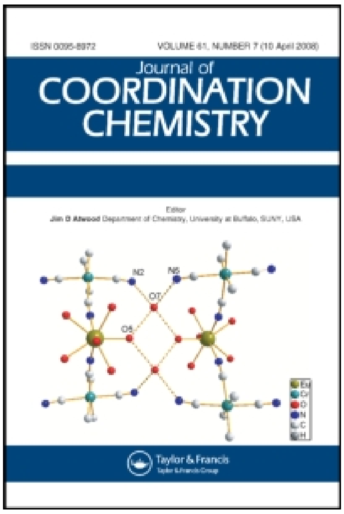

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Benzoylation and Properties of 14-π Nickel(II)-Tetraazaannulene Complexes with Substituents on the Phenyl Ring

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BENZOYLATION AND PROPERTIES OF 14-π NICKEL(II)-TETRAAZAANNULENE COMPLEXES WITH SUBSTITUENTS ON THE PHENYL RING

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The benzoylated asymmetrical nickel(II) complexes, 2,4,9,11-tetramethyl-3,10-dibenzoyl-1,5,8,12-([14]-Xbenzo)tetraazacyclotetradecinato(2-)nickel(II) (**A$_{1-4}$**) and 2,4,10,12-tetramethyl-3,11-dibenzoyl-1,5,9,13-([15]-Xbenzo)tetraazacyclotetradecinato(2-)nickel(II) (**B$_{1-4}$**), wherein $X = CH_3$ (**A$_1$** and **B$_1$**), H (**A$_2$** and **B$_2$**), Cl (**A$_3$** and **B$_3$**) and NO_2 (**A$_4$** and **B$_4$**), have been synthesized and characterized by analysis, IR, electronic, ^{1}H- and ^{13}C-NMR spectra. An intense IR band due to C=O stretching is present in the range 1630–1650 cm^{-1} upon benzoylation. Electronic spectra show bands at 375–390 nm with $\varepsilon_{max} = 10000$–$26000\,M^{-1}cm^{-1}$ due to $\pi \rightarrow \pi^*$ transitions of macrocycles and at 500–550 nm with $\varepsilon_{max} = 1000$–$5000\,M^{-1}cm^{-1}$ attributable to LMCT for each of the complexes. The proton peaks of methine sites in the NMR spectra disappear on benzoylation. Results of the carbon-13 NMR spectra are compatible with those of the proton NMR. Cyclic voltammograms of the complexes in acetonitrile exhibit two successive and reversible (irreversible in DMSO) oxidation peaks for the macrocycle ($Mc \rightarrow Mc^{\bullet +}$ and $Mc^{\bullet +} \rightarrow Mc^{2+}$) in the ranges $+0.31 - +0.51$ and $+0.60 - +0.84$ V, respectively. In the reduction area, a reversible wave is followed by reduction of metal {Ni(II) → Ni(I) at around −2.32 V}. Unlike analogous complexes without the benzoyl group, those compounds are not electropolymerized by cyclic voltammetry.

Keywords: Asymmetric 14-π nickel(II)-tetraazaannulene; Benzoylation; Substituent effect; Electrochemistry

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INTRODUCTION

The tetraazaannulenenickel(II) complexes first described by Jaeger [1,2] have attracted considerable attention because of their utility to model porphyrins and corrins in biological systems [3–7]. The potential of these macrocyclic complexes as catalysts has also fostered some interest [6,7]. Most tetraazaannulene complexes have been synthesized by the condensation of 1,2-phenylenediamine or substituted 1,2-phenylenediamine with 2,4-pentanedione, but asymmetrical annulene complexes substituted by the benzoyl group at the methine sites of the macrocyclic ring have not been reported.

In previous papers, we reported a series of asymmetrical tetraazaannulenenickel(II) complexes with mono- or disubstituted benzo N_4 macrocycles, [Ni(Me$_4$-{14 or 15}XbenzotetraeneN$_4$)] [8,9] or [Ni(Me$_4$-X$_2$benzo{14 or 15}tetraeneN$_4$)] [10], where $X = CH_3$, H, Cl or NO_2, prepared by template condensation. These complexes contain the 14-π electron system with one saturated five (or six-membered) chelate ring and unsaturated five-membered chelate ring and two nucleophilic methine centres. It is expected that the properties of these 14-π complexes would be considerably affected by substituents at methine sites.

In this study, we report the benzoylation of asymmetrical 14-π nickel(II) complexes with substituted monobenzoN4 macrocycles, [Ni(Me$_4$-dibenzoyl-{14 or 15}-XbenzotetraeneN$_4$)] by modifying a method described in the literature [8–10]. We also consider the effect of varying the substituent X ($X = CH_3$, H, Cl and NO_2). These new complexes are studied in order to better understand the mechanism of tetraazaannulene metal complex-catalyzed olefin oxidation.

EXPERIMENTAL

Materials and Physical Measurements

$Ni(OAc)_2 \cdot 4H_2O$ was purchased from Aldrich. All reagents used were of analytical grade. Acetonitrile was distilled according to the published method [11]. Tetraethylammonium perchlorate (TEAP) used as supporting electrolyte was prepared and purified by the method described by Kolthoff and Coetzee [12].

Microanalyses of the complexes prepared were carried out on a Carlo-Ebra, EA 1108 instrument. IR spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr pellets. Electronic spectra were recorded using chloroform solutions on a Jasco V 550 spectrophotometer at room temperature. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Brucker instrument at room temperature and chemical shifts in $CDCl_3$ are given in ppm relative to tetramethylsilane as internal reference.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50 W electrochemical analyzer and C2 cell stand at room temperature. For the electrochemical measurements, a three electrode system consisting of a GC working electrode, an Ag/Ag^{+} (0.1 M $AgNO_3$ in 0.1 M TEAP actonitrile solution) reference electrode and a platinum wire as auxiliary electrode was used.

Synthesis of Complexes

2,4,9,11-Tetramethyl-3,10-dibenzoyl-1,5,8,12-([14]-methylbenzo)-tetraazacyclotetradecinato(2-)nickel(II) (A_1)

A mixture of complex **1** (n = 2) (0.36 g, 0.001 mol) prepared by the method reported in the literature [9,10] was dissolved in benzene (40 cm^3) containing triethylamine (0.28 cm^3, 0.002 mol) and benzoyl chloride (0.23 cm^3, 0.002 mol). The mixture was heated under reflux for 5 h with stirring and protecting from moisture. The reaction mixture was left to stand at room temperature for one day and filtered to remove triethylamine hydrochloride. The filtrate was evaporated to dryness under reduced pressure and the resulting solid was chromatographed on aluminium oxide and eluted with chloroform. The second effluent was collected, evaporated to dryness *in vacuo* and dried to give fine, dark violet crystals. Yield 65%. *Anal.* Calcd. (%) for $NiC_{33}H_{32}N_4O_2$: C, 68.9; H, 5.50; N, 9.74. Found: C, 69.10; H, 5.30; N, 9.80. IR (KBr disc, cm^{-1}): ν(C=C), 1545; ν(C=N), 1595; ν(aromatic), 752 and 804; ν(C=O), 1647. UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in $CHCl_3$ 503 and 4850, and 376 and 25400.

2,4,9,11-Tetramethyl-3,10-dibenzoyl-1,5,8,12-([14]-Hbenzo)-tetraazacyclotetradecinato(2-)nickel(II) (A_2)

$\mathbf{A_2}$ was prepared from a mixture of complex **1**, benzoyl chloride and triethylamine according to the procedure described above. The dark violet product was obtained by recrystallizing from chloroform. Yield 78%. *Anal.* Calcd. (%) for $NiC_{32}H_{30}N_4O_2$: C, 68.47; H, 5.39; N, 9.98. Found: C, 68.54; H, 5.37; N, 9.82. IR (KBr disc, cm^{-1}): ν(C=C), 1548; ν(C=N), 1597; ν(aromatic), 725 and 804; ν(C=O), 1655. UV–vis: λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) in $CHCl_3$ 502 and 5190, and 374 and 27500.

2,4,9,11-Tetramethyl-3,10-dibenzoyl-1,5,8,12-([14]-chlorobenzo)-tetraazacyclotetradecinato(2-)nickel(II) (A_3) and 2,4,9,11-Tetramethyl-3,10-dibenzoyl-1,5,8,12-([14])-nitrobenzo)-tetraazacyclotetradecinato(2-)nickel(II) (A_4)

The products were isolated by chromatography to give fine, dark violet crystals, following the above mentioned procedures. Yields 72 and 53%, respectively. For $NiC_{32}H_{29}N_4O_2Cl$ (**A₃**): *Anal.* Calcd. (%): C, 64.52; H, 4.87; N, 9.41. Found: C, 64.63; H, 4.89; N, 9.38. IR (KBr disc, cm^{-1}): ν(C=C), 1547; ν(C=N), 1593; ν(aromatic), 752 and 804; ν(C=O), 1651. UV–vis: λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 514 and 4470, and 378 and 26500. For $NiC_{32}H_{29}N_5O_4$ (**A₄**): *Anal.* Calcd. (%): C, 63.40; H, 4.75; N, 11.56; Found: C, 63.52; H, 4.81; N, 11.39. IR (KBr disc, cm^{-1}): ν(C=C), 1552; ν(C=N), 1593; ν(aromatic), 748 and 806; ν(C=O), 1655; $\nu(NO_2)$, 1319. UV–vis: λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 518 and 10700, and 396 and 22000.

2,4,10,12-Tetramethyl-3,11-dibenzoyl-1,5,9,13-([15]-methylbenzo)tetraazacyclotetradecinato(2-)nickel(II) (B_1)

Complex **2** (n = 3) was synthesized according to the published procedure [9,10]. Complex **2** (0.001 mol), benzoyl chloride (0.23 cm^3, 0.002 mol) and triethylamine (0.28 cm^3, 0.002 mol) were dissolved in benzene and refluxed for 3 h followed by the above procedure to give the product that was fine, dark violet crystals. Yield 70%. *Anal.* Calcd. for $NiC_{34}H_{32}N_4O_2$: C, 69.31; H, 5.77; N, 9.51. Found: C, 69.50; H, 5.71; N, 9.45. IR (KBr disc, cm^{-1}): ν(C=C), 1531; ν(C=N), 1595; ν(aromatic), 752 and 802; ν(C=O), 1628. UV–vis: λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 531 and 2710, and 376 and 19100.

2,4,10,12-Tetramethyl-3,11-dibenzoyl-1,5,9,13-([15]-Hbenzo)tetraazacyclotetradecinato(2-)nickel(II) (B_2), 2,4,10,12-tetramethyl-3,11-dibenzoyl-1,5,9,13-([15]-chlorobenzo)tetraazacyclotetradecinato(2-)nickel(II) (B_3) and 2,4,10,12-Tetramethyl-3,11-dibenzoyl-1,5,9,13-([15]-nitrobenzo)-tetraazacyclotetradecinato(2-)nickel(II) (B_4)

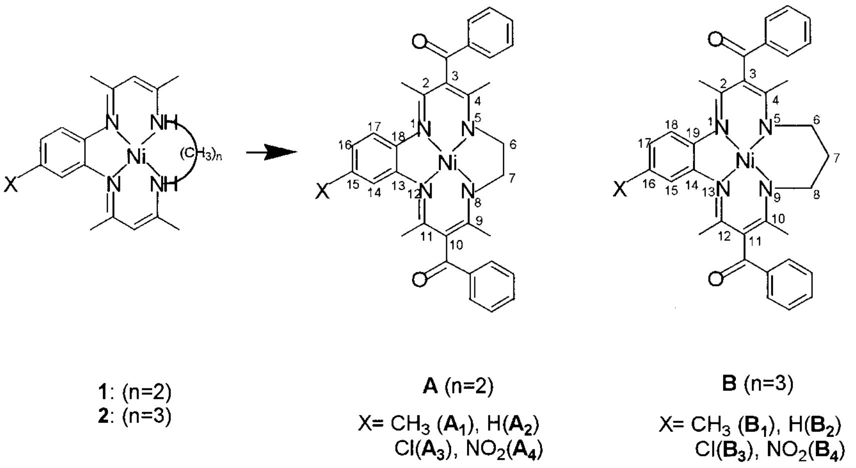
The products were isolated by chromatography to give fine, dark violet crystals. Yield 64, 68 and 58%, respectively. For $NiC_{33}H_{32}N_4O_2$ (**B₂**): *Anal.* Calcd. (%): C, 68.89; H, 5.61; N, 9.74. Found: C, 69.98; H, 5.57; N, 9.82. IR (KBr disc, cm^{-1}): ν(C=C), 1531; ν(C=N), 1597; ν(aromatic), 717 and

802; ν(C=O), 1629. UV–vis: λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 531 and 1850, and 376 and 11300. For $NiC_{33}H_{31}N_4O_2Cl$ (**B**$_3$): *Anal.* Calcd. (%): C, 65.01; H, 5.09; N, 9.13. Found: C, 65.23; H, 5.03; N, 9.13. IR (KBr disc cm^{-1}): ν(C=C), 1531; ν(C=N), 1575; ν(aromatic), 752 and 802; ν(C=O), 1631. UV–vis: λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 550 and 1250, and 382 and 12200. For $NiC_{33}H_{31}N_5O_4$ (**B**$_4$): *Anal.* Calcd. (%): C, 63.90; H, 5.00; N, 11.30. Found: C, 64.05; H, 4.89; N, 11.21. IR (KBr disc cm^{-1}): ν(C=C), 1533; ν(C=N), 1595; ν(aromatic), 748 and 802; ν(C=O), 1639; ν(NO_2), 1319. UV–vis, λ_{max} (nm) and ε_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$ 552 and 5100, 443 and 9840, and 392 and 14400.

RESULTS AND DISCUSSION

The condensation reaction between complex **1** (or **2**) and benzoyl chloride in a 1 : 2 molar ratio in the presence of triethylamine was performed in refluxing benzene to give the corresponding 3,10-dibenzoylated (**A**$_{1-4}$) or 3,11-dibenzoylated (**B**$_{1-4}$) products in 53–78% yields. The reaction was completed within 4–5 h. Purification of the crude products was achieved by column chromatography on activated aluminium oxide.

The synthesis of complexes (**A**$_{1-4}$ and **B**$_{1-4}$) is illustrated in Scheme 1. Since the electronic structure between the diiminate chelate ring of tetraaza-[14 or 15]annulene and the diketonate chelate ring of 2,4-pentanedione is



SCHEME 1

very similar, both are supposed to possess similar reactivity and structure patterns. The methine sites of tetraazaannulene have nucleophilicity and the nickel(II) ion protects nitrogen centres [13–15]. Elemental analyses given in the Experimental section are consistent with these formulations.

Spectroscopic Studies

IR absorption data for the complexes ($\mathbf{A}_{1\text{–}4}$ and $\mathbf{B}_{1\text{–}4}$) are summarized in the Experimental section. The complexes have very intense bands in the regions 1647–1655 cm^{-1} ($\mathbf{A}_{1\text{–}4}$) and 1628–1639 cm^{-1} ($\mathbf{B}_{1\text{–}4}$) attributable to the stretching modes of C=O, indicating the benzoylation in both series. The benzoyl group has a characteristic mode around 800 cm^{-1}. $\mathbf{A}_4$ and $\mathbf{B}_4$ exhibit strong bands at around 1320 cm^{-1} due to the NO_2 group. The C=O stretching modes of $\mathbf{A}_{1\text{–}4}$ shift to higher frequencies by about 20 cm^{-1} than those of $\mathbf{B}_{1\text{–}4}$. Spectra also show strong bands due to ν(C=C) at 1545–1552 cm^{-1} for $\mathbf{A}_{1\text{–}4}$ and at around 1530 cm^{-1} for $\mathbf{B}_{1\text{–}4}$, and ν(C=N) at around 1595 cm^{-1} for both $\mathbf{A}_{1\text{–}4}$ and $\mathbf{B}_{1\text{–}4}$.

The electronic absorption of $\mathbf{A}_{1\text{–}4}$ and $\mathbf{B}_{1\text{–}4}$ exhibit two bands in the region 370–550 nm. Complex $\mathbf{B}_4$ exhibits an additional band at 440 nm which may be due to charge transfer. In general the features for $\mathbf{A}_{1\text{–}4}$ (or $\mathbf{B}_{1\text{–}4}$) are similar not only to one another, but also to the starting complexes (**1** and **2**). This indicates that the delocalization of the conjugated system in the complexes is approximately analogous and that the electronic effects of the benzoyl group on the tetraaza[14 or 15]annulene chelate ring is small. The bands in the near UV region (375–390 nm) with molar absorptivities ranging from 10000 to 26000 $M^{-1}\,cm^{-1}$ could be attributed to $\pi \rightarrow \pi^*$ transitions and are almost independent of the size of the macrocycle rings (14- or 15-membered). Spectra in the visible region show bands at 500–550 nm (ε_{max}=1000–5000 $M^{-1}\,cm^{-1}$) attributed to charge transfer (CT) transitions from the highest occupied ligand molecular orbital to the lowest empty d-orbital of nickel. The values of ε_{max} are much larger than those commonly assigned to ligand field transitions [16]. This behaviour is comparable to that observed for D_{4h} nickel(II) complexes with four nitrogen donors [9,17,18]. The maximum wavelengths (λ_{max}) of the **A** series have almost 20 nm smaller shifts relative to **B** complexes. This observation is attributed to different ring sizes in agreement with other tetraazaannulene complexes [9,18]. One other feature of the electronic spectra is the variation of the band maximum for the CT transitions according to the substituent in the phenyl ring on the macrocycle. For example, $1/\lambda_{max}$ of 14-membered

A complexes is linearly and negatively dependent on the electron-withdrawing (σ_p) [19] nature of the substituents on the phenyl group as shown in Fig. 1. The slope (ρ) of the plot of $1/\lambda_{max}$ against σ_p was -0.83, indicating that the bands at 500–550 nm are due to the CT transitions. Such a conclusion is supported by similar observations with dibenzo[14]tetraazaannulene complexes ($\rho = -0.72$) [17].

The complexes $\mathbf{A}_{1-4}$ and $\mathbf{B}_{1-4}$ give well-resolved proton NMR spectra. Chemical shift assignments are accomplished on the basis of comparisons with those for complexes reported earlier [7–10]. Proton NMR data and their assignments for $\mathbf{A}_{1-4}$ and $\mathbf{B}_{1-4}$ are collected in Table I. Olefinic proton signals of the methine sites disappear on benzoylation. Methyl proton signals at the 2,4,9,11-positions exhibit upfield shifts by 0.101–0.181 ppm on benzoylation, indicating that the methyl groups are within the shielding zone caused by the magnetic anisotropy of the benzene ring

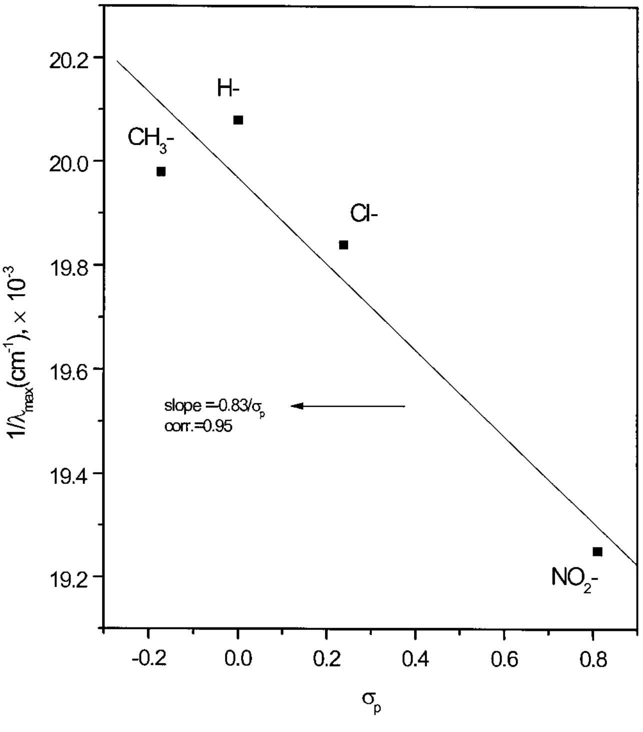


FIGURE 1 Correlation between the maximum energy of the LMCT of $\mathbf{A}_{1-4}$ and Hammett σ_p parameters.

TABLE I ^{1}H-NMR data for the nickel(II)-tetraazaannulene complexes, $\mathbf{A_{1\text{–}4}}$ and $\mathbf{B_{1\text{–}4}}$

Complexes	*Methyl*	*Toluene Methyl*	*Ethylene* $-N-CH_2$	*Propylene* $-N-CH_2,-CH_2$	*Aromatic (macrocyle)*	*Aromatic (benzoyl)*
$\mathbf{A_1}$	1.87(s) 2.27(s) 2.94(s)	2.25	3.49		6.54–6.96	7.44–7.97
$\mathbf{A_2}$	1.88 2.28		3.50		6.71–7.06	7.45–7.97
$\mathbf{A_3}$	1.89 2.90 3.24 2.25		3.52		6.68–7.01	7.46–7.98
$\mathbf{A_4}$	1.95 2.25 2.31		3.59		7.03–7.06	7.49–8.00
$\mathbf{B_1}$	1.74 2.19 2.21	2.24		2.89, 2.72	6.55–6.72	7.45–8.02
$\mathbf{B_2}$	1.75 2.20			2.90, 2.72	6.73–6.83	7.46–8.02
$\mathbf{B_3}$	1.76 1.76 2.14 2.14			2.90, 2.72	6.70–6.76	7.47–8.01
$\mathbf{B_4}$	1.80 2.82 3.12 2.14			2.95, 2.72	6.80–6.83	7.50–8.05

Chemical shifts in ppm from internal TMS; measured in Chloroform-*d*; multiplicity of a proton signal is given in parantheses after δ-value; s = singlet, m = multiplet, br = broad.

of the benzoyl group. Peaks of $\mathbf{A_1}$ and $\mathbf{B_1}$ show appreciable upfield shifts (0.106–0.177 and 0.108–0.180 ppm) relative to $\mathbf{A_2}$ and $\mathbf{B_2}$ with no substituent on the phenyl ring, respectively. On the other hand, peaks of complexes ($\mathbf{A_3}$, $\mathbf{A_4}$, $\mathbf{B_3}$ and $\mathbf{B_4}$) with an electron withdrawing group show slightly downfield shifts (0.040–0.071 ppm) relative to $\mathbf{A_2}$ and $\mathbf{B_2}$. The results are attributed to the shielding and deshielding effects of the substituents on the phenyl ring.

Carbon-13 NMR data and their assignments for $\mathbf{A_{1\text{–}4}}$ and $\mathbf{B_{1\text{–}4}}$ are listed in Table II. All methyl carbon peaks of $\mathbf{A_{1\text{–}4}}$ and $\mathbf{B_{1\text{–}4}}$ show upfield shifts resulting from the same shielding effects as in the proton NMR. Signals of the aromatic carbons at the 2-, 4-, 9- (or 10-) and 10- (or 11-) positions with the methyl group also exhibit slight upfield shifts upon benzoylation, while carbon peaks at the 6-, 7-, 13- (or 14-), 14- (or 15-), 16- (or 17-) and 18- (or 19-) positions shift slightly downfield. The carbon signals at the 3- and 10- (or 11-) positions show downfield

TABLE II ^{13}C-NMR data for the nickel(II)-tetraazaannulene complexes, $\mathbf{A_{1-4}}$ and $\mathbf{B_{1-4}}$

Complexes	*Methyl*	*Toluene Methyl*	*Ethylene –N–C*	*Propylene –N–C, –C–C*	*Methine*	*Aromatic (aromatic)*	*Diiminate*	*Aromatic (Benzoyl)*	*C=O*
A$_1$	19.9	20.9	52.8		115.6	120.8	155.7	128.5	199.2
	23.1		52.9		116.1	121.2	155.9	129.3	199.3
						121.7	158.5	130.3	
						140.9	158.7	132.4	
						142.9			
						145.1			
A$_2$	20.1		53.0		116.1	120.7	156.1	128.6	199.5
	23.2					121.5	158.8	129.4	
						140.9		132.6	
						145.2			
A$_3$	20.2		52.9		116.1	119.6	155.3	125.2	199.2
	22.8		53.0		116.4	120.7	155.5	128.6	
						121.1	158.8	129.3	
						140.5	158.9	132.7	
						143.7			
						145.9			
A$_4$	20.0		52.9		115.5	116.8	154.3	128.8	198.9
	22.6		53.4		116.2	118.5	154.9	129.4	199.2
						119.2	159.3	133.1	
						139.5	159.7	133.2	
						144.6			
						150.6			
B$_1$	20.9	21.6		50.9,	117.6	121.3	158.9	128.3	197.4
	21.7			32.1	117.9	122.2	159.2	129.1	
						122.3	163.1	131.4	
						142.5	163.4	131.6	
						143.8			
						146.0			
B$_2$	22.1			50.9,	117.9	121.4	159.0	128.3	197.5
	21.8			32.0		121.8	163.2	128.9	
						146.1		129.2	
								131.7	
								142.4	
B$_3$	20.9			51.2,	118.1	121.4	158.5	126.3	197.7
	21.9			32.2	118.3	121.6	158.7	128.5	197.8
						122.1	163.4	129.3	
						142.2	163.5	132.1	
						145.1			
						147.3			
B$_4$	20.9			51.4,	116.1	118.4	157.1	128.6	197.8
	21.6			31.9	117.5	119.4	157.7	129.2	197.9
						120.3	163.4	132.4	
						141.3	163.6	132.6	
						146.5		140.9	
						152.3		141.3	

Chemical shifts in ppm from internal TMS; measured in chloroform-*d* at room temperature.

shifts by *ca* 10–12 ppm upon benzoylation, supporting the idea that complex **1** (or **2**) is benzoylated at the 3- and 10- (or 11-) positions. New carbon peaks for the benzoyl groups are observed in the range 125–200 ppm.

TABLE III Redox potential data for the nickel(II)-tetraazaannulene complexes, $\mathbf{A}_{1\text{–}4}$

Comp.	$E_{1/2}$, V $MC \rightarrow Mc^{\bullet 2+}$	$E_{1/2}$, V $Mc^{\bullet +} \rightarrow Mc^{\bullet 2+}$	$E_{1/2}$, V $Ni(II) \rightarrow Ni(I)$
$\mathbf{A}_1$	+0.31	+0.60	−2.32
$\mathbf{A}_2$	+0.34	+0.76	−2.32
$\mathbf{A}_3$	+0.45	+0.69	−2.30
$\mathbf{A}_4$	+0.52	+0.84	−2.33

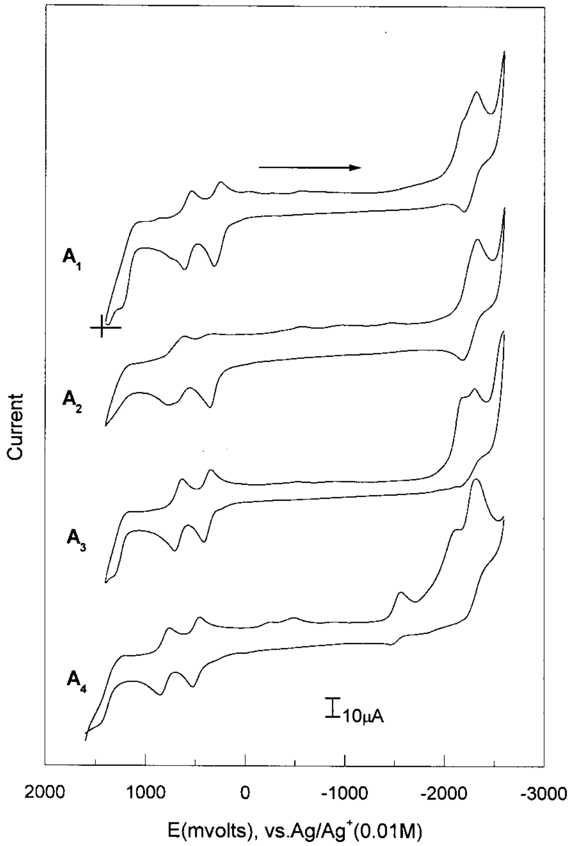


FIGURE 2 Cyclic voltammograms of $[\mathbf{A}_{1\text{–}4}] = 1.1 \times 10^3$ M in 0.1 M TEAP-AN solutions *vs.* Ag/Ag$^+$ (0.01 M) at 25°C and sweep rates 100 mV/s.

Electrochemical Behaviour

Redox potentials of the new benzoylated complexes measured in 0.1 M TEAP-AN solutions *vs* Ag/Ag^+ (0.01 M) at 25°C and sweep rates of 100 mV/s are listed in Table III. Typical voltammograms in the potential range from +1.06 to −2.6 V *vs* Ag/Ag^+ are shown in Fig. 2. Processes are much more reversible than those for the nonbenzoylated tetraazaannulene complexes [20,21]. The voltammogram for each complex $\mathbf{A_{1\text{–}4}}$ shows two successive and appreciablely reversible (irreversible in DMSO) oxidation peaks of the tetraazaannulene in the ranges of +0.31 to +0.52 V and +0.60 to +0.84 V for $Mc \rightarrow Mc^{\bullet+}$ and $Mc^{\bullet+} \rightarrow Mc^{\bullet 2+}$, respectively and one reasonably reversible reduction peak which is metal-based. The number of electron involved in each oxidation step is 1. Oxidation potentials of the tetraazaannulenes are shifted to more positive values according to the electron withdrawing power of the substituent attached to the phenyl ring; this is attributed to a decrease of electron density of the methine site. The order of increase in each oxidation potential $Mc \rightarrow Mc^{\bullet+}$ and $Mc^{\bullet+} \rightarrow Mc^{\bullet 2+}$ is equal to the increase in σ_p values of the substituents. Such an electronic effect is completely different to that on the nonbenzoylated tetraazaannulenenickel(II) complexes in which the oxidation potentials are not affected by substituents [21]. On the other hand, there is no electronic effect of substituent on the reduction potentials of the metal ($E_{pc} = -2.32$ V for $Ni^{2+} \rightarrow Ni^{1+}$). However, the reversibilities of both the oxidation of the ligand and the reduction of metal decrease in the order of the electron withdrawing groups as shown in Fig. 2. The other feature is that unlike complexes without the benzoyl group the new ones are not electropolymerized by cyclic voltammetry, indicating directly that the electropolymerization of nickel(II)-tetraazaannulene on glassy carbon [21–23] occurs at the methine centre on the macrocycle.

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References

[1] E.Z. Jaeger, *Anorg. Allg. Chem.*, **76**, 346 (1966).
[2] E.Z. Jaeger, *Chem.*, **8**, 392 (1968).
[3] D.R. Neves and J.C. Daborwiak, *Inorg. Chem.*, **15**, 129 (1976).
[4] K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta*, **83**, L67 (1984).

[5] H. Nishihara, M. Noguchi and K. Armaki, *Inorg. Chem.*, **26**, 2862 (1987).
[6] D.A. Gangi and R.R. Durand, Jr., *J. Chem. Soc. Chem. Comm.*, 697 (1986).
[7] C.L. Bailey, R.D. Bereman, D.P. Rillema and R. Nowak, *Inorg. Chim. Acta*, **116**, 245 (1986).
[8] Y.C. Park, Z.U. Bae, S.S. Kim and S.K. Baek, *Bull. Korean Chem. Soc.*, **16**, 287 (1995).
[9] Y.C. Park, S.S. Kim, D.C. Lee and C.H. An, *Polyhedron*, **16**, 253 (1997).
[10] Y.C. Park, S.S. Kim, Y.I. Noh and H.G. Na, *J. Coord. Chem.*, **41**. 191 (1997).
[11] J.F. Coetzee, *Anal. Chem.*, **34**, 1139 (1962).
[12] I.M. Kolthoff and J.F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).
[13] K. Sakata, H. Tagami and M. Hashimoto, *J. Heterocyclic Chem.*, **26**, 805 (1989).
[14] K. Sakata and M. Itoh, *J. Heterocyclic Chem.*, **32**, 329 (1995).
[15] K. Sakata, M. Hashimoto, T. Kashiwamura and A. Tsuge, *Synth. React. Inorg. Met-Org. Chem.*, **27**, 797 (1997).
[16] A.B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn. (Elsevier, Amsterdam, 1984).
[17] C.L. Bailey, R.D. Bereman, D.P. Rillema and R. Nowak, *Inorg. Chem.*, **23**, 3956 (1984).
[18] Y.C. Park, Z.U. Bae, S.S. Kim and S.K. Baek, *Bull. Korean Chem. Soc.*, **16**, 287 (1995).
[19] N. Issaacs, *Physical Organic Chemistry*, 2nd Ed. pp. 146–192 (Longman Scientific & Technical, 1995).
[20] A. Detonizer and M-J. Marques, *Electrochim. Acta*, **39**, 1377 (1994).
[21] D.C. Lee, *Ph.D. Dissertation* (1998), Kyungpook Nat. University, Taegu 702–701, Korea.
[22] P.J. Hochgesang, *Ph.D. Dissertation* (1987), North Carolina State University, Raleigh, U.S.A.
[23] Z.U. Bae and Y.C. Park, *Bull. Korean Chem. Soc.*, **21**, 749 (2000).