Synthesis and Characterization of 7,16-Dinicotinoyl- and 7,16-Diisonicotinoyltetraaza[14]annulene and their Nickel(II) and Copper(II) Complexes

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The reaction of tetraaza[14]annulene and its complexes with nicotinoyl chloride hydrochloride and/or isonicotinoyl chloride hydrochloride produced the 7,16-dinicotinoylated and/or 7,16-diisonicotinoylated corresponding products in satisfactory yields. The mass spectra reveal the molecular ion peaks due to the 7,16-diacylated products. A strong ir band which is correlated with a C=O stretching mode is freshly observed in the 1635-1670 cm^{-1} region upon the acylation. The electronic spectra for the complexes hardly change upon the acylation, but those for the ligands change slightly. The olefinic proton signals at the 7- and 16-positions disappear on the acylation in ^{1}H-nmr spectra and the substituted pyridine proton signals are newly observed. The proton nmr results are consistent with those of the carbon-13 nmr. The spin Hamiltonian parameters for the acylated copper(II) complexes are comparable with those for the copper(II) complex which is not acylated. The copper(II) complexes assume the square-planar coordinations with an unpaired electron in the $d_{x^2-y^2}$ orbital.

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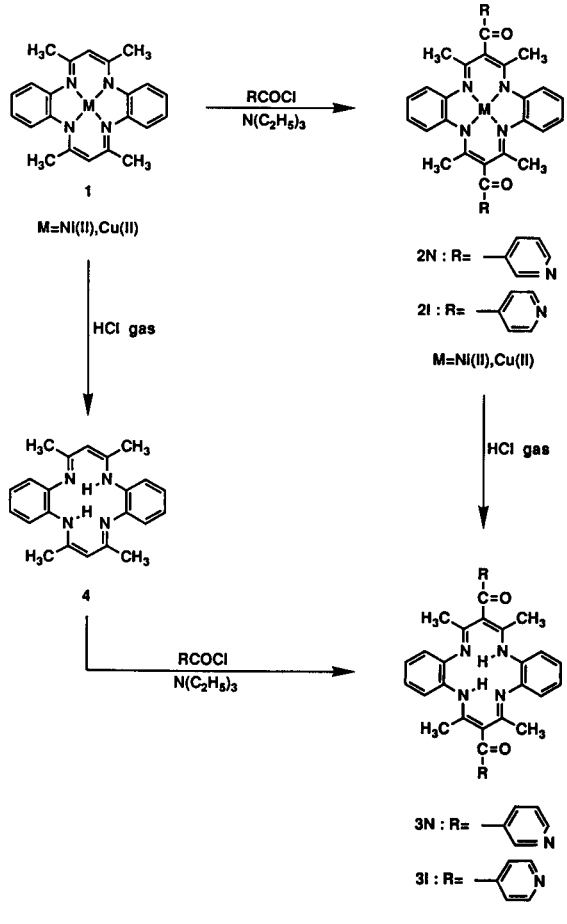
Introduction.

The reactivity of tetraaza[14]annulene complexes to various reagents can be used to introduce a number of substituents into the macrocyclic skeleton. These substituents provide points of attachment for further structural modifications which provide the capability of preparing more complex compounds employed as models for biologically significant macrocyclic systems. Thus, the 7,16-positions of tetraaza[14]annulene nickel(II) complexes have been found to be a reactive nucleophilic center [1]. In previous papers, the reaction of the metal-free tetraaza[14]annulene **4** with a series of *p*-substituted benzoyl chlorides and the reaction of a tetraaza[14]annulene nickel(II) complex with 3,3'-(octamethylenedioxy)dibenzoyl chloride were described [2,3]. Eilmes *et al.* presented only the reaction of tetraaza[14]annulene nickel(II) complexes with benzoyl chloride, *p*-nitrobenzoyl chloride, acetyl chloride, glutaryl chloride, and pimelic acid dichloride [4-7]. Dzugan and Busch reported also the reaction of tetraaza[14]annuleme nickel(II) complex with perfluorobenzoyl chloride and trifluoroacetic anhydride and the characterization of these products [8]. Nevertheless, the reaction of tetraaza[14]annulene nickel(II) and copper(II) complexes with nicotinoyl- and isonicotinoyl chlorides has never been investigated because of the poor solubility of the complexes in benzene, toluene, *etc.*

In the present work, we prepared nickel(II) and copper(II) complexes of the tetraaza[14]annulene, that is, (6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (**Ni(1)**) and (6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)copper(II) (**Cu(1)**), indicating that the results of the reaction of **Ni(1)** and **Cu(1)** with nicotinoyl- and isonicotinoyl chloride hydrochloride were productive. The spectral properties of the present products, namely 7,16-disubstituted tetraaza[14]annulenes and their nickel(II) and copper(II) complexes have also been studied by mass, infrared, electronic, nmr and esr spectroscopy.

Scheme I



Results and Discussion.

Acylation of Tetraaza[14]annulene and its Nickel(II) and Copper(II) Complexes.

The reaction between the **Ni(1)** and/or **Cu(1)** complexes and isonicotinoyl chloride hydrochloride in a 1:5 molar ratio in the presence of triethylamine was carried out in boiling toluene and gave the corresponding 7,16-diisonicotinoylated complexes of **Ni(2I)** and **Cu(2I)**, in 85-93% yields. Dinicotinoylation of the **Ni(1)** and **Cu(1)** complexes was accomplished in the above manner and the products were obtained in 91-94% yields. The treatment of **4** with nicotinoyl chloride hydrochloride and/or isonicotinoyl chloride hydrochloride led to the 7,16-dinicotinoylated **3N** and/or 7,16-diisonicotinoylated **3I** products in 55-80% yields according to the above procedure. The preparation of these compounds is illustrated in Scheme I. This acylation required a good deal of nicotinoyl chloride and/or isonicotinoyl chloride hydrochloride owing to the poor solubility in benzene and/or toluene. The acylation for the metal free macrocycle **4** was done under milder conditions than those for the nickel(II) and copper(II) complexes in order to prevent a lowering of the yield. It appears that the coordinated nickel(II) and copper(II) ions in the complexes protect the potentially nucleophilic nitrogen centers from attack by electrophilies, allowing only the olefinic carbons at the 7- and 16-positions to be susceptible to an electrophilic substitution reaction. The analytical data and melting points for **Ni(2N)**, **Ni(2I)**, **Cu(2N)**, **Cu(2I)**, **3N**, and **3I** are summarized in Table I. Elemental analyses of these crystalline samples were consistent with compounds of these compositions.

Mass Spectra.

Mass spectral data for the macrocycles and their complexes are given in the Experimental. The EI mass spectra for the macrocycles, **3N**, **3I**, and their copper(II) complexes, **Cu(2N)**, **Cu(2I)**, show the presence of a molecular ion M^+ at m/z 554 and 615, respectively. These are the base peaks in each mass spectrum. The mass of the major fragment at m/z 510 corresponds to $[M-C_5H_4NCO+H]^+$ in the copper(II) complexes. On the other hand, the masses of the major fragment at m/z 448 and 539 correspond to $[M-C_5H_4NCO+H]^+$ and $[M-CH_3]^+$, respectively, in the metal-free macrocycles. The nickel(II) complexes exhibit a molecular ion M^+ at m/z 610 which is not a base peak. The masses of the major fragment at m/z 400 and 505 correspond to $[M-2C_5H_4NCO+2H]^+$, and to $[M-C_5H_4NCO+H]^+$, respectively, and the latter peak becomes the base peak in each mass spectrum.

Table I

Analytical Data and Melting Points for New Tetraaza[14]annulenes and their Metal(II) Complexes

Compound	Mp (°C)	Empirical Formula	Elemental Analyses Calcd./Found % C	H	N
3N	213.2-214.9 dec	$C_{34}H_{30}N_6O_2$	73.63	5.45	15.15
			73.49	5.37	14.90
3I	249.8-250.3 dec	$C_{34}H_{30}N_6O_2$	73.63	5.45	15.15
			73.51	5.32	14.92
Ni(2N)	>300	$C_{34}H_{28}N_6O_2Ni$	66.80	4.62	13.75
			67.04	4.68	13.62
Ni(2I)	>300	$C_{34}H_{28}N_6O_2Ni$	66.80	4.62	13.75
			66.79	4.65	13.63
Cu(2N)	>300	$C_{34}H_{28}N_6O_2Cu$	66.27	4.58	13.64
			66.21	4.55	13.44
Cu(2I)	>300	$C_{34}H_{28}N_6O_2Cu$	66.27	4.58	13.64
			65.94	4.68	13.41

Infrared Spectra.

The characteristic ir absorption bands are listed in the Experimental. The macrocycles, **3N**, **3I** freshly show a strong band about 1640 cm^{-1} which is correlated with a C=O stretching mode upon acylation. This band shifts to higher frequency by 20-30 cm^{-1} on metal-coordination. This seems to suggest that electronic interaction between the carbonyl and pyridine moieties is weakened by an increase of the steric hindrance effect between the carbonyl and methyl groups in order to be nearly fixed in one plane upon formation of the nickel(II) and copper(II) complexes, resulting in the absorption band at higher frequency part than that of **3N** and **3I**.

Electronic Spectra.

Visible and ultraviolet spectra for **3N**, **Ni(2N)**, and **Cu(2N)** as an example are shown in Figure 1, covering the 12500-40000 cm^{-1} region. The spectral features for **3N** and

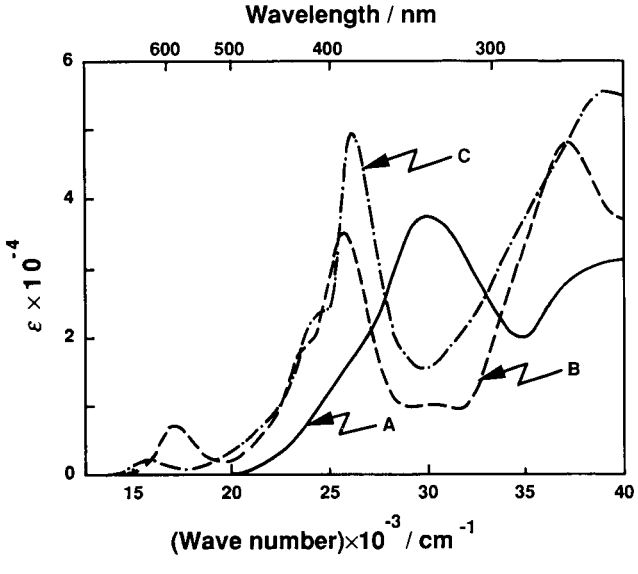


Figure 1. Electronic spectra for the macrocyclic complexes at room temperature in chloroform. **A, 3N; B, Ni(2N); C, Cu(2N).**

3I, and **Ni(2N)** and **Ni(2I)**, and **Cu(2N)** and **Cu(2I)** respectively, are similar to each other and are scarcely influenced by acylation such as nicotinoylation and isonicotinoylation. This suggests that the delocalization of a conjugated system in two isomers on a relative position of a nitrogen atom is approximately analogous to one another. Moreover, the general features of the spectrum for the acylated macrocyclic complex, **Ni(2N)**, **Ni(2I)**, **Cu(2N)**, and **Cu(2I)**, are similar to that for the unacylated macrocyclic complex, **Ni(1)** and **Cu(1)**, as shown in Figure 2. On the other hand, an extremely intense absorption band observed at 28700 cm^{-1} in **4** shows a shift to higher energy

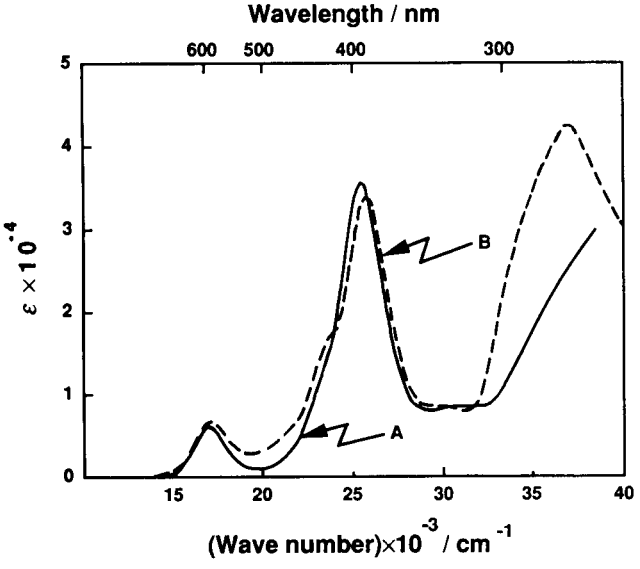


Figure 2. Electronic spectra for the macrocyclic nickel(II) complexes at room temperature in chloroform **A, Ni(1); B, Ni(2I)**.

upon acylation. This seems to indicate that the steric hindrance effect by dinicotinoyl and/or diisonicotinoyl groups gives strain to the tetraaza[14]annulene skeleton **4** and then the length of the conjugated system in **4** slightly decreases. The absorption bands lying above 23000 cm^{-1} are reasonably attributed 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 larger than those usually assigned to $d \rightarrow d^*$ transitions [10-12]. The nickel(II) and copper(II) complexes have a weak absorption band in the 15700-17100 cm^{-1} region which is due to a $d \rightarrow d^*$ transition [12]. The spectral behavior is consistent with that of the square-planar coordination of nickel(II) and copper(II) [11,12]. The $d \rightarrow d^*$, $\pi \rightarrow \pi^*$, and CT transitions for the macrocycles and their complexes are collected in Table II. Consequently, it is contemplated that the macrocyclic skeleton of the metal-free ligand is slightly distorted with the acylation, but that of the nickel(II) and copper(II) complexes is hardly distorted in order to protect the macrocyclic ring with metal-coordination.

Table II

Electronic Absorption Bands for Macrocycles and their Complexes [a]

Compound	Transition energy in cm^{-1} (ε)
4	28700 (47800), 38800 (22300)
3N	29900(37800), 38200 sh (30200)
3I	30300 (34400), 38200 sh (27900)
Ni(1)	17000 (6300), 23300 sh (13000), 25500 (36000), 30700 (8640), 35700 sh (21100)
Ni(2N)	17100 (7330), 23900 sh (19100), 25800 (35600), 29900 (10300), 37000 (48700)
Ni(2I)	17100 (6800), 24000 sh (17900), 25800 (34300), 29900 (8890), 37000 (42700)
Cu(1)	15700 (2160), 24000 (23400), 26000 (58500), 34200 (28000), 39400 (36700)
Cu(2N)	15700 (2300), 24300 sh (23400), 26200 (50900), 38800 (55500)
Cu(2I)	15700 (2120), 24500 sh (22500), 26200 (46400), 35700 sh (38800), 38800 (48500)

[a] Measured in chloroform at room temperature.

NMR Spectra.

Consistent with a diamagnetism of the present macrocyclic nickel(II) complexes, **Ni(2N)** and **Ni(2I)**, gave well-resolved proton nmr spectra. Chemical shift assignments were made on the basis of comparisons with **4** and **Ni(1)** [2,9]. Proton nmr data and their assignments for **3N**, **3I**, **Ni(2N)**, and **Ni(2I)** are compiled in Table III. The amine proton peaks show downfield shifts by *ca.* 2 ppm upon dinicotinoylation and diisonicotinoylation. The downfield shift is due to the deshielding effect of the substituted carbonyl group. The olefinic proton signals of the 7- and 16-positions disappears on acylation at these positions. The aromatic proton signals show upfield shifts by 0.53 ppm on nickel-coordination. This seems to suggest that the upfield shifts are subjected to the shielding effect caused by the magnetic anisotropy of the chelating rings formed. The substituted pyridine proton peaks have downfield shifts by the deshielding effect of the chelating rings. The methyl proton signals show upfield shifts upon acylation since the methyl groups are within the shielding zone that is produced by the magnetic anisotropy of the substituted pyridine ring.

Carbon-13 nmr data and their assignments for **4**, **Ni(1)**, **3N**, **Ni(2N)**, **3I**, and **Ni(2I)** are listed in Table IV. All carbon peaks show a singlet. All methyl carbon signals show upfield shifts which are associated with the shielding effect due to the substituted pyridine rings. The carbon peaks at the 7- and 16-positions show downfield shifts by *ca.* 10 ppm upon dinicotinoylation and diisonicotinoylation. This seems to indicate that the tetraaza[14]annulenes and their complexes are acylated at 7- and 16-positions.

Table III

Proton NMR Data for the Tetraaza[14]annulenes and their Nickel(II) Complexes [a]

Compound	Methyl $-CH_3$	Aromatic	Pyridinic 1'-H	2'-H	6'-H	3'-H	5'-H	Amine -NH
3N	2.01 (s)	7.09 (s)	8.79(dd) (J = 4.8 Hz) (J = 2.0 Hz)		7.47 (ddd) (J = 8.0 Hz) (J = 4.8 Hz) (J = 0.7 Hz)	9.19 (dd) (J = 2.0 Hz) (J = 0.7 Hz)	8.29 (dt) (J = 8.0 Hz) (J = 2.0 Hz)	14.54 (s)
3I	1.99 (s)	7.09 (m)		8.83 (dd) (J = 4.4 Hz) (J = 1.7 Hz)		7.78 (dd) (J = 4.4 Hz) (J = 1.7 Hz)		14.59 (s)
Ni(2N)	1.93 (s)	6.65 (s)	8.84 (dd) (J = 4.8 Hz) (J = 2.0 Hz)		7.53 (ddd) (J = 8.1 Hz) (J = 4.8 Hz) (J = 0.7 Hz)	9.45 (dd) (J = 2.0 Hz)	8.51 (dt) (J = 8.1 Hz) (J = 2.0 Hz)	
Ni(2I)	1.91 (s)	6.66 (s)		8.92 (dd) (J = 4.5 Hz) (J = 1.5 Hz)		8.01 (dd) (J = 4.5 Hz) (J = 1.5 Hz)		

[a] Chemical shifts in ppm from TMS. Multiplicity of a proton signal is given in parentheses after δ-value; s = singlet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublets of doublets.

Table IV

Carbon ^{13}NMR Data for the Macrocycles and their Nickel(II) Complexes [a]

Compound	$-CH_3$	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(1')	C(2')	C(6')	C(3')	C(5')	C(4')	C=O
4	20.79	97.66	122.52	122.71	138.13	158.40							
Ni(1)	21.95	110.87	120.51	121.49	146.94	154.96							
3N	19.72	108.48	123.74	124.60	137.29	161.86	150.77		124.77	152.88	136.37	136.77	196.44
Ni(2N)	20.63	120.60	121.91	123.05	147.12	154.09	151.28		123.91	153.63	136.71	134.60	198.61
3I	19.83	108.25	122.25	124.65	137.17	162.66		150.94		125.00		147.97	196.61
Ni(2I)	20.69	120.25	121.97	122.31	147.06	154.37		151.28		123.17		145.34	199.07

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

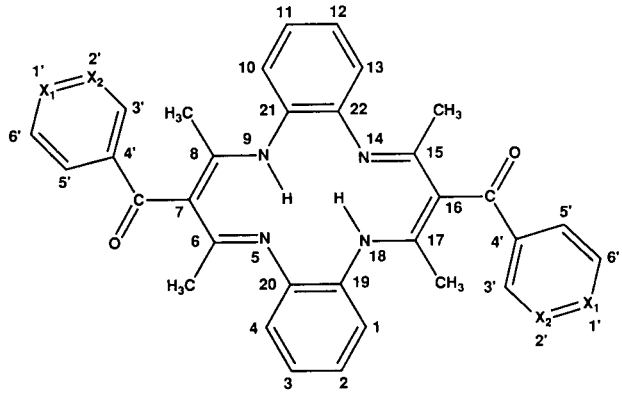
Table V

Spin Hamiltonian Parameters for the Macrocyclic Copper(II) Complex

Complex	Medium	$\bar{g}$	$g_{\parallel}$	$g_{\perp}$	$\bar{A}^{Cu}\times10^4$ (cm^{-1})	$A_{\parallel}^{Cu}\times10^4$ (cm^{-1})	$\bar{A}^{N}\times10^4$ (cm^{-1})	$A_{\parallel}^{N}\times10^4$ (cm^{-1})	$A_{\perp}^{N}\times10^4$ (cm^{-1})
Cu(1)	[a]	2.085			89.4		12.4		
Cu(2N)	[b]	2.086			89.9		12.6		
Cu(2I)	[b]	2.086			89.9		12.8		
Cu(1)	[c]		2.168	2.040		199.9		12.7	16.0
Cu(2N)	[d]		2.171	20.43		200.1		12.3	12.6
Cu(2I)	[d]		2.171	2.043		199.9		12.1	12.7

[a] In benzene-xylenee (1:1 v/v) at room temperature. [b] In benzene-xylene (2:3 v/v) at room temperature. [c] Doped in the **Ni(1)** complex at room temperature. [d] In benzene-xylene (2:3 v/v) at 77 K.

The new carbon signals for the carbonyl and pyridyl groups on the basis of the acylation are newly observed at 196-200 ppm and 123-152 ppm, respectively. These results are consistent with the corresponding proton nmr spectral behaviors.



3N X_1=CH, X_2=N
3I X_1=N, X_2=CH

ESR Spectra.

The esr spectrum for **Cu(2I)** complex in benzene-xylene (2:3 v/v) at 77 K is shown in Figure 3. The general features of the spectra for **Cu(2N)** and **Cu(2I)** are similar to each other and to that observed for the square-planar copper(II) complexes derived from porphyrins [13,14] and from phthalocyanine [15]. A set of four copper hyperfine lines on the $g_{\parallel}$ componet, which lie in the lower field region, can be observed, while such hyperfine lines are not obvious on the $g_{\perp}$ component in the higher field region. Super-hyperfine lines due to the nitrogen nuclei appear on the $g_{\parallel}$ and $g_{\perp}$ componets. The spectrum in benzene-xylene (2:3 v/v) at room temperature also shows four hyperfine lines due to the copper atom and additional splitting caused by the nitrogen nuclei in the higher field range. The spin Hamiltonian parameters are very comparable with those for **Cu(1)** which is not acylated, as given in Table V. Accordingly, **Cu(2N)** and **Cu(2I)** complexes assume the square-planar coordinations with an unpaired electron in the $d_{x^2-y^2}$ orbital.

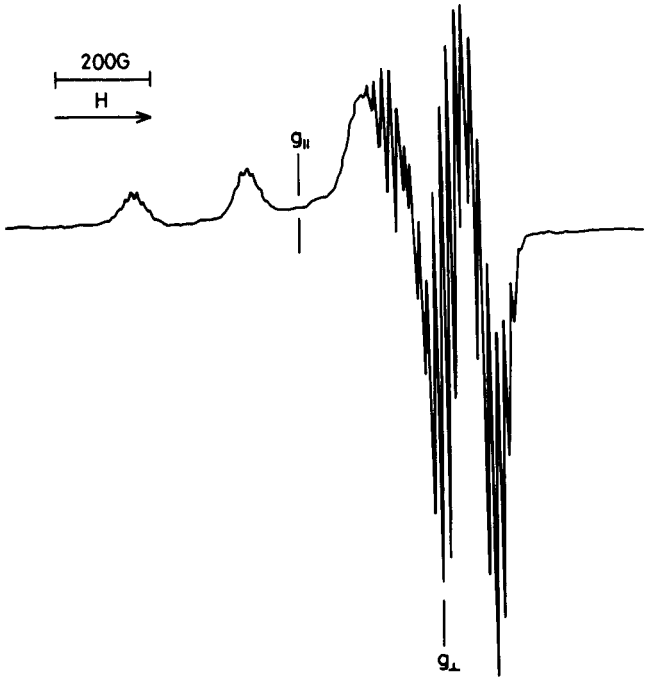


Figure 3. ESR spectrum of **Cu(2I)** complex in benzene-xylene (2:3 v/v) at 77 K.

EXPERIMENTAL

The EI mass spectra (at 23 eV) for the metal-free tetraaza[14]-annulenes and their nickel(II) and copper(II) complexes were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. The infrared spectra in the range of the 400-4000 cm^{-1} were taken on a Hitachi 260-30 spectrophotometer and a JEOL JIR-5500 FT-IR spectrophotometer at room temperature with potassium bromide disks. The ultraviolet and visible spectra covering the 13000-40000 cm^{-1} region were obtained on a Shimadzu UV 200S double beam spectrophotometer for chloroform solutions at room temperature. The proton and carbon-13 nmr spectra were recorded on a JEOL JNM-FX 60 spectrometer in chloroform-d at room temperature and the chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard. The esr spectra were performed on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The copper(II) complexes were measured in benzene-xylene (2:3 v/v) at room temperature and 77 K, the concentrations being maintained in the 10^{-3} mol dm^{-3}. The manganese ion diffused thermally into magnesium oxide was employed in order to obtain the standard reference signals for measurements. All melting points were observed on a Yanaco MP-500D micro melting point apparatus (hot-plate type).

Preparation of Macrocycles and their Complexes.

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

The preparative procedures for **Ni(1)** and **Cu(1)** complexes have been described previously [2,9].

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

A mixture of **Ni(1)** (2.41 g) and nicotinoyl chloride hydrochloride (5.34 g) was dissolved in dry toluene (1500 ml) containing triethylamine (12.15 g), and heated under reflux for a week with stirring and protected from moisture. The reaction mixture was cooled down at room temperature and filtered to take off triethylamine hydrochloride. The filtrate was evaporated to dryness under reduced pressure, and then resulting solid was chromatographed on silica gel (40-100 mesh, Wako Pure Chemical Industries, Ltd.) and eluted with ethyl acetate. The third effluent was

collected, evaporated to dryness *in vacuo*, and vacuum dried to give fine dark violet crystals (**Ni(2N)**). The yield was 3.46 g (94%); ir: ν C=O 1660, ν C=C and C=N 1581, 1535, 1381 cm^{-1}; ms: m/z (relative intensity) 613 (10.0), 612 (32.9), 611 (27.2), 610 (69.5), 508 (15.5), 507 (43.8), 506 (35.9), 505 (100), 402 (15.2), 401 (11.3), 400 (37.7).

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

This was prepared from **Ni(1)** (2.41 g), isonicotinoyl chloride hydrochloride (5.34 g), dry toluene (1500 ml) and triethylamine (12.15 g), following the above procedure, and chromatographed on silica gel using ethyl acetate as an eluent to yield 3.42 g (93%) of fine dark violent crystals (**NI(2I)**); ir: ν C=O 1664, ν C=C and C=N 1537, 1381 cm^{-1}; ms: m/z (relative intensity) 613 (12.5), 612 (39.7), 611 (35.5), 610 (84.2), 508 (15.9), 507 (44.2), 506 (38.3), 505 (100), 402 (27.5), 401 (19.5), 400 (65.8).

7,16-Dinicotinoyl-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)copper(II) (**Cu(2N)**).

A mixture of **Cu(1)** (0.61 g), nicotinoyl chloride hydrochloride (1.07 g) and dry benzene (500 ml) containing triethylamine (5.08 g) was kept under reflux for four days with stirring and protected from moisture. After being allowed to stand at room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was freed of solvent *in vacuo*. The resulting solid was chromatographed on silica gel eluted with ethyl acetate. The third fraction was collected, evaporated to dryness by diminished pressure and dried *in vacuo* to obtain 0.84 g (91%) of fine dark violet crystals (**Cu(2N)**); ir: ν C=O 1660, ν C=C and C=N 1581, 1531, 1383 cm^{-1} ms: m/z (relative intensity) 618 (21.9), 617 (56.2), 616 (44.6), 615 (100), 513 (5.4), 512 (17.9), 511 (19.3), 510 (38.3).

7,16-Diisonicotinoyl-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato)copper(II) (**Cu(2I)**).

Triethylamine (12.15 g) was added to a mixture of **Cu(1)** (2.44 g), isonicotinoyl chloride hydrochloride (5.34 g) and dry toluene (1500 ml). The reaction mixture was held under reflux for a week with stirring and protecting from the moisture, and then allowed to cool. Triethylamine hydrochloride was removed by filtration and evaporation of the filtrate was carried out to dryness under reduced pressure. The resulting solid was chromatographed on silica gel using ethyl acetate as an eluent. The third band was collected and the bulk of the solvent was removed *in vacuo*, and then vacuum dried to afford 3.14 g (85%) of fine dark violet crystals (**Cu(2I)**); ir: ν C=O 1668, ν C=C and C=N 1533, 1387 cm^{-1} ms: m/z (relative intensity) 617 (54.0), 616 (6.3), 615 (100), 512 (24.4), 510 (49.4).

5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**4**).

The synthetic procedure for **4** has been reported previously [2].

5,14-Dihydro-7,16-dinicotinoyl-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**3N**).

(a) A stirred suspension of **Ni(2N)** (1.46 g) in acetonitrile (50 ml) was treated with excess anhydrous hydrogen chloride gas during *ca.* 15 minutes until the orange-colored ligand salt precipitated. The precipitate was separated by filtration and washed with acetonitrile until the washings were no longer colored. The solid was dissolved in water (150 ml) and treated with sodium carbonate to afford a yellow precipitate. The crystalline product was filtered, recrystallized from 2-methoxyethanol and vacuum dried to yield 0.78 g (59%) of orange plates (**3N**); ir: ν C=O 1641, ν C=C and C=N 1581, 1551, 1416, 1367 cm^{-1}; ms: m/z (relative intensity) 556 (5.3), 555 (46.0), 554 (100), 540 (11.2), 539 (28.6), 449 (22.6), 448 (52.9).

(b) A mixture of **4** (2.07 g) and nicotinoyl chloride hydrochloride (5.34 g) was dissolved in dry toluene (1500 ml) containing triethylamine (12.15 g) under argon atmosphere and heated under gentle reflux for six days with stirring and protecting from the moisture. To the reaction mixture was added further nicotinoyl chloride hydrochloride (0.50 g) and triethylamine (0.29 g), and then this mixture was refluxed for two days with stirring and protecting from the moisture again. Triethylamine hydrochloride was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. 1,2-Dichloroethane solution of the resulting solid was applied on the top of a chromatographic column of activated aluminium oxide (200 mesh, Wako Pure Chemical Industries, Ltd.). A deeply colored band on the top of the column was eluted with 1,2-dichloroethane, and then with chloroform. The second deep yellow effluent (chloroform as an eluent) was collected and evaporated to dryness under reduced pressure. The oily residue was crystallized from ethyl acetate to afford 1.84 g (55%) of orange plates (**3N**).

5,14-Dihydro-7,16-diisonicotinoyl-6,8,15,17-tetramethyldibenzo-[*b,i*][1,4,8,11]tetraazacyclotetradecine (**3I**).

A mixture of **4** (2.07 g), isonicotinoyl chloride hydrochloride (5.34 g), dry toluene (1500 ml), and triethylamine (12.15 g) was heated under gentle reflux for three days with stirring and protecting from the moisture under argon atmosphere. Triethylamine hydrochloride was removed by filtration and the filtrate was evaporated to dryness by diminished pressure. The resulting solid was chromatographed on activated aluminium oxide using chloroform as an eluent. The first effluent was collected and evaporated to dryness *in vacuo*. The oily residue was crystallized from ethyl acetate to obtain 2.64 g (79%) of fine yellow crystals (**3I**); ir ν C=O 1637, ν C=C and C=N 1578, 1551, 1406, 1365 cm^{-1}; ms: m/z (relative intensity) 556 (6.5), 555 (38.9), 554 (100), 540 (5.1), 539 (14.7), 449 (11.7), 448 (20.9).

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