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SYNTHESIS AND CHARACTERIZATION FOR FIVE 7,16-DIBENZYLATED TETRAAZA[14]ANNULENE NICKEL(II) COMPLEXES

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Abstract—The substitution reaction of tetraaza[14]annulene nickel(II) (1) with five various *para*-substituted benzyl bromides led to the corresponding 7,16-dibenzylated complexes in 43–60% yields. The mass spectra indicate the existence of molecular ion peaks due to the 7,16-dibenzylated products. The macrocyclic skeleton of the five complexes and their electronic spectra are hardly changed by the benzylation. The five nickel(II) complexes are in almost square-planar coordination, judging from the ligand-field transition bands. The olefinic proton signals at the 7- and 16-positions disappear on benzylation in the ¹H NMR spectra. The off-resonance decoupling peak at the 7- and 16-positions changes from a doublet to a singlet by the benzylation of 1 in ¹³C NMR spectra. The ¹³C NMR results are comparable with those of ¹H NMR.

In previous papers we have reported the reaction of the tetraaza[14]annulene nickel(II) complex (1) with 3,3'-(octamethylenedioxy)dibenzoyl dichloride, ^{1a} 3,3'-(2,6-pyridyldimethyleneoxy)dibenzoyl dichloride, ^{1b} nicotinoyl chloride hydrochloride, isonicotinoyl chloride hydrochloride^{1c} and/or six types of *para*-substituted benzoyl chlorides.^{1d} Although there have been extensive investigations for the substitution reaction of 1 with acid chlorides,²⁻⁴ little attention has been devoted to the substitution reaction between 1 and benzyl bromide, etc.

In the present work, for the purpose of making a further exploration into the reactivity for the 7,16-positions of 1, we have shown that the results for the reaction of 1, namely (6,8,15,17-tetra-methyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II), with a series of *para*-substituted benzyl bromides were productive. We also characterized the spectral properties of the present products by means of mass, IR, electronic and NMR spectroscopy.



EXPERIMENTAL

Physical measurements

EI mass spectra for tetraaza[14]annulene nickel(II) complexes 2–6 were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer at 70 eV using a direct inlet system. Melting points were obtained with a Yanaco MP-500D

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micro melting point apparatus (hot-plate type). Elemental analyses were determined with a Yanaco C.H.N recorder MT3. IR spectra in the 400–4000 cm⁻¹ range were taken on a Hitachi 260–30 spectrophotometer at room temperature by the potassium bromide disk technique. Electronic spectra covering the 12 000–40 000 cm⁻¹ region were obtained on a Shimadzu UV 200S double-beam spectrophotometer for chloroform solutions at room temperature. Proton and ¹³C NMR spectra were recorded on a JEOL JNM-A500 spectrometer in chloroform-d at room temperature and the chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard.

Preparation of macrocyclic nickel(II) complexes

(6,8,15,17-*Tetramethyldibenzo* [b,i] [1,4,8,11]*tetraazacyclotetradecinato*)*nickel*(II) (1). The preparative procedure for complex 1 has been reported previously.^{1a,5}

(7,16-Dibenzyl-6,8,15,17-tetramethyldibenzo [b,i]-[1,4,8,11] tetraazacyclotetradecinato) nickel(II) (2). A mixture of 1 (1.21 g, 3.00 mmol) and benzyl bromide (2.06 g, 12.0 mmol) was dissolved in dry xylene (650 cm³) containing triethylamine (1.51 g, 15.0 mmol), and heated under reflux for a week with stirring, protected from moisture. The reaction mixture was cooled down at room temperature. Precipitated triethylamine hydrobromide was removed by filtration and the filtrate was evaporated to dryness in vacuo. The resulting solid was chromatographed on activated aluminium oxide (200 mesh, Wako Pure Chemical Industries, Ltd) and eluted with dichloromethane. The second effluent was collected, evaporated to dryness under reduced pressure, and vacuum-dried to give fine green crystals (2). The yield was 1.14 g (65%); m.p. 235–239°C (dec); IR (KBr disk): v(C=C) and v(C=N) 1530, 1425, 1375 cm⁻¹; EIMS: m/z 580 $(M^+, {}^{58}Ni), 581.40$ (Calc. for molecular weight).

(7,16-Bis (4-methylbenzyl)-6,8,15,17-tetramethyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecinato)nickel(II) (3). This was prepared from 1 (1.21 g, 3.00 mmol), 4-methylbenzyl bromide (2.22 g, 12.0 mmol), dry xylene (650 cm³) and triethylamine (1.51 g, 15.0 mmol), following the above procedure, and chromatographed on activated aluminium oxide using dichloromethane as an eluent to yield 0.92 g (50%) of fine yellow green crystals (3); m.p. 252–256°C (dec); IR (KBr disk): v(C=C) and v(C=N) 1535, 1428, 1365 cm⁻¹; EIMS: m/z 608 (M⁺, ⁵⁸Ni), 609.45 (Calc. for molecular weight).

(7,16-*Bis*(4-*bromobenzyl*)-6,8,15,17-*tetramethyldibenzo*[*b*,*i*][1,4,8,11]*tetraazacyclotetradecinato*)*nickel*-(II) (4). 4-Bromobenzyl bromide (3.00 g, 12.0 mmol) and 1 (1.21 g, 3.00 mmol) were reacted in dry xylene (650 cm³) containing triethylamine (1.51 g, 15.0 mmol), as described above. The product was chromatographed on activated aluminium oxide eluted with dichloromethane to obtain 0.95 g (43%) of fine green crystals (4); m.p. 177–183°C (dec); IR (KBr disk): v(C=C) and v(C=N) 1536, 1426, 1372 cm⁻¹; EIMS: m/z 736 (M⁺, ⁵⁸Ni, ⁷⁹Br), 739.19 (Calc. for molecular weight).

(7,16-Bis (4-chlorobenzyl)-6,8,15,17-tetramethyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecinato)nickel(II) (5). 4-Chlorobenzyl bromide (2.47 g, 12.0 mmol) and 1 (1.21 g, 3.00 mmol) were reacted in dry xylene (650 cm³) containing triethylamine (1.51 g, 15.0 mmol), as described above. The reaction product was chromatographed on activated aluminium oxide using dichloromethane as an eluent to afford 1.08 g (55%) of fine dark green crystals (5); m.p. 192–195°C (dec); IR (KBr disk): ν (C=C) and ν (C=N) 1528, 1422, 1360 cm⁻¹; EIMS: m/z 648 (M⁺, ⁵⁸Ni, ³⁵Cl), 650.29 (Calc. for molecular weight).

(7,16-*Bis*(4-*nitrobenzyl*)-6,8,15,17-*tetramethyldibenzo*[*b*,*i*][1,4,8,11]*tetraazacyclotetradecinato*)*nickel*-(II) (**6**). 4-Nitrobenzyl bromide (2.59 g, 12.0 mmol) and **1** (1.21 g, 3.00 mmol) were reacted in dry xylene (650 cm³) containing triethylamine (1.51 g, 15.0 mmol), as described above. The reaction product was chromatographed on activated aluminium oxide eluted with dichloromethane to yield 1.21 g (60%) of fine dark green crystals (**6**); m.p. 166– 178°C (dec); IR (KBr disk): v(C==C) and v(C==N) 1530, 1425; v(NO₂) 1520, 1350 cm⁻¹; EIMS: *m*/*z* 670 (M⁺, ⁵⁸Ni), 671.39 (Calc. for molecular weight).

RESULTS AND DISCUSSION

Benzylation of the tetraaza[14]annulene nickel(II) complex (1)

The preparation of 2-6 is given in Scheme 1. The substitution reaction between 1 and five benzyl bromides in a 1:4 molar ratio in the existence of triethylamine was carried out in refluxing xylene and led to the corresponding 7,16-dibenzylated complexes 2-6 in 43–60% yields. This molar ratio was employed to produce the 7,16-dibenzylated products. The reaction takes a week since the reactivity of benzyl bromides is much poorer than that of benzoyl chlorides. The crude complexes were purified by the use of column chromatography on activated aluminium oxide. The yield for the reaction between complex 1 and the benzyl bromide containing a *para*-substituted electron-withdrawing group is approximately similar to that of the *para*-





substituted electron donating group. This suggests that the reaction is not susceptible to an electronic effect of the *para*-substituent because of a methylene linkage between the tetraaza[14]annulene group and the substituted benzene ring. The result indicates that complex 1 undergoes an electrophilic substitution reaction at the olefinic carbons of the 7and 16-positions as with the olefinic carbon of the 3position in metal acetylacetonates.⁶ The analytical data for **2–6** are compiled in Table 1. The elemental analyses of the crystalline complexes are consistent with the expected compositions.

Mass spectra

The EI mass spectra of **2–6** exhibit the molecular ion M^+ at 580, 608, 736 (⁷⁹Br), 648 (³⁵Cl) and 670, respectively. These parent peaks substantiate the

	comple	exes		
		Elementa Calc./Fo	lanalyses und (%)	
Complex	Empirical formula	С	Н	Ν
2	C ₃₆ H ₃₄ N ₄ Ni	74.4	5.9	9.6
		74.0	5.8	9.8
3	$C_{38}H_{38}N_4Ni$	74.9	6.3	9.2
		74.6	6.3	9.1
4	$C_{36}H_{32}Br_2N_4Ni$	58.5	4.4	7.6
		58.9	4.4	7.4
5	C ₃₆ H ₃₂ Cl ₂ N ₄ Ni	66.5	5.0	8.6
		66.2	5.0	8.5
6	$C_{36}H_{32}N_6O_4N_1$	64.4	4.8	12.5
	00 02 0 7	64.5	4.9	12.2

Table 1. Analytical data for novel tetraaza[14]annulene nickel(II) complexes



Fig. 1. Electronic spectra for the tetraaza[14]annulene nickel(II) complexes at room temperature in cholorform : (A) 1; (B) 6.

7,16-dibenzylated complexes. The mass of the major fragment at m/z 400 for all complexes corresponds to $[M-2RC_6H_4CH_2+2H]^+$ and the frag-

ment peaks at m/z 490, 504, 568 (⁷⁹Br), 524 (³⁵Cl) and 535, respectively, also accords with $[M - RC_6H_4CH_2 + H]^+$.

IR spectra

The characteristic IR bands of **2–6** reveal very strong bands about 1530, 1425 and 1365 cm⁻¹ which are correlated with the C=C and C=N stretching modes of the tetraaza[14]annulene skeleton as in complex $1.^5$ Moreover, **6** indicates strong bands at 1520 and 1350 cm⁻¹ due to the NO₂ stretching mode.^{1d}

Electronic spectra

The electronic spectra covering the 12 500–40 000 cm^{-1} area are shown in Fig. 1 for 1 and 6. The general feature of the spectra for 2–6 are analogous to each other and to that for 1 which is not benzylated. This suggests that the delocalization of the

Complex	Transition energy $(cm^{-1})(\varepsilon)$
1	17 000(6300), 23 300sh(13 000), 25 500(36 000),
	30 700(8640), 35 700sh(21 100)
2	16 100(6030), 22 600(14 200), 25 100(22 200),
	36 600(29 500)
3	16 100(6420), 22 500(15 500), 25 200(25 000),
	36 400 (31 700)
4	16 200(6360), 22 800sh(15 900), 25 000(25 900).
	36 800(35 700)
5	16 200(6560), 22 600(15 400), 25 100(26 500).
	36 500(33 200)
6	16 300(6970), 22 800(16 600), 25 200(29 200).
	36 000(53 300)

 Table 2. Electronic absorption bands for the tetraaza[14]annulene nickel(II) complexes^a

"Measured in chloroform at room temperature.

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Table 3. Pr	oton NMR	data for the	tetraaza[14]annu	ilene nickel(II)) complexes ^{<i>a</i>}
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Complex	Methyl 6,8,15,17-CH ₃	Olefinic 7,16-H	Aromatic (Macrocyclic)	Aromatic	Methyl <i>p</i> -CH ₃	Methylene —CH ₂ —Ph
1	2.07(s)	4.85(s)	6.61(s)			
2	2.03(s)		6.53(s)	7.39(m)	2.36(s)	3.72(s)
3	2.02(s)		6.52(s)	7.25(m)		3.67(s)
4	2.00(s)		6.54(s)	7.28(d, J = 8.8 Hz) 7.51(d, J = 8.8 Hz)		3.65(s)
5	2.00(s)		6.54(s)	7.36(s)		3.67(s)
6	2.00(s)		6.57(s)	7.57(d, J = 8.8 Hz) 8.26(d, J = 8.8 Hz)		3.81(s)

"Chemical shifts in ppm from internal TMS. Measured in chloroform-d. Multiplicity of a proton signal is given in parentheses after the δ value; s = singlet; d = doublet; m = multiplet.

conjugated system on the nickel(II) complexes 1-6 is almost similar. This may be due to the fact that the electronic interaction between the tetraaza[14]annulene skeleton and the benzvlated group scarcely happens. The absorption bands observed above 22 500 cm⁻¹ are attributable to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal-to-ligand since the molar extinction coefficients of the bands are much larger than those commonly assigned to ligand-field transitions.⁷ The weak bands in the 16 100–16 300 cm⁻¹ region are attributed to ligand-field transition.⁷ The spectral behaviour is in fair agreement with that of the square-planar nickel(II) complexes.⁷ The ligand-field, charge-transfer and $\pi \rightarrow \pi^*$ transitions bands of 1-6 are listed in Table 2.

NMR spectra

Consistent with a diamagnetism of the present macrocyclic nickel(II) complexes, 2-6 gave wellresolved ¹H NMR spectra. The chemical shift assignments were performed on the basis of comparisons with 1.5 The ¹H NMR data and their assignments for 2-6 are compiled in Table 3. The signals for the olefinic protons at the 7- and 16positions are extinguished on benzylation at these positions, and then the methylene and the aromatic proton signals newly appear in the 3.65-3.81 and 7.25–8.26 ppm ranges on benzylation, respectively. The signals for the methyl protons at the 6-, 8-, 15and 17-positions reveal very slight upfield shifts on the benzylation since the methyl groups are within the shielding zone which is produced by the magnetic anisotropy of the substituted benzene rings. The aromatic proton signals of the macrocyclic skeleton in 2-6 also show upfield shifts by 0.04-0.09 ppm. The aromatic proton signal of the benzyl group in 2, 3 and 5 is a singlet. On the other hand, the aromatic peaks of the benzyl group in complexes 4 and 6 represent an approximately firstorder A_2B_2 system and thereby each proton peak is represented by a doublet.

The 13 C NMR data and their assignments for 1– 6 are collected in Table 4. All methyl carbon peaks of 2–6 show upfield shifts that are correlated with the shielding effect caused by the magnetic anisotropy of the benzene ring in the benzyl group. The olefinic carbon peaks at the 6-, 8-, 15- and 17positions bonded to the methyl group show slight downfield shifts. The aromatic carbon peaks at the 2-, 3-, 11-, 12-, 1-, 4-, 10-, 13-, 19-, 20-, 21- and 22-positions show slight downfield shifts also. The carbon peaks at the 7- and 16-positions exhibit downfield shifts by 1.3–2.7 ppm on the benzylation. The off-resonance decoupling carbon peak at the 7-

	C(6) C(8) C(15)	C(19) C(20) C(21)	C(1) C(1) C(11)	C(4) C(10)	C(7)							
olex	C(17)	C(22)	C(12)	C(13)	C(16)	C(1')	C(2')	C(3')	C(4′)	CH ₂	-CH ₃	p -CH $_3$
	155.0(s)	146.9(s)	121.5(d)	120.5(d)	(p)6.011						22.0(q)	
_ `	156.3(s)	148.2(s)	121.7(d)	121.4(d)	113.5(s)	141.6(s)	127.6(d)	128.5(d)	125.9(d)	36.1(t)	20.6(q)	
	156.2(s)	148.1(s)	121.6(d)	121.4(d)	113.6(s)	138.4(s)	129.2(d)	127.4(d)	135.2(s)	35.6(t)	20.5(q)	21.0(q)
_	156.2(s)	148.1(s)	121.7(d)	121.6(d)	113.0(s)	140.7(s)	129.4(d)	131.6(d)	119.6(s)	35.6(t)	20.5(q)	
	156.1(s)	148.1(s)	121.7(d)	121.6(d)	113.1(s)	140.1(s)	128.6(d)	128.3(d)	131.5(s)	35.5(t)	20.5(q)	
	156.0(s)	147.9(s)	121.9(d)	121.8(d)	112.2(s)	149.9(s)	128.3(d)	123.8(d)	146.5(s)	36.2(t)	20.5(q)	

Comp

 δ value: s = singlet; d = doublet; t = triplet; q = quartet

[able 4. ¹³C NMR data for the tetraaza[14]annulene nickel(11) complexes^a

and 16-positions of 1 is split into a doublet owing to coupling with the proton at these positions, but that of 2-6 is a singlet due to having no proton at these positions. This indicates that complex 1 is benzylated at the 7- and 16-positions. New carbon peaks for the benzyl group are observed in the 35– 150 ppm region.

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