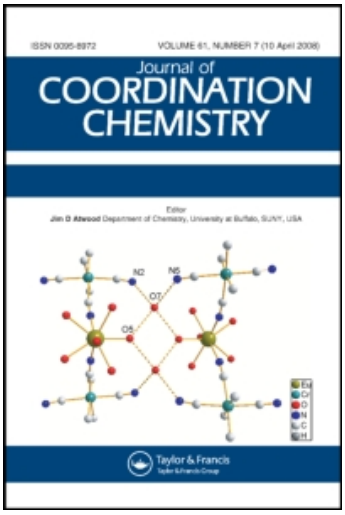

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Synthesis and Reaction of Novel (Tetraaza[14]Annulene)Nickel(II) Complexes with Amino Groups in Their Side Chains

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SYNTHESIS AND REACTION OF NOVEL (TETRAAZA[14]ANNULENE)NICKEL(II) COMPLEXES WITH AMINO GROUPS IN THEIR SIDE CHAINS

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The replacement reaction of a (tetraaza[l4]annulene)nickel(II) (**1**) with 3- and/or 4-nitrobenzoyl chlorides led to the corresponding 7,16-dibenzoylated products (**2m**, **2p**). (7,16-Bis(3-aminobenzoyl)tetraaza[14]annulene)nickel(II) (**3m**) and (7,16-bis(4-aminobenzoyl)tetraaza[14] annulene)nickel(II) (**3p**) were prepared by hydrogenation of the corresponding dinitro-analogues (**2m**, **2p**). The reaction of **3m** with pivaloyl chloride, nicotinoyl chloride hydrochloride and/or isonicotinoyl chloride hydrochloride gave the corresponding amido products (**4**, **5**β, **5**γ). Methylation of pyridine comprised in **5**β using iodomethane afforded the corresponding dimethylated product (**6**β). The strapped tetraaza[14]annulene nickel(II) (**7**β) was synthesized from **5**β and α,α'-dibromo-*m*-xylene. These reactions smoothly proceed on the nickel(II) complexes, but do not occur on the metal-free tetraaza[14]annulenes under these conditions except for the nitrobenzoylation.

Keywords: Nickel(II) complexes; Macrocycles; Acid chlorides; Hydrogenation; Amino groups; NMR spectra

INTRODUCTION

For several years we have been studying the reactivity of the 7,16-positions of a (tetraaza[14]annulene)nickel(II) (**1**) towards a number of electrophilic reagents to introduce various substituent groups in the framework.

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These reactions provide the possibility of modifying complicated compounds used as models for biologically significant macrocycles. Several workers, including ourselves, have described the replacement reaction of **1** with acid chlorides [1] and/or benzyl bromide [2]. In a previous paper, we have presented the diazo coupling reaction between **1** and phenyldiazonium salts [3]. Although substantial effort has been expended on the study of the replacement reaction between **1** and acid chlorides, there is no information on the reaction of the substituents at the 7,16-positions of **1**.

In the present work, we report the syntheses of (7,16-bis(3-aminobenzoyl)-6, 8, 15, 17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecianto) nickel(II) (**3m**) and (7,16-bis(4-aminobenzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecianto)nickel(II) (**3p**) and the reactivities of the amino groups in their side chains towards acid chlorides. Further, we describe the methylation of pyridine included in **5**β and **5**γ and the synthesis of the strapped (tetraaza[14]annulene)nickel(II) (**7**β). Their spectroscopic properties have been investigated by mass, vibrational and NMR spectroscopy.

EXPERIMENTAL

Materials and Physical Measurements

Elemental analyses were determined with a Yanaco CHN Corder MT-3. FAB mass spectra were carried out with a JEOL JMS-SX 102A gas chromatograph-mass spectrometer in a magic bullet matrix employing xenon in the fast atom beams. Infrared spectra in the $400-4000\,cm^{-1}$ region were recorded on a Hitachi 260–30 spectrophotometer at room temperature and KBr disk techniques were used. Electronic spectra covering the $14000-35000\,cm^{-1}$ range were obtained with a Shimadzu UV 200 S double beam spectrophotometer in chloroform and *N*,*N*-dimethylformamide (DMF) at room temperature. ^{1}H NMR spectra were recorded with a JEOL JNM-A500 spectrometer in chloroform-*d* or in dimethyl sulfoxide-d_6 at room temperature and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference. Melting points were observed with a Yanaco MP-500 D micro melting point apparatus. Conductivity measurements were made in DMF kept at $25.0 \pm 0.1°C$ with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics LTD, CM-20E instrument.

(6,8,15,17-Tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (1)

The synthetic method for **1** has been described previously [4].

(7,16-Bis(3-nitrobenzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (2m)

A mixture of **1** (1.02 g, 2.54 mmol), 3-nitrobenzoyl chloride (2.51 g, 13.5 mmol), triethylamine (3.43 g) and dry toluene (200 cm^3) was heated under reflux for 4 h with stirring. After cooling to room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness under reduced pressure. The resulting solid was chromatographed on activated aluminum oxide (200 mesh, Wako Pure Chemical Industries, Ltd.) and eluted with dichlormethane. The second eluted band was collected, evaporated to dryness *in vacuo* and vacuum dried to afford **2m** as fine dark violet crystals; yield 1.77 g (99.3%); mp 263–270°C(dec); IR (KBr): ν C═O 1670, ν C═C and C═N 1605, 1540, 1389, NO_2 1520 sh, 1355 cm^{-1}; MS (FAB): *m*/*z* 699 ($[M+l]^+$). *Anal*. Calcd. for $C_{38}H_{28}N_6O_6Ni$ (%): C, 61.83; H, 4.04; N, 12.02. Found: C, 61.91; H, 4.52; N, 12.12.

(7,16-Bis(4-nitrobenzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (2p)

The synthetic procedure for **2p** has been reported previously [1(k)].

(7,16-Bis(3-aminobenzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (3m)

A 300 cm^3 autoclave was charged with a mixture of **2m** (1.74 g, 2.49 mmol), tetrahydrofuran (THF) (200 cm^3) and 5% palladium carbon (0.197 g, Wako Pure Chemical Industries, Ltd.). The mixture was hydrogenated at 50°C under a hydrogen pressure of 5 kg/cm^2 for 8 h with stirring. The reaction mixture was cooled to room temperature and filtered to remove the catalyst. The filtrate was evaporated to dryness under reduced pressure. The resulting solid was chromatographed on activated aluminum oxide (200 mesh) using chloroform as eluent. The second band was collected and evaporated to dryness *in vacuo*. The powdered residue was reprecipitated with chloroform-hexane to obtain 1.02 g (64.0%) of fine, dark green crystals (**3m**); mp

288–295°C(dec); IR (KBr); ν N—H 3350, ν C═O 1650, ν C═C and C═N 1600, 1535, 1388 cm^{-1}; MS (FAB): m/z 639 ($[M+1]^+$). *Anal.* Calcd. for $C_{36}H_{32}N_6O_4Ni \cdot H_2O$ (%): C, 65.77; H, 5.21; N, 12.78. Found: C, 66.05; H, 5.14; N, 12.78.

(7,16-Bis(4-aminobenzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (3p)

A mixture of **2p** (0.494 g, 707 μmol), THF (100 cm^3) and 5% palladium carbon (0.471 g) was hydrogenated at 50°C under a hydrogen pressure of 40 kg/cm^2 for 4 h with stirring in an autoclave. After standing at room temperature, the catalyst was removed by filtration. The filtrate was evaporated to dryness under reduced pressure. A chloroform solution of the residue was applied on the top of a chromatographic column of activated aluminum oxide (200 mesh). A deeply coloured band was eluted with chloroform, and then with THF. The second fraction (THF as eluent) was collected and evaporated to dryness *in vacuo* to give fine, dark violet crystals (**3p**), yield 0.065 g (15.0%); mp > 300°C; IR (KBr): ν N—H 3400, ν C═O 1640, ν C═C and C═N 1600, 1535, 1390 cm^{-1}; MS (FAB): m/z 639 ($[M+1]^+$). *Anal.* Calcd. for $C_{36}H_{32}N_6O_4Ni \cdot H_2O$ (%): C, 65.77; H, 5.21; N, 12.78. Found: C, 65.88; H, 5.12; N, 12.65.

(7,16-Bis(3-(*N*-pivaloylamino)benzoyl)-6,8,15,17-tetramethyl-dibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (4)

Into a solution of **3m** (0.103 g, 161 μmol) in dichloromethane (20 cm^3) were added pivaloyl chloride (1.0 cm^3) and triethylamine (2 cm^3). The reaction mixture was stirred for 4 h at room temperature while protecting the mixture from moisture. To the reaction mixture was added water (20 cm^3). The organic layer was separated and dried over anhydrous sodium sulfate overnight. The drying agent was removed by filtration and the filtrate evaporated to dryness *in vacuo*. The residue was chromatographed on activated aluminum oxide (200 mesh) using chloroform-ethyl acetate (98 : 2 vol/vol) as eluent. The first effluent was collected and the solvent was removed. The resulting product was dried to yield 0.103 g (79.2%) of fine, dark violet crystals (**4**); mp > 300°C; IR (KBr): ν N—H 3350, ν C—H 2950, ν C═O 1670, 1650, ν C═C and C═N 1590, 1530, 1385 cm^{-1}; MS (FAB): m/z 807 ($[M+1]^+$). *Anal.* Calcd. for $C_{46}H_{48}N_6O_4Ni \cdot 0.5H_2O$ (%): C, 67.66; H, 6.05: N, 10.29. Found: C, 67.77; H, 6.07; N, 10.27.

(7,16-Bis(3-(*N*-nicotinoylamino)benzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (5*β*)

A mixture of **3m** (0.202 g, 317 μmol) and nicotinoyl chloride hydrochloride (1.91 g, 10.7 mmol) was dissolved in dry THF (40 cm^3) containing triethylamine (6.20 g) and heated under reflux for 8 h with stirring and protection from moisture. The reaction mixture was cooled to room temperature and filtered to remove triethylamine hydrochloride. The filtrate was freed of solvent under reduced pressure and the residue reprecipitated with THF-water. The resulting solid was filtered off and chromatographed on activated aluminum oxide (200 mesh) and successively eluted with chloroform, THF and THF-ethanol (95 : 5 vol/vol). The third fraction (THF-ethanol as eluent) was collected and evaporated to dryness under diminished pressure. The residue was reprecipitated with THF-hexane to afford 0.180 g (66.8%) of fine, green crystals (**5***β*); mp > 300°C; IR (KBr): ν N—H 3400, ν C=O 1675, 1650, ν C=C and C=N 1595, 1530, 1350 cm^{-1}; MS (FAB): *m*/*z* 849 ($[M+l]^+$). *Anal.* Calcd. for $C_{48}H_{38}N_6O_4Ni \cdot H_2O$ (%): C, 66.45; H, 4.65; N, 12.92. Found: C, 66.59; H, 4.79; N, 12.94.

(7,16-Bis(3-(*N*-isonicotinoylamino)benzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (5*γ*)

This was prepared from **3m** (0.120 g, 188 μmol), isonicotinoyl chloride hydrochloride (1.00 g, 5.62 mmol) and triethylamine (3.01 g) in refluxing dry THF (20 cm^3) for 8 h. Following the above procedure, the product was isolated by column chromatography on activated aluminum oxide (200 mesh) to give 0.099 g (62.0%) of fine, green crystals (**5***γ*); mp > 300°C; IR (KBr): ν N—H 3400, ν C=O 1680, 1655, ν C=C and C=N 1600, 1540, 1385 cm^{-1}; MS (FAB): *m*/*z* 849 ($[M+l]^+$). *Anal.* Calcd. for $C_{48}H_{38}N_8O_4Ni \cdot H_2O$ (%): C, 66.45; H, 4.65; N, 12.92. Found: C, 66.64; H. 4.84; N, 12.97.

(7,16-Bis(3-(*N*-(*N*-methylnicotinoylamino)benzoyl)-6,8,15,17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)-nickel(II) diiodide (6*β*)

Iodomethane (2.0 cm^3) and **5***β* (0.023 g, 72 μmol) were dissolved in dichlormethane (40 cm^3), and the reaction solution was stirred at room temperature for 3 days in the dark. The deposited crystalline solid was filtered off and washed with dichloromethane until the washings were no

longer coloured. The product was dried to give 0.016 g (48.0%) of fine, deep green crystals (**6**β); mp > 300°C; IR (KBr): ν C—H 3050, ν C=O 1680, 1650, ν C=C and C=N 1600, 1530, 1388 cm^{-1}; MS (FAB): m/z 879 ($[M+l]^+$). *Anal*. Calcd. for $C_{50}H_{44}I_2N_8O_4Ni \cdot H_2O$ (%): C, 52.01; H, 4.11; N, 9.70. Found: C, 52.63; H, 3.90; N, 9.39.

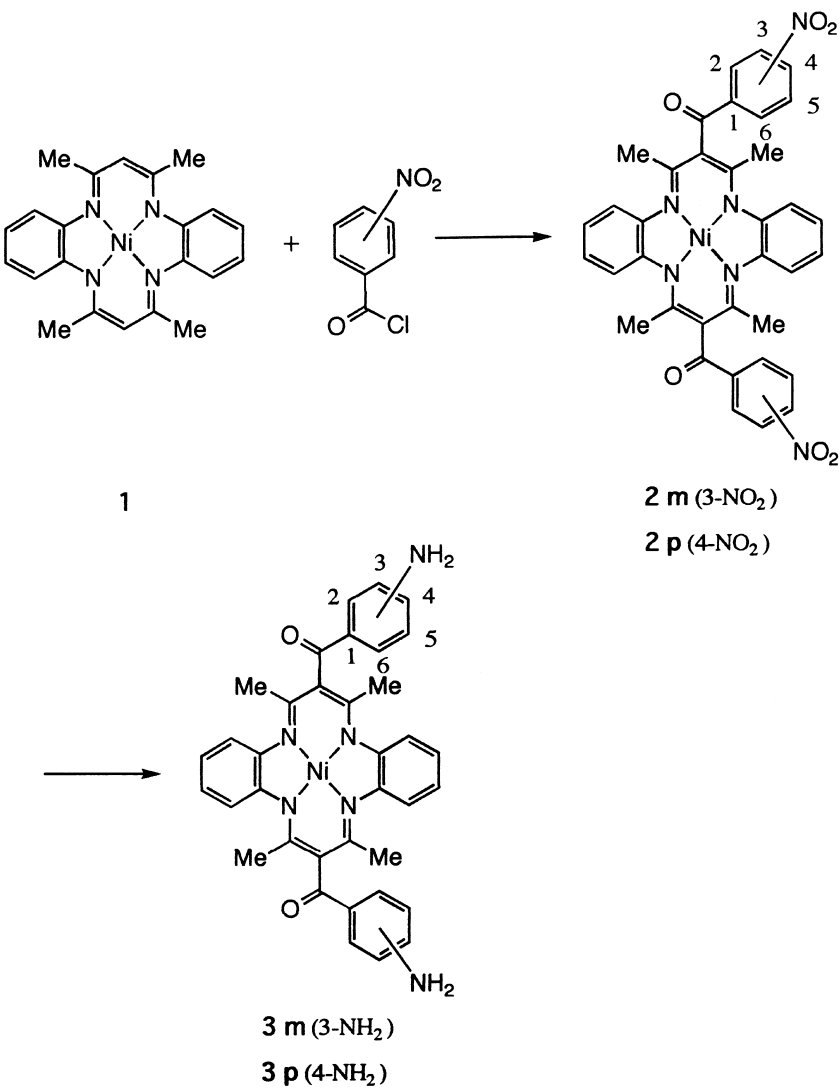
(7,16-(3,3′-(*N*,*N*′-(*m*-xylene-α,α′-diryl)dinicotinoyl)diamino)dibenzoylo-6,8,15,17-tetramethyldibenzo[*b*, *i*][1,4,8,11]tetraazacyclotetradecinato)-nickel(II) dihexafluorophosphate (7β)

α,α′-Dibromo-*m*-xylene (0.022 g, 83 μmol) and **5**β (0.073 g, 86 μmol) were dissolved in 1,4-dioxane (20 cm^3). The reaction solution was heated at 80°C for 2 days with stirring and protection from moisture. After being allowed to stand at room temperature, the precipitate was separated by filtration and washed with dichloromethane. The resulting solid was dissolved in dimethyl sulfoxide (10 cm^3) and the slight amount of the insoluble material was removed by filtration. To the filtrate was added a solution of potassium hexafluorophosphate (0.53 g) in a mixed solvent composed of dimethyl sulfoxide (10 cm^3) and water (10 cm^3). The reaction mixture was stirred at room temperature for 20 min. The crystalline product was isolated by filtration to yield 0.064 g (60.0%) of **7**β as fine, dark green crystals; mp > 300°C; IR (KBr): ν C=O 1680, 1640, ν C=C and C=N 1595, 1535, 1390 cm^{-1}. *Anal* calcd. for $C_{56}H_{46}N_8O_4P_2F_{12}Ni \cdot H_2O$(%): C, 53.32; H, 3.68; N, 8.88. Found: C, 52.96; H, 3.39; N, 8.56.

RESULTS AND DISCUSSION

Preparation of Nitrobenzoylated Nickel(II) (2m, 2p) and Reduction of their Nitro Groups

The replacement reaction between **1** and *meta*- or *para*-nitrobenzoyl chlorides in a 1 : 5.3 mol ratio and in the presence of triethylamine was undertaken in refluxing toluene to give the corresponding 7,16-dinitrobenzoylated products (**2m**, **2p**) in very high yields. The synthesis of **2m** and **2p** is illustrated in Scheme 1. This reaction is scarcely associated with the positions of the nitro groups. FAB mass spectra of **2m** and **2p** reveal molecular ions $[M+1]^+$ at m/z 699. This parent peak suggests the 7,16-dinitrobenzoylated products (**2m**, **2p**). In the IR spectra **2m** and **2p** show very strong bands in the range 1660 – 1670 cm^{-1} correlated with the C=O



SCHEME 1

stretching modes upon benzoylation, [1(k), 6] and exhibit strong bands at about 1520 and 1350 cm^{-1} due to the NO_2 stretching mode [1(k), 6]. ^1H NMR data and their assignments of **2m** and **2p** are listed in Table I. The signals for the olefinic protons at the 7- and 16-positions vanish upon benzoylation at these positions. These results support the formation of **2m** and **2p**.

TABLE I ^{1}H NMR data for (tetraaza[14]annulene)nickel(II) complexes with nitro or amino groups[a]

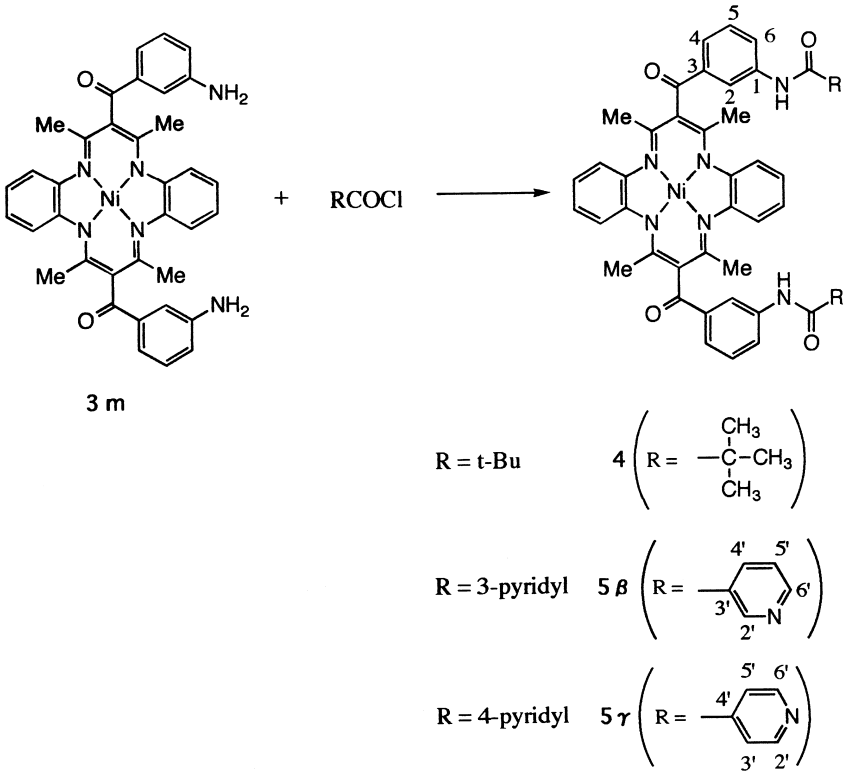
Complex	*Methyl* $-CH_3$	*Macrocycle* (*Aromatic*)	*Benzoyl group* 2-*H*	3-*H*	4-*H*	5-*H*	6-*H*	NH_2
2m	1.93(s)	6.67(m)	9.06(s)		8.65(d) $J = 7.9$ Hz	7.85(t) $J = 7.9$ Hz	8.50(d) $J = 7.9$ Hz	
2p	1.91(s)	6.66(s)	8.39(s)	8.39(s)		8.39(s)	8.39(s)	
3m	1.92(s)	6.68(m)	7.51(s)		6.93(d) $J = 7.8$ Hz	7.35(t) $J = 7.8$ Hz	7.62(d) $J = 7.8$ Hz	3.94(s)
3p	1.84(s)	6.68(m)	7.77(d) $J = 8.2$ Hz	6.68(d) $J = 8.2$ Hz		6.68(d) $J = 8.2$ Hz	7.77(d) $J = 8.2$ Hz	5.94(s)

[a] Chemical shifts in ppm from internal TMS; measured in chloroform-*d* at room temperature; multiplicity of a proton signal is given in parentheses after the δ-value; s = singlet, d = doublet, t = triplet, m = multiplet.

Products **3m** and **3p** with amino groups are prepared from **2m** and **2p** with dinitro groups by hydrogenation over palladium-carbon [5]. The reactivity of **2p** is poorer than that of **2m** since the reaction for the former only occurs under more severe conditions. It is thought that the extension of the conjugated system for **2p** is larger than that for **2m**. Product **3m** is very soluble in alcoholic solvents but is not very soluble in the benzene series. Purification of **3m** is achieved by column chromatography on activated aluminum oxide employing chloroform as eluent. However, the solubility of **3p** is very poor in organic solvents, so that the technique of isolation, separation and purification is a matter of immediate importance. The syntheses of **3m** and **3p** are shown in Scheme 1. The metal-free compounds do not proceed in the reduction reaction of the nitro groups under the hydrogenation condition but cause the reduction of the 2,4-pentanediiminate rings. It thus appears that the coordinated nickel(II) ion in **2m** and **2p** protects the 2,4-pentanediiminate rings. In the IR spectra **3m** and **3p** exhibit broad medium bands in the region $3300-3500\,cm^{-1}$, concerned with N—H stretching modes on reduction of nitro groups in **2m** and **2p** [6]. FAB mass spectra of **3m** and **3p** indicate molecular ions $[M+1]^+$ at m/z 639, which suggest the corresponding amino products. ^1H NMR data and their assignments of **3m** and **3p** are collected in Table I. The signals for the amino protons in the benzoyl groups appear at the range 3.94 – 5.95 ppm upon hydrogenation of the nitro groups in **2m** and **2p** [6]. The structures of **3m** and **3p** were confirmed with the above data.

Preparation of Nickel(II) Complexes (4, 5β, 5γ) Containing Amido Groups

The synthesis of **4**, **5**β and **5**γ is depicted in Scheme 2; **3m** gave product **4** in an excellent yield within 4 h at room temperature when treated with pivaloyl chloride. In addition, **3m** led to **5**β or **5**γ in good yield under refluxing conditions when reacted with nicotinyl chloride hydrochloride or isonicotinyl chloride hydrochloride. These results indicate that the reactivity of aliphatic acid chlorides is much greater than that of aromatic acid chlorides. On the other hand, the reaction between **3p** and acid chlorides was not carried out since **3p** is too insoluble in organic solvents to react with acid chlorides. FAB mass spectra of **4**, **5**β and **5**γ show molecular ions $[M+1]^+$ at m/z 807 and 849, respectively. These parent peaks substantiate the corresponding amide products. In IR spectra **4**, **5**β and **5**γ reveal very strong bands in the area $1650-1680\,cm^{-1}$, associated with C=O stretching modes upon amidation [7], and exhibit broad medium bands in the



SCHEME 2

3350 – 3400 cm^{-1} range due to N—H stretching modes in the amide groups [7]. ^1H NMR data and their assignments are compiled in Table II. The signal for the amino protons in the benzoyl groups disappear on amidation, and signals for the amide protons appear at 7.97, 10.72 and 10.77 ppm, respectively. Furthermore, aromatic and aliphatic proton signals appear at 1.41 ppm and in the region 7.91 – 9.17 ppm, respectively. These data attest to the expected products.

N-Methylation of 5β and 5γ

N-Methylation of **5**β is shown in Scheme 3. *N*-Methylation of pyridine comprised in the substituents using iodomethane in l,2-dichloroethane afforded the corresponding dimethylated products (**6**β) for **5**β. The product is soluble in polar solvents such as methanol and acetone. On the other

TABLE II ^{1}H NMR data for (tetraaza[14]annulene)nickel(II) complexes with amide groups[a]

			Benzoyl group					*Pyridine*					
Complex	*Methyl* —CH_3	*Aromatic* (*Macrocycle*)	2-*H*	4-*H*	5-*H*	6-*H*	*Amide* N—*H*	2′-*H*	3′-*H*	4′-*H*	5′-*H*	6′-*H*	*t-Butyl* —CH_3
4	1.91(s)	6.63(m)	7.68(s)	8.02(d) $J = 7.9$ Hz	7.57(t) $J = 7.9$ Hz	8.22(d) $J = 7.9$ Hz	7.97(s)						1.41(s)
5β	1.88(s)	6.67(m)	8.41(s)	7.88(d) $J = 7.9$ Hz	7.62(t) $J = 7.9$ Hz	7.89(d) $J = 7.9$ Hz	10.72(s)	9.17(s)		8.34(d) $J = 7.9$ Hz	8.27(dd) $J = 7.9$ Hz $J = 1.6$ Hz	8.41(s)	
5γ	1.88(s)	6.76(m)	8.41(s)	7.88(d) $J = 7.9$ Hz	7.61(t) $J = 7.9$ Hz	8.19(d) $J = 7.9$ Hz	10.77(s)	7.91(dd) $J = 7.9$ Hz $J = 1.6$ Hz	8.82(dd) $J = 7.9$ Hz $J = 1.6$ Hz	8.82(dd) $J = 7.9$ Hz $J = 1.6$ Hz	7.91(dd) $J = 7.9$ Hz $J = 1.6$ Hz		

[a] Chemical shifts in ppm from internal TMS; measured in chloroform-*d* for **4** and in dimethyl sulfoxide-d_6 for **5**β and **5**γ at room temperature; multiplicity of a proton signal is given in parentheses after the δ-value; s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.

hand, *N*-methylation of **5**γ with iodomethane or dimethyl sulfate did not proceed and recover the starting material alone. Moreover, reaction of **5**γ with methyl trifluoromethanesulfonate (a strong methylation reagent) did not lead to the anticipated product and caused cleavage of **5**γ, which is not identified by spectroscopy. This seems to indicate that the difference in the chemical reactivity is associated with electronic effects. That is to say, the *N*-positions of **5**β are the *meta*-positions, but those of **5**γ are the *para*-positions. Consequently, it can therefore be presumed that the electron density for *N*-positions of **5**γ is poorer due to the electron withdrawing effect of the *para*-amido carbonyl groups. FAB mass spectra of **6**β exhibit a molecular ion $[M+1]^+$ at m/z 879, which supports the corresponding dimethylated product. IR spectra of **6**β do not show remarkably distinct bands compared with **5**β. This is due to the absence of newly IR active groups in **6**β. In the electronic spectra, the general features of **6**β are very similar to those of **5**β. These are hardly influenced by methylation of the pyridine rings. Thus the delocalization of the more highly conjugated system remains nearly unaltered upon *N*-methylation of the substituent groups in the complex [8]. ^{1}H NMR data for these complexes and their assignments are summarized in Table III. The signal for the methyl group in the pyridine ring appears at 4.47 ppm as a singlet. These results support the expected structure of **6**β.

Synthesis of Strapped Nickel(II) (7β)

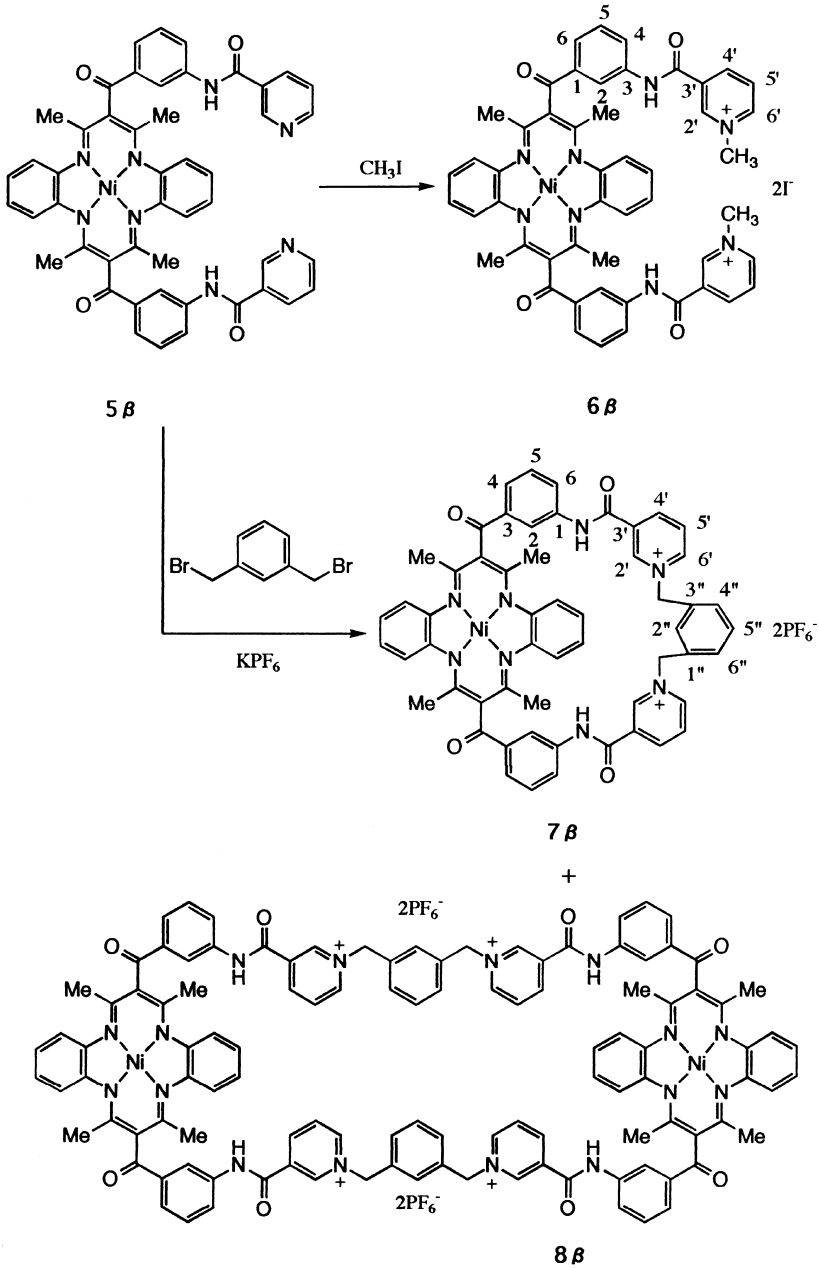
The synthesis of **7**β is shown in Scheme 3. Benzylation of pyridine implicit in the substituent groups utilizing α,α'-dibromo-*m*-xylene in 1,2-dichloroethane provided the corresponding strapped complex (**7**β). The product was isolated from the reaction mixture by anion exchange. ^{1}H NMR data and assignments for **7**β are listed in Table III. The aliphatic proton signal for benzylation of the pyridine ring appears at 6.00 ppm as a singlet and the aromatic proton signals emerge in the 7.56 – 7.93 ppm range as a multiplet. NMR data support the possibility of the formation of two products as shown in Scheme 3 since the FAB mass spectra do not reveal the presence of a molecular ion $[M+1]^+$. The molar conductance of the product is consistent with a 1 : 2 electrolyte in DMF (see Tab. IV) [9]. The results substantiate the anticipated structure of **7**β.

Consequently, these reactions except for the nitrobenzoylation, do not proceed on the metal-free macrocycle but do so on the nickel(II) complexes without difficulty.

TABLE III ^{1}H NMR data for (tetraaza[14]annulene)nickel(II) complexes with *N*-alkylpyridinium salts[a]

			Benzoyl					*Pyridine*						*m-Xylene*
Complex	*Methyl* —CH_3	*Aromatic* (*Macrocycle*)	2-*H*	4-*H*	5-*H*	6-*H*	*Amide* N—*H*	2′-*H*	4′-*H*	5′-*H*	6′-*H*	N—CH_3	*Benzyl* —CH_2—	*Aromatic* 2-*H″*, 4-*H″*, 5-*H″*, 6-*H″*
6β	1.89(s)	6.77(m)	8.36(s)	8.17(d) $J=7.9$ Hz	7.70(t) $J=7.9$ Hz	7.92(d) $J=7.9$ Hz	11.07(s)	9.55(s)	9.09(d) $J=8.1$ Hz	8.33(dd) $J=8.1$ Hz $J=6.1$ Hz	9.16(d) $J=6.1$ Hz	4.47(s)		
7β	1.88(s)	6.76(m)	8.35(s)	8.15(d) $J=5.8$ Hz	7.68(t) $J=5.8$ Hz	7.93(d) $J=5.8$ Hz	11.11(s)	9.71(s)	9.16(d) $J=5.8$ Hz	8.39(t) $J=5.8$ Hz	9.28(d) $J=5.8$ Hz		6.00(s)	7.56–7.93(m)

[a] Measured in dimethyl sulfoxide-d_6; multiplicity of a proton signal is given in parentheses after the δ-value; s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.



SCHEME 3

TABLE IV Molar conductance for the new (tetraaza[14]annulene)nickel(II) complexes at 25°C[a]

Complex	$\Lambda_M S$ ($cm^2 mol^{-1}$)	*Type of electrolyte* [b]
6β	131	1:2
7β	140	1:2

[a] Measured in DMF; *ca* 10^{-3} mol dm^{-3} solutions.
[b] Assignment of the type of electrolyte present in solution was made on the basis of the conductance data compiled by Geary [9].

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