Synthesis and Spectroscopic Properties for Six 7,16-Dibenzoylated Tetraaza[14]annulene Nickel(II) Complexes

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The condensation reaction between tetraaza[14]annulene nickel(II) complex and a series of *para*-substituted benzoyl chlorides gave the corresponding 7,16-dibenzoylated products in 53-98% yields. The mass spectra exhibit molecular ion peaks ascribed to the 7,16-dibenzoylated products. The intense ir band due to the C=O stretching mode in these nickel(II) complexes is present in the 1650-1658 cm^{-1} range upon the benzoylation. Even though the ligand moiety of these six complexes is changed by benzoylation, the electronic spectra hardly vary. These nickel(II) complexes assume roughly the square-planar coordinations as judged by the ligand-field transition bands. The olefinic proton peaks at the 7- and 16-positions vanish on benzoylation in the proton nmr spectra and the proton signals of the *para*-substituted benzoyl groups are observed in the 2.4-8.4 ppm region. The results of the carbon-13 nmr spectra are compatible with those for the proton nmr spectra.

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Introduction.

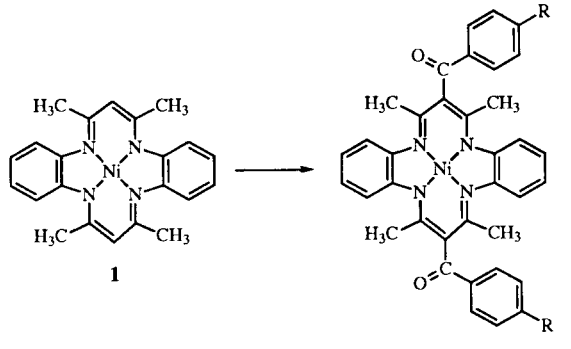
In order to make a further exploration into the reactivity for the 7,16-positions of tetraaza[14]annulene nickel(II) complex (**1**), six kinds of *para*-substituted benzoyl chlorides are allowed to react with complex **1** in this work. In previous papers, we have reported the reaction of complex **1** with 3,3'-(octamethylenedioxy)dibenzoyl chloride [1a] and/or with 3,3'-(2,6-pyridyldimethyleneoxy)dibenzoyl chloride [1b] and the reaction of **1** and its copper(II) analogue with nicotinoyl and/or isonicotinoyl chloride hydrochloride [2]. Eilmes *et al.* published the reaction of tetraaza[14]annulene nickel(II) complexes with benzoyl chloride, *p*-nitrobenzoyl chloride, acetyl chloride, glutaryl chloride and pimelic acid dichloride [3]. Dzugan and Busch reported the reaction of complex **1** with perfluorobenzoyl chloride and trifluoroacetic anhydride and the characterization of the reaction products [4]. Through these studies, the 7,16-positions of tetraaza[14]annulene nickel(II) complexes are known to be reactive nucleophilic centers [5]. Although Eilmes *et al.* carried out nmr studies on the products formed from complex **1**, their information is rather limited due to non-systematic utilization of reaction reagents with respect to substituent groups. The present study provides thorough information on the reactivity of the 7,16-positions of complex **1**, and the spectroscopic properties of the reaction products.

Results and Discussion.

Benzoylation of the Tetraaza[14]annulene Nickel(II) Complex.

The condensation reaction between complex **1** and six benzoyl chlorides in a 1:5 molar ratio in the presence of triethylamine was performed in refluxing toluene to give the corresponding 7,16-dibenzoylated products **2-7** in 53-98% yields. A 1:2 molar ratio of these reagents produced a mixture of approximately equal quantities of the 7-monobenzoylated and the 7,16-dibenzoylated products. Purification of the crude product was achieved by column chromatography on activated aluminium oxide. The synthesis of complexes **2-7** is illustrated in Scheme 1. Complex **1** gave product **6** or **7** in excellent yield within one hour when treated with *p*-chlorobenzoyl chloride or *p*-nitrobenzoyl chloride, respectively. On the other hand, product **3** or **4** was obtained in about 50% yield in four hours or longer, when **1** was allowed to react with *p*-methylbenzoyl chloride or *p*-methoxybenzoyl chloride, respectively. Thus, reaction between complex **1** and the benzoyl chloride containing a *p*-substituted electron withdrawing group gave the product in a much better yield than that with the *p*-substituted electron donating group. These results imply that the reaction is susceptible to an electronic effect of the *para*-substituent. Also the results indicate that the olefinic carbons at the 7- and 16-positions

Scheme 1



1

2: R = H
3: R = CH_3
4: R = OCH_3
5: R = OCH_2–C6H5
6: R = Cl
7: R = NO_2

in complex **1** undergo an electrophilic substitution reaction like the olefinic carbon at the 3-position in the chelate ring of 2,4-pentanedione metal complexes [6]. The analytical data for complexes **2-7** are listed in Table 1.

Table 1

Analytical Data for the Tetraaza[14]annulene Nickel(II) Complexes

Complex	Empirical Formula	Elemental Analyses Calcd./Found % C	H	N
2	$C_{36}H_{30}N_4O_2Ni$	70.96	4.96	9.19
		71.17	5.05	9.17
3	$C_{38}H_{34}N_4O_2Ni$	71.60	5.38	8.79
		71.69	5.39	8.71
4	$C_{38}H_{34}N_4O_4Ni$	68.18	5.12	8.37
		67.95	5.00	8.12
5	$C_{50}H_{42}N_4O_4Ni$	73.09	5.15	6.82
		72.82	5.21	6.52
6	$C_{36}H_{28}N_4O_2Cl_2Ni$	63.75	4.16	8.26
		63.46	4.25	8.00
7	$C_{36}H_{28}N_6O_6Ni$	61.83	4.04	12.02
		61.66	4.15	11.98

Mass Spectra.

The EI mass spectra for complexes **2-7** show the presence of a molecular ion M^+ at m/z 608, 636, 668, 820, 676 (^{35}Cl) and 698, respectively, as given in the Experimental. These parent peaks support the 7,16-dibenzoylated products. The mass of the major fragment at m/z 400 for all products corresponds to $[M\text{-}2RC_6H_4CO\text{+}2H]^+$ and the fragment peaks at m/z 504, 518, 534, 610, 538 (^{35}Cl) and 549, respectively, also correspond to $[M\text{-}RC_6H_4CO\text{+}H]^+$.

Infrared Spectra.

The characteristic ir absorption bands are summarized in the Experimental. Complexes **2-7** exhibit very intense bands in the 1650-1658 cm^{-1} region which are associated with the C=O stretching modes upon the benzoylation [2]. A shift of the C=O stretching mode is scarcely observed with changing the *para*-substituent of the benzoyl group. This indicates that the electronic effect of the *para*-substituent in the benzoyl group does not influence the C=O stretching mode. Moreover, complex **7** exhibits strong bands at 1520 and 1350 cm^{-1} which correlate with the NO_2 stretching mode [7].

Visible and Ultraviolet Spectra.

The visible and ultraviolet spectra covering the 12500-40000 cm^{-1} region are shown in Figure 1 for complexes **1** and **2**. The general spectral features for complexes **2-7** are similar to one another and to that for the complex **1** which is not benzoylated. This seems to indicate that the delocalization of the conjugated system in the nickel(II) complexes **1-7** is approximately analogous to each other and that the electronic interaction between the tetraaza[14]-annulene chelate ring and the benzoylated group is hardly formed. The absorption bands appearing at energy greater than 23000 cm^{-1} can be attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand, because the molar extinction coefficients of the bands are much larger in magnitude than those normally assigned to ligand-field transitions [8]. The weak absorption bands in the 16700-17000 cm^{-1} range can be attributed to ligand-field transitions [8]. This spectral behavior is compatible with that observed for the square-planar coordination of nickel(II) complexes [8]. The CT, $\pi \rightarrow \pi^*$ and ligand-field transitions for the complexes **1-7** are compiled in Table 2.

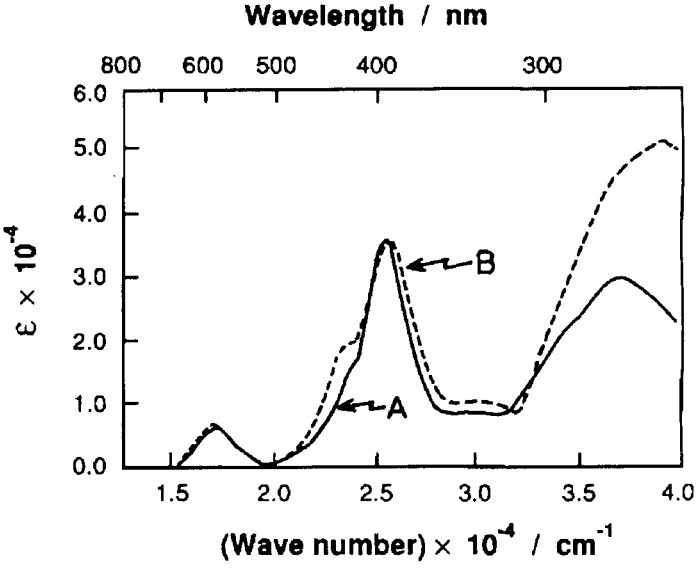


Figure 1. Electronic spectra for the tetraaza[14]annulene nickel(II) complexes at room temperature in chloroform; **A**, **1**; **B**, **2**.

Table 2

Electronic Absorption Bands for the Tetraaza[14]annulene Nickel(II) Complexes [a]

Complex	Transition Energy in cm^{-1} (ε)
1	17000 (6300), 23300 sh (13000), 25500 (36000), 30700 (8640), 35700 sh (21100)
2	16900 (6800), 23300 sh (18400), 25600 (35700), 29900 (10500), 37900 sh (48900)
3	16900 (7160), 23400 sh (16500), 25600 (36200), 29900 (9790), 37300 (63900)
4	16900 (6160), 23300 sh (15600), 25500 (27900), 30300 sh (10800), 35300 (42900)
5	16700 (6480), 23300 sh (16000), 25500 (33200), 30500 sh (10600), 35100 (66200)
6	17000 (6370), 23500 sh (16900), 25600 (33000), 29900 (8580), 37600 (60000)
7	16800 (6200), 23700 sh (13200), 25700 (27500), 30500 sh (14300), 37000 (53200)

[a] Measured in chloroform at room temperature.

Table 3

Proton NMR Data for the Tetraaza[14]annulene Nickel(II) Complexes [a]

Complex	Methyl 6,8,15,17-CH_3	Olefinic 7,16-H	Aromatic (Macrocyclic)	Aromatic	Methyl *p*-CH_3	Methoxy *p*-OCH_3	Methylene *p*-OCH_2-
1	2.07 (s)	4.85 (s)	6.61 (s)				
2	1.92 (s)		6.62 (s)	7.41-8.33 (m)			
3	1.91 (s)		6.61 (s)	7.36 (d, J = 8.1 Hz) 8.14 (d, J = 8.1 Hz)	2.47 (s)		
4	1.92 (s)		6.61 (s)	7.05 (d, J = 8.9 Hz) 8.23 (d, J = 8.9 Hz)		3.93 (s)	
5	1.91 (s)		6.60 (s)	7.12 (d, J = 8.8 Hz) 8.22 (d, J = 8.8 Hz) 7.42 (s)			5.18 (s)
6	1.90 (s)		6.62 (s)	7.54 (d, J = 8.4 Hz) 8.18 (d, J = 8.4 Hz)			
7	1.91 (s)		6.66 (s)	8.39 (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 δ-value; s = singlet, d = doublet, m = multiplet.

Table 4

Carbon-13 NMR Data for the Tetraaza[14]annulene Nickel(II) Complexes [a]

Complex	-CH_3	C(7) C(16)	C(1) C(4) C(10) C(13)	C(2) C(3) C(11) C(12)	C(19) C(20) C(21) C(22)	C(6) C(8) C(15) C(17)	C(3') C(5')	C(2') C(6')	C(4')	C(1')	C=O	R -CH_3	-OCH_3	-CH_2-	-Ph
1	22.0	110.9	120.5	121.5	146.9	155.0									
2	20.5	121.3	121.9	122.8	147.4	153.9	129.1	129.8	133.5	139.3	200.3				
3	20.5	121.5	121.9	122.7	147.5	153.7	129.7	130.0	144.4	136.8	200.0	21.9			
4	20.4	121.5	121.9	122.7	147.5	153.6	114.3	132.2	164.0	132.3	199.0		55.7		
5	20.4	121.4	121.8	122.6	147.5	153.6	115.1	132.4	163.1	132.1	198.9			70.4	127.5 128.8 128.3 136.3
6	20.5	120.8	121.9	122.9	147.3	153.9	129.4	131.2	140.0	137.7	199.0				
7	20.8	121.1	122.1	123.4	147.2	154.4	124.4	130.7	154.8	144.2	197.0				

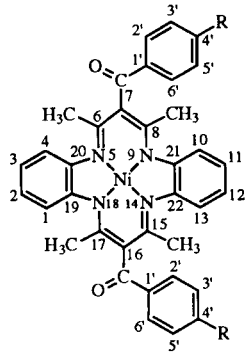
[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d at room temperature.

NMR Spectra.

Nickel(II) complexes **2-7** gave well-resolved proton nmr spectra owing to the diamagnetism. The chemical shift assignments were accomplished on the basis of comparisons with complex **1** [9]. The proton nmr data and their assignments for complexes **1-7** are collected in Table 3. The signals for the olefinic protons at the 7- and 16-positions disappear on benzoylation at these positions. The methyl proton signals at the 6,8,15,17-positions exhibit upfield shifts by 0.15-0.17 ppm on the benzoylation. This indicates that the methyl groups are within the shielding zone caused by the magnetic anisotropy of the benzene ring of the benzoyl group. The aromatic proton signals of the macrocyclic skeleton in complexes **2-7** do not shift upon the benzoylation since the aromatic protons are not within the shielding zone of the substituted benzene rings. In the *para*-substituted benzoyl group, the protons *ortho* to the carbonyl group are chemically equivalent to each other and the protons *ortho* to the R group are also chemically equivalent to each other. The spectrum of the benzoyl group represents a nearly first-order A_2B_2 system. Hence, each proton except for the complex **7** is represented by a doublet. The aromatic proton peak of the benzoyl groups in complex **7** is a singlet, since the electron withdrawing effect of the nitro group is nearly equal to that of the carbonyl group.

Carbon-13 nmr data and their assignments for complexes **1-7** are listed in Table 4. All carbon peaks are singlets. All methyl carbon peaks of **2-7** show upfield shifts resulting from the shielding effect produced by the magnetic anisotropy of the substituted benzene ring. The signals of the aromatic carbons at the 6-, 8-, 15- and 17-positions bonded to the methyl carbons also show a slight upfield shift upon the benzoylation. On the other hand, the aromatic carbon peaks at the 2-, 3-, 11-, 12-, 1-, 4-, 10-, 13-, 19-, 20-, 21- and 22-positions show slight downfield shifts. The carbon signals at the 7- and 16-positions

show downfield shifts by *ca.* 10 ppm upon the benzoylation. This supports that complex **1** is benzoylated at the 7- and 16-positions. New carbon peaks for the benzoyl groups are observed in the 21-201 ppm range.



EXPERIMENTAL

The EI mass spectra for tetraaza[14]annulene nickel(II) complexes **2**-**7** were determined with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer at 70 eV using a direct inlet system. The infrared spectra in the area of the 400-4000 cm^{-1} were obtained on a Hitachi 260-30 spectrophotometer at room temperature with potassium bromide disks. The ultraviolet and visible spectra covering the 12500-40000 cm^{-1} range were taken on a Shimadzu UV 200S double beam spectrophotometer for chloroform solutions at room temperature. All melting points were performed with a Yanaco MP-500D micro melting point apparatus (hot-plate type). Elemental analyses were measured with a Yanaco CHN corder MT3. Proton and carbon-13 nmr spectra were recorded on a JEOL JNM-FX 60 spectrometer in chloroform-d and dimethyl sulfoxide-d_6 at room temperature and the chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard.

Preparation of Tetraaza[14]annulene Nickel(II) Complexes. (6,8,15,17-Tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (**1**).

The synthetic procedure for complex **1** has been reported [9].

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

The method of Eilmes was modified for the preparation of this complex [3c]. A solution of complex **1** (2.01 g) and benzoyl chloride (3.55 g) in dry toluene (600 ml) containing triethylamine (6.09 g) was heated under reflux for twenty hours with stirring while protecting the mixture from moisture. After being allowed to stand at room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness under reduced pressure. The resulting solid was chromatographed on activated aluminium oxide (200 mesh, Wako Pure Chemical Industries, Ltd.) and eluted with dichloromethane. The third effluent was collected, evaporated to dryness *in vacuo* and vacuum dried to obtain **2** as fine dark violet crystals. The yield was 3.55 g (82%), mp 354.0-355.6° dec; ir: ν C=O 1655, ν C=C and C=N 1578, 1525, 1370 cm^{-1}; ms: m/z (relative intensity) 610 (44.2), 609 (42.0), 608 (93.5), 538 (10.8), 504 (13.3), 400 (25.0).

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

This was prepared from complex **1** (2.01 g), *p*-methylbenzoyl chloride (3.87 g) and triethylamine (6.07 g) in refluxing dry toluene (600 ml) for four hours, following the above procedure. The product was chromatographed on activated aluminium oxide using dichloromethane as an eluent to give 2.46 g (77%) of fine dark violet crystals **3**, mp 328.7-329.8° dec; ir: ν C=O 1655, ν C=C and C=N 1600, 1530, 1375 cm^{-1}; ms: m/z (relative intensity) 638 (3.8), 637 (3.9), 636 (8.2), 520 (24.5), 519 (21.8), 518 (54.0), 402 (42.5), 401 (28.1), 400 (100).

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

p-Methoxybenzoyl chloride (4.27 g) and complex **1** (2.01 g) were reacted in dry toluene (600 ml) containing triethylamine (6.07 g) for eight hours as described above to yield 1.75 g (52%) of **4** as fine dark violet crystals, mp 311.5-313.0° dec; ir: ν C=O 1650, ν C=C and C=N 1601, 1535, 1382 cm^{-1}; ms: m/z (relative intensity) 670 (16.4), 669 (15.5), 668 (33.2), 536 (5.2), 535 (5.1), 534 (11.9), 402 (5.7), 400 (13.6).

p-Benzyloxybenzoic Acid.

Into a solution of sodium hydroxide (4.08 g) in water (250 ml) were added *p*-hydroxybenzoic acid (6.91 g) and benzyl bromide (8.56 g). The reaction solution was kept under reflux with stirring for ten hours. Upon cooling the solution in a refrigerator overnight, sodium bromide and unreacted compounds which separated were filtered. The precipitate obtained by the addition of hydrochloric acid was recovered by filtration, washed repeatedly with water and dried *in vacuo* for one day to afford 5.35 g (47%) of white powder, mp 165.7-166.6° dec; ir: ν OH 2900 (br), ν C=O 1670, ν C-O 1255, 1020 cm^{-1}; ms: m/z (relative intensity) 229 (2.4), 228 (16.4), 138 (2.8), 92 (8.8), 91 (100); ^{1}H-nmr (dimethyl sulfoxide-d_6): 5.18 (s, 2H, O-CH_2-), 7.42 (m, 9H, aromatic), 12.60 ppm (s, 1H, COOH).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.53; H, 5.37.

p-Benzyloxybenzoyl Chloride.

A mixture of *p*-benzyloxybenzoic acid (3.42 g) and thionyl chloride (15 ml) was hold under reflux with stirring for five hours. After removal of the unreacted thionyl chloride benzene (5 ml) was added and the solvent was removed *in vacuo*. The oily residue was permitted to stand overnight at room temperature under an argon atmosphere to give 3.62 g of white powder (98%), mp 93.4-97.8° dec; ir: ν C=O 1770, 1740, ν C-O 1260, 1050 cm^{-1}; ms: m/z (relative intensity) 248 (34.2), 247 (16.6), 246 (100), 211 (62.8), 106 (13.9), 91 (100); ^{1}H-nmr (chloroform-d): 5.15 (s, 2H, O-CH_2-), 7.39 (m, 9H, aromatic).

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: C, 68.16; H, 4.49. Found: C, 68.46; H, 4.64.

(7,16-Bis(*p*-benzyloxobenzoyl)-6,8,15,17-tetramethyldibenzo-[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (**5**).

This complex was prepared from complex **1** (1.20 g), *p*-benzyloxobenzoyl chloride (3.77 g) and triethylamine (4.48 g) in refluxing dry toluene (300 ml) for 25 hours. Following the above procedure, the product was isolated by chromatography to

yield 1.75 g (52%) of fine dark violet crystals, mp 157.9-160.9° dec; ir: ν C=O 1650, ν C=C and C=N 1598, 1530, 1377 cm^{-1}; ms: m/z (relative intensity) 820 (1.0), 612 (35.2), 611 (31.1), 610 (74.2), 519 (17.8), 402 (42.0), 401 (26.2), 400 (100).

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

p-Chlorobenzoyl chloride (4.38 g) and complex **1** (2.01 g) were treated in dry toluene (600 ml) containing triethylamine (6.07 g) for one hour. Following the above procedure, **6** was obtained as fine dark violet crystals. The yield was 2.95 g (88%), mp 249.7-250.7° dec; ir: ν C=O 1658, ν C=C and C=N 1590, 1535, 1380 cm^{-1}; ms: m/z (relative intensity) 678 (25.0), 677 (10.5), 676 (59.5), 540 (40.6), 538 (53.8), 400 (21.0).

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

A mixture of complex **1** (2.01 g), *p*-nitrobenzoyl chloride (4.63 g), triethylamine (6.07 g) and dry toluene (600 ml) was kept under reflux for 15 minutes with stirring. After being permitted to stand at room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness under diminished pressure. The residue was chromatographed on activated aluminium oxide using dichloromethane as an eluent. The second fraction was collected, evaporated to dryness under reduced pressure to afford 3.45 g (99%) of fine dark violet crystals, mp 274.5-280.4° dec; ir: ν C=O 1658, ν C=C and C=N 1602, 1535, 1384, ν NO_2 1520sh, 1350 cm^{-1}; ms: m/z (relative intensity) 700 (6.4), 699 (4.1), 698 (12.8), 551 (33.8), 550 (26.1), 549 (73.1), 402 (41.5), 401 (26.2), 400 (100).

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