, 4.78; N, 13.88. *Found:* C, 51.26; H, 4.92; N, 14.11%. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1533; $\nu(\text{C}=\text{N})$, 1483 and 1411; $\nu(\text{aromatic})$, 733. UV-Vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) in CHCl_3 381 and 542, and 22440 and 2720. ^1H NMR (CDCl_3 , 300 MHz): δ 2.07 and 2.35 (s, MeH), 3.37 (s, ethyleneH), 5.07 (s, methineH), 7.18 (s, ArH). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 20.51 22.90, 52.75, 104.84 (methine), 119.93, 121.27, 144.65, 154.24, 158.77. EI MS: m/z 420 $[\text{M}]^+$.

2,4,9,11-Tetramethyl-16,17-dimethylbenzo-1,5,8,12-tetraaza[15]cyclotetradecinato(2-)-nickel(II) (15-2Me) was prepared from 2,4-pentanedione (0.06 mol), nickel(II) acetate tetrahydrate (0.03 mol), 4,5-dimethyl-1,2-phenylenediamine (0.03 mol) and propylenediamine (0.03 mol), following the above-mentioned procedures. Yield: 33%. *Anal. Calc.* for $\text{NiC}_{21}\text{H}_{28}\text{N}_4$: C, 63.83; H, 7.14; N, 14.18. *Found:* C, 64.02; H, 7.13; N, 14.06%. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1,525; $\nu(\text{C}=\text{N})$, 1470 and 1410; $\nu(\text{aromatic})$, 748. UV-Vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) in CHCl_3 397 and 583, and 13380 and 1810. ^1H NMR (CDCl_3 , 300 MHz): δ 2.09 and 2.13 (s, MeH), 1.90 (s, ArMeH), 2.30 (m) and 2.79 (t) (propyleneH), 4.86 (s, methineH), 6.63 (s, ArH). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 21.01, 21.22, 19.60, 31.90, 50.86, 103.48, 127.83 (methineC), 121.66, 160.46, 146.10, 154.61, 154.83. EI MS: m/z 394 $[\text{M}]^+$, 379 $[\text{M}-\text{CH}_3]^+$.

2,4,9,11-Tetramethyl-16,17-dichlorobenzo-1,5,8,12-tetraaza[15]cyclotetradecinato(2-)-nickel(II) (15-2Cl) was synthesized from 2,4-pentanedione (0.06 mol), nickel(II) acetate tetrahydrate (0.03 mol), 4,5-dichloro-1,2-phenylenediamine (0.03 mol) and propylenediamine (0.03 mol) by following the above procedure. Yield: 51%. *Anal.* Calc. for $\text{NiC}_{19}\text{H}_{22}\text{N}_4\text{Cl}_2$: C, 52.34; H, 5.09; N, 12.85. Found: C, 52.06; H, 5.15; N, 13.05%. IR (KBr disc, cm^{-1}): $\nu(\text{C}=\text{C})$, 1,527; $\nu(\text{C}=\text{N})$, 1,474 and 1,420; $\nu(\text{aromatic})$, 748. UV-Vis: λ_{max} (nm) and ϵ_{max} ($\text{M}^{-1}\text{cm}^{-1}$) in CHCl_3 388 and 565, and 19 310 and 1480. ^1H NMR (CDCl_3 , 300 MHz): δ 1.92 and 2.07 (s, MeH), 2.34 (m) and 2.82 (s) (propyleneH), 4.91 (s, methineH), 6.84 (s, ArH). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 20.78, 21.45, 31.66, 50.96, 104.85 (methineC), 120.73, 121.84, 145.68, 154.40, 161.38. EI MS: m/z 434 $[\text{M}]^+$, 419 $[\text{M}-\text{CH}_3]^+$.

The asymmetric nickel(II) complexes with monosubstituted tetraazaannulene macrocycles, 2,4,9,11-tetramethyl-Xbenzo-1,5,8,12-tetraaza[14]cyclotetradecinato(2-)-nickel(II) and 2,4,9,11-tetramethyl-Xbenzo-1,5,8,12-tetraaza[15]cyclotetradecinato(2-)-nickel(II), wherein X = H (14-H and 15-H), X = Cl (14-Cl and 15-Cl), X = CH_3 (14-Me and 15-Me) and X = NO_2 (14- NO_2 and 15- NO_2), were prepared as reported previously [12,13].

2.3. Electropolymerization of the complexes on GCE

Before GCE (GC-20S Tokai Carbon, $\phi = 5$ mm) modification, it was polished with alumina slurry (1.0, 0.3 and 0.05 μm) on carborundum papers, washed with deionized water, and then dried. After polishing, any residual material was removed by sonication (Branson co. Model 1210) for 1 min, and then it was dried. The electrochemical behavior of the modified electrode was greatly influenced by the solvent used. The reproducibility and stability of a given GCE surface was examined using a $\text{K}_2\text{Fe}(\text{CN})_6$ solution which was accomplished by scanning the respective CV curve, briefly stirring the solution and rescanning the CV curve. Preliminary voltammetric evaluation indicated acceptable electrode behaviors. The repeated scanning (in a dioxygen saturated solution) between +1.0 and -2.0 V versus Ag/Ag^+ (0.01 M AgNO_3 in 0.1 or 0.05 M TEAP acetonitrile solution) caused a relative standard deviation of only 3% of the peak currents of ferri/ferro at the scan rates 100 mV s^{-1} for ten cycles. The oxidation potential had a deviation of about 0.005 V for four to ten scans, which were within the precision of the experimental measurement. Electropolymerization of the complexes as electrode modifiers was mostly carried out by cycling the potential between +0.5 and -2.5 V at 200 mV s^{-1} in freshly distilled acetonitrile solutions containing 1×10^{-4} M complexes and 5×10^{-2} M TEAP under a nitrogen atmosphere. After ten cycles,

the electrode was removed from the solution, rinsed with water and dried in air.

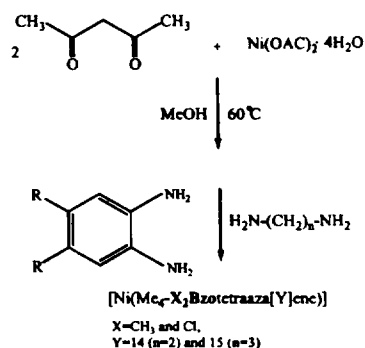
3. Results and discussion

The complexes 14-2Cl, 14-2Me, 15-2Cl and 15-2Me were prepared by the synthetic procedure as illustrated in Scheme 1. Template condensation of a (1:1) mixture of 4,5-disubstituted(2Cl or 2 CH_3)-1,2-diaminobenzene and ethylenediamine (or propylenediamine) with 2,4-pentanedione in the presence of nickel(II) ion gave the disubstituted complexes of the 14-2X and 15-2X series with a range of yields from 33% to 65%. Elemental analyses of these new complexes collected in the experimental part were consistent with their formulations.

3.1. Spectral properties of complexes with disubstituents

The EI mass spectra for 14-2Cl, 14-2Me and 15-2Me exhibited the presence of a molecular ion M^+ at m/z 420 (^{35}Cl , ^{58}Ni), 380 (^{58}Ni) and 394 (^{58}Ni), respectively, which are the base peaks in each mass spectrum. The 15-2Cl showed a molecular ion M^+ at m/z 434 (^{35}Cl , ^{58}Ni) that is not a base peak. The IR spectra of the new complexes exhibited bands at around 1530 cm^{-1} due to the vibrations of $\text{C}=\text{C}$ and 1475 and 1410 cm^{-1} due to $\text{C}=\text{N}$ modes but no $\text{N}-\text{H}$ absorption at around 3200 cm^{-1} . The aromatic band occurred at around 750 cm^{-1} . These observations reflect the formation of $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds, and the disappearance of $\text{N}-\text{H}$ groups, and the formation of a conjugated six membered chelate ring in the reaction [16].

The electronic absorption spectra of these asymmetric complexes were examined over the 370–700 nm range. The bands in the near UV regions (375–390 nm) with molar absorptivities (ϵ_{max}) ranging from 10 000 to 25 000 $\text{M}^{-1}\text{cm}^{-1}$ for each of the new complexes could be attributed to the $\pi \rightarrow \pi^*$ transitions of the macrocycles and are almost independent of the macrocycle rings (14- or 15-membered). The bands in the visible region had



Scheme 1.

energies between 500 and 550 nm ($\epsilon_{\max} = 2660\text{--}3220 \text{ M}^{-1} \text{ cm}^{-1}$) which are attributed to charge transfer (CT) transitions from the highest occupied ligand molecular orbital to the lowest empty d-orbital of the nickel. Their values of ϵ_{\max} are much larger than those commonly assigned to ligand field transitions. This behaviour is comparable to that observed for D_{4h} nickel(II) complexes with four nitrogen donors [10,12,13]. The spectra of the 15-2X series showed shifts of λ_{\max} to longer wavelengths compared with 14-2X ones. This observation is attributed to the different ring size between the 14-membered and 15-membered macrocycles, which is in agreement with other tetraazaannulene complexes [12,13]. Another feature of the electronic spectra is the variation of the band maximum according to the substituents of the phenyl ring on the macrocycle. The spectra of 14-2Me and 15-2Me with an electron-donating group showed 5 and 13 nm shifts of λ_{\max} to longer wavelengths compared with 14-2H and 15-2H, respectively, while those of 14-2Cl and 15-2Cl with an electron-withdrawing group did relatively hypsochromic shifts. Such an electronic effect of the substituent group is supported by similar observations with nickel(II) tetraaza N_4 macrocycles [12,13,17,18].

The 14-2X and 15-2X complexes gave well-resolved ^1H and ^{13}C NMR spectra. The assignments of the chemical shifts were made mostly characterized by comparisons of the data with those of other nickel(II) macrocyclic complexes reported earlier [5,12,13]. The carbon sites of the diaminate framework of nickel(II)-tetraazaannulene complexes have been found to be a reactive nucleophilic centre named a methine site [13,19,20]. Thus, the resonance energies of the methine sites for the new complexes and the effects of macrocyclic rings are worth special mentioning. The methine proton peaks for 14-2Me and 15-2Me with two methyl substituents and those for 14-2Cl and 15-2Cl with two chloro substituents on the phenyl rings were equivalent and showed one singlet. The proton peaks of 14-2Me and 15-2Me, and 14-2Cl and 15-2Cl were shifted by about 0.05 and 0.02 ppm upfield, and 0.04 and 0.03 ppm downfield relative to 14-2H and 15-2H, respectively. The ^{13}C NMR peaks of 14-2Me and 15-2Me, and 14-2Cl and 15-2Cl were shifted by about 0.58 and 0.49 ppm upfield, and 0.98 and 0.88 ppm downfield relative to 14-2H and 15-2H, respectively. Such results are attributed to the shielding and deshielding effects of the substituents of the phenyl group on the macrocycle rings. The ^{13}C data was mostly in agreement with the corresponding ^1H NMR behaviour.

3.2. Electrochemical studies of complexes with a monosubstituent

Redox potentials of the monosubstituted nickel(II) complexes measured using cyclic voltammetry are given

in Table 1. The cyclic voltammograms of 14- NO_2 and free base ligand, for example, are illustrated in Fig. 1 and exhibited cyclic voltammetric behaviors characterized by, two appreciably irreversible one electron waves corresponding to oxidation of the macrocycle (Mc), $\text{Mc} \rightarrow \text{Mc}^+ +$ and $\text{Mc}^+ \rightarrow \text{Mc}^{2+}$, and only one regular and reversible wave ($\text{Ni}^{2+} \rightarrow \text{Ni}^+$). The number of electrons involved in each redox reaction could be determined by electrolyzing the complex relating to the more positive potential by 0.2 V more than that of each wave according to the method reported.[26] As listed in Table 1, the 1st and 2nd ligand based oxidations were detected at in the ranges of +0.01–+0.30 V and +0.36–+0.81 V versus Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TEAP acetonitrile solution), and the reduction of metal at $E_{1/2} = -1.65$ to -2.65 V in DMSO solution. The waves were of similar pattern to those exhibited by the symmetric nickel(II) tetraazaannulene, [10] indicating that diffusion coefficients of nickel(II) tetraazaannulene macrocycles do not appreciably differ with respect to symmetric or asymmetric complexes. The complexes, 14-X and 15-X contain macrocycles with various electron donor and withdrawing groups (X) that have different σ values [21]. As pointed out elegantly by Kadish et al. in ref. [21], the exact choice of Hammett parameters to use, i.e. σ_p , σ^+ , σ^- , etc., is not clear. We have chosen σ_p ($\sigma_p = -0.17$ for CH_3 , 0.00 for H, 0.23 for Cl and 0.78 for NO_2) because the correlation between redox potentials and σ_p are linear and it offers comparisons to the widest range of literature data. Totally the substituents effect on the reduction potential of the complexes was not large, but clearly appeared. The correlation between the substituent effect and the redox potentials of the complexes was examined by means of a Hammett plot. As shown in Fig. 2, the relationships between the 1st oxidation potentials (E_{ap1}) and σ_p were linear with a slopes of 0.23 V for both 14-X and 15-X series (correlation coefficients of 0.99), reflecting the similarity of structures of the 14-X and 15-X series. Interestingly, these slopes are similar to those of the oxidation potentials for metalloporphyrins with substituents located on the pyrrole residues of the porphyrin ligand [22,23].

The modification of a GCE could be carried out by scanning repeatedly in the range of a given potential and the modified electrodes were relatively stable even in air or solution. For example, the asymmetric complexes 14-H were electropolymerized by cycling from +1.0 to -2.0 V versus Ag/Ag^+ (0.01 M AgNO_3 in a 0.1 M TEAP acetonitrile solution) giving thin films on the GCE (Fig. 3). The nickel(II) complexes of tetraazaannulenes with benzoyl groups at the methine sites of the macrocycle are not electropolymerized on the GCE by cyclic voltammetry [24] supporting directly that the electropolymerization of nickel(II)-tetraazaannulene [25,26] occurs at the methine site on macrocycle. According to

Table 1
Redox potentials of 14-CH₃, 14-H, 14-Cl, 14-NO₂, 15-CH₃, 15-H, 15-Cl and 15-NO₂ vs. Ag/Ag⁺ (0.01 M AgNO₃ in a 0.1 M TEAP^a and in a 0.05 M TEAP^b acetonitrile solution) at 25 °C

M	Composition	$E_{p(1)}$ (mV)	$E_{p(2)}$ (mV)	$E_{1/2}$ (V)	σ_p ^c
Ni	14-CH ₃	56	582	-2.65 ^d	-0.17
	14-H	96	620	-2.65 ^d	0.00
	14-Cl	152	683	-2.65 ^d	0.23
	14-NO ₂	282	805	-1.55 ^d	0.78
H ₂	14-H	238	614	-	0.00
Ni	15-CH ₃	5 ^d	360 ^d	-2.45 ^d	-0.17
	15-H	107	645	-2.45 ^d	0.00
	15-Cl	174	705	-	0.23
	15-NO ₂	287	787	-1.56 ^d	0.78
H ₂	15-H	194	606	-	0.00

^a All 14-X data were measured from 1×10^{-4} M complexes in 0.1 M TEAP–acetonitrile solutions vs. Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) at 25 °C.

^b All 15-X data were measured from 1×10^{-4} M complexes in 0.05 M TEAP–acetonitrile solutions vs. Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) at 25 °C and sweep rates 200 mV s^{-1} .

^c The σ_p values are from, Swain, C.G., Lupton, E.C., J. Am. Chem. Soc., 1968, 90, 4328.

^d Data from 1×10^{-3} M complexes in 0.1 M TEAP–DMSO solutions vs. Ag/Ag⁺ (0.01 M) at 25 °C and sweep rates 200 mV s^{-1} .

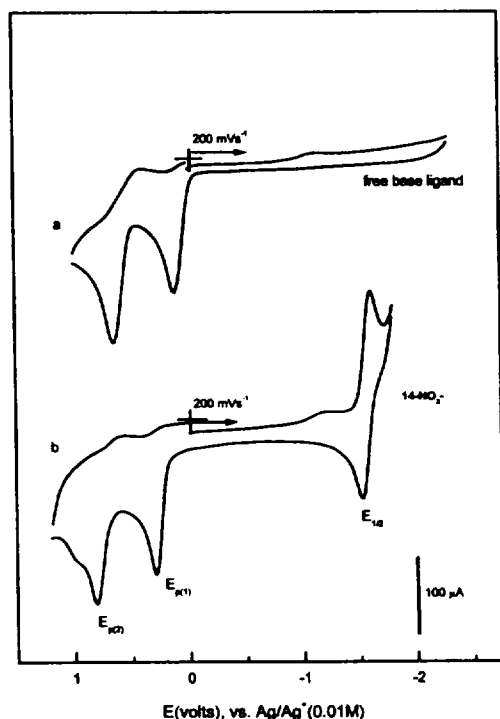


Fig. 1. Cyclic voltammograms of the free base ligand (a) and its complex, 14-NO₂ (b) in a 0.1 M TEAP acetonitrile solution at 25 °C and 200 mV s^{-1} .

the pattern of electropolymerization and the electron number observed in each oxidation step and the results reported, we concluded that the polymer is formed at the electrode surface via a radical cation and dication.

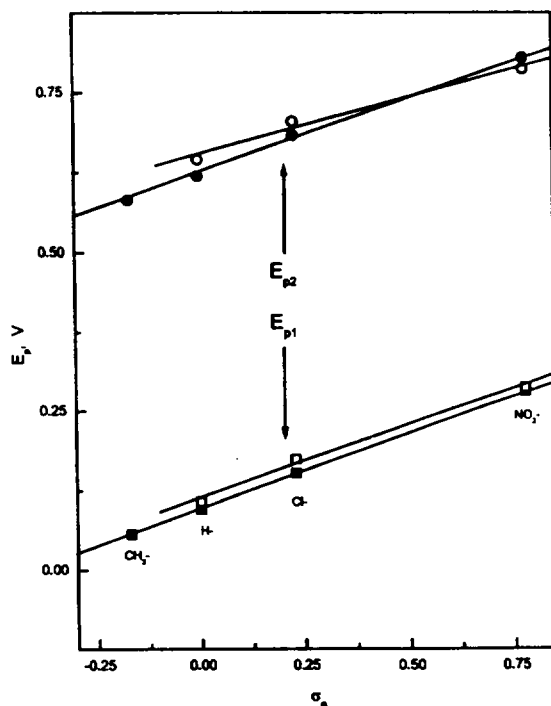


Fig. 2. Hammett plots of the first and second oxidation potentials (E_{p1} and E_{p2}) of the 14-X (■ and ●) and 15-X (□ and ○) series against the substituent constants (σ_p).

That is the mechanism for the electropolymerization of the asymmetric complex is thought to be similar to that of the symmetric one. The cyclic voltammograms of the modified electrode in neat 0.1 M TEAP acetonitrile exhibited both the Mc/Mc^{+} and $\text{Mc}^{+}/\text{Mc}^{2+}$ irrever-

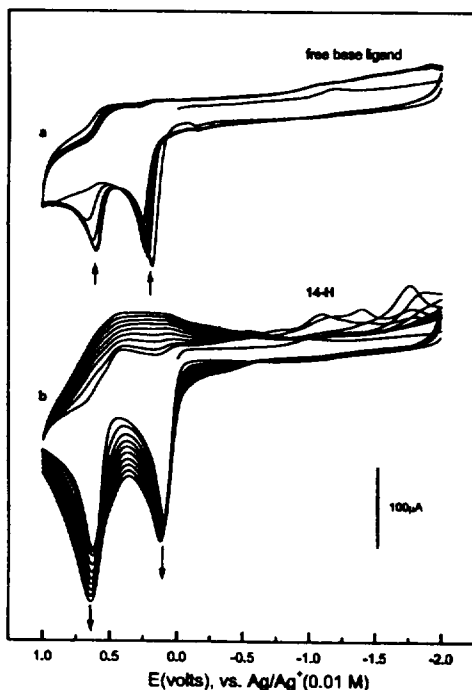


Fig. 3. Cyclic voltammograms of the free base ligand (a) and its complex, 14-H (b) cycling from +1.0 to -2.0 V vs. Ag/Ag⁺ (0.01 M AgNO₃ in a 0.1 M TEAP acetonitrile) at 25 °C and 200 mV s⁻¹.

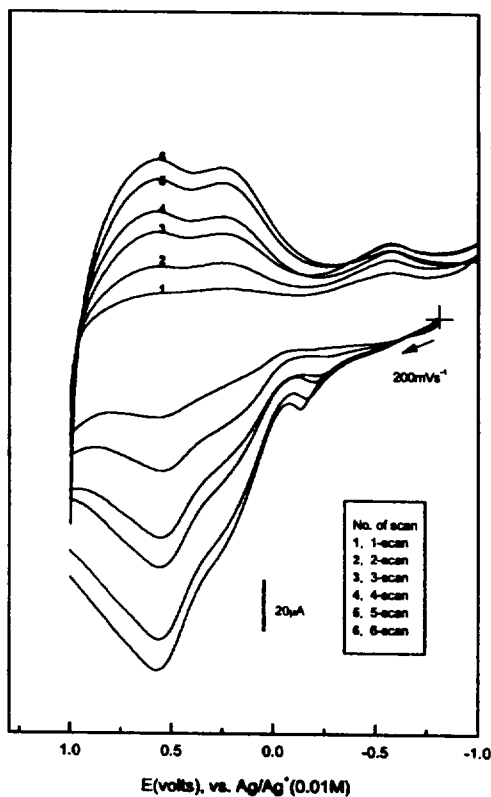


Fig. 4. Cyclic voltammograms of the GCE electropolymerized by the 14-H in a neat 0.1 M TEAP acetonitrile solutions at 25 °C and 200 mV s⁻¹.

sible waves at around +0.10 and +0.60 V, respectively, as shown in Fig. 4. The first and second oxidation waves (Fig. 4) of the GCE electropolymerized by 14-H showed at almost the same potentials as those of the complex 14-H (Fig. 3), while no other chemical reaction following the electropolymerization on GCE could be found.

The applications of the GCEs modified by 14-H, 14-NO₂ and 15-NO₂ for dioxygen electroreduction were illustrated in Fig. 5. The traces a, b and c indicate the cyclic voltammograms for the GCEs electropolymerized by 14-H, 14-NO₂ and 15-NO₂ in an oxygen-saturated acetonitrile solution, respectively, while trace d is for the bare GCE in the same solution. The potential difference between the modified and bare electrodes was often used to evaluate the catalytic activity of the modifier. On comparing the voltammograms, the reduction potentials of dioxygen by the modified GCEs were reduced by about 400 mV compared with the bare one. In the case of the 14-X series, the catalytic reduction of dioxygen occurred at potentials somewhat more positive than in the 15-X series. Based upon the results herein (Fig. 5), it was shown that the electropolymerized electrodes using 14-H, 14-NO₂ and 15-NO₂ have good catalytic activities for use in electrocatalytic reduction of dioxygen. On the other hand, the same modified electrodes showed scarcely any catalytic activity in the electrooxidation of L-ascorbate [27].

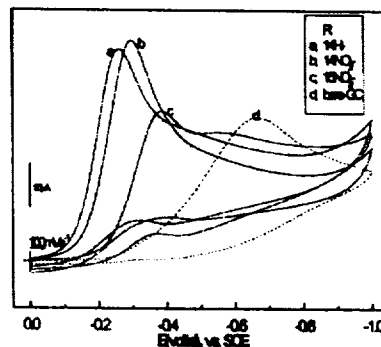


Fig. 5. Cyclic voltammograms of catalytic dioxygen reduction by the electropolymerized and bare GCEs in a 0.1 M phosphate buffer (pH 7.0) at 25 °C and 100 mV s⁻¹: (a), 14-H; (b), 14-NO₂; (c), 15-NO₂; (d), bare GCE.

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