Preparation and Characterization of Tetraaza[14]annulene and its Nickel(II) and Copper(II) Complexes with Crown Ether Functionalities

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Three new organic hosts are described that contain a tetraaza[14]annulene core to which two crown ether voids are attached. These hosts include a free base tetraaza[14]annulene and/or its complexes with benzo-15-crown-5 rings. The crown tetraaza[14]annulene is synthesized from tetraaza[14]annulene and 4'-chloroformylbenzo-15-crown-5. Its nickel(II) and copper(II) complexes are prepared in a similar manner as above. In solution the compounds do not tend to form aggregates. However, aggregation is affected by the presence of alkali-metal salts, which coordinate to the crowns. Li^+ and Na^+ cations with diameters that match the diameters of the crown ether rings form 1:2 host-guest complexes. Complexes with 2:2 host-guest stoichiometry are formed when the diameters of K^+ and Cs^+ cations exceed that of the crown ether rings. Nevertheless, it is weak for the present macrocycle and its complexes to be inclined to form dimers owing to the steric hindrance of the substituent groups and owing to restraining the rotation of the carbonyl bond connecting the crown ether group.

Introduction.

Although lots of papers have been published about dimerization of crown porphyrins [1] and crown phthalocyanines [2], little has been reported on that of crown tetraaza[14]annulenes. Kruse and Breitmaier presented the syntheses of nickel(II) and cobalt(II) complexes with 2,3,11,-12-bis(1',4',7',10',13'-pentaoxatridecamethylene)-5,14-di-hydro-7,16-diisopropyl[b,i][1,4,8,11]tetraazacyclotetrade-cine without the work of spectral properties [3]. We also described the syntheses and characterization of nickel(II), copper(II) and oxovanadium(IV) complexes with

2,3,11,12-bis(1',4',7',10',13'-pentaoxatridecamethylene)-5,14-dihydro-7,16-diethyldibenzo[b,i][1,4,8,11]tetraazacy-clotetradecine that causes dimerization of crown phthalocyanine type [4].

In the present work, we report the syntheses of tetraaza[14]annulene functionalized with two crown ether voids at the 7,16-positions, namely 7,16-bis((3',4'-(1'',4'',7'',10'',13''-pentaoxatridecamethylene))benzoyl)-5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11] tetraazacyclotetradecine (**H₂L**) and its nickel(II) (**NiL**) and copper(II) (**CuL**) complexes which give rise to dimerization of crown porphyrin type. We also report the spectral properties and the cation and/or solvent-induced dimerization of the present crown tetraaza[14]annulene and its complexes.

Results and Discussion.

Synthesis of the Crown Side-Chain.

2,3-(4'-Chloroformylbenzo)-1,4,7,10,13-pentaoxacyclo-pentadeca-2-ene (**6**) was synthesized with a maximum overall yield of 14%. 2,3-(4'-Carboxybenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (**5**) was prepared from catechol through four steps according to the method of Smid *et al.* [5,6]. Acid chloride **6** was prepared in 95% yield under vigorous stirring and with refluxing a mixture of compound **5** and a large excess thionyl chloride. Compound **6** is pretty stable on exposure to air because of aromatic acyl halides. Compounds **1-6** have been adequately characterized by elemental analyses and infrared and ¹H nmr spectroscopies as given in the Experimental.

Synthesis of the Crown Tetraaza[14]annulene and its Complexes.

H₂L

ML
M = Ni(II), Cu(II)

Since tetraaza[14]annulene and its complexes containing crown ether voids at their 7,16-positions have never been reported, the treatment of compounds **7L**, **7Ni** and **7Cu** with compound **6** in a 1:4 molar ratio was carried out in refluxing toluene in the presence of triethylamine and led to the corresponding 7,16-disubstituted compounds **H₂L**, **NiL** and **CuL** in 37-60% yields. Purification of the crude products was performed with column chromatography on activated aluminium oxide eluted with chloroform, dichloromethane and/or dichloromethane-benzene. The acylation for macrocycle **7L** was made under argon atmosphere and under gentler condition than that of complexes **7Ni** and **7Cu** for the sake of preventing a lowering of the yield. It seems likely that the coordinated metal ion of complexes **7Ni** and **7Cu** protects the potentially nucleophilic nitrogen centers against attack by electrophilies, permitting only the olefinic carbons at the 7,16-positions to be sensitive to substitution reactions like the olefinic carbon at the 3-position in 2,4-pentandione metal complexes [7]. The analytical data and melting points for compounds **H₂L**, **NiL** and **CuL** are collected in the Experimental. Elemental analyses of these crystalline products were consistent with the expected compositions.

Mass Spectra.

The mass spectral data for compounds **H₂L**, **NiL** and **CuL** are summarized in the Experimental. Their FD mass spectra exhibit the presence of a molecular ion M^+ at 932, 988 and 993, respectively, which are the base peaks in each mass spectrum. The mass spectra indicate the absence of fragment ions because of FD mass spectra using a soft ionization system. Their EI mass spectra do not reveal the existence of a molecular ion since it may be easy to be broken upon the ionization of their compounds.

Infrared Spectra.

The characteristic ir absorption bands are given in the Experimental. Compounds **H₂L**, **NiL** and **CuL** newly indicate very intense bands about 1640 cm⁻¹ that are associated with the C=O stretching modes accompanied by the substitution reaction of acid chloride **6**. Moreover, they also exhibit strong bands in the 1260-1268 and 1127-1138 cm⁻¹ ranges which are correlated with C-O-C stretching mode in the substituent groups of the 7,16-positions. These show that the acylation takes place at the 7,16-positions of tetraaza[14] annulene and its complexes.

Visible and Ultraviolet Spectra.

The electronic spectra for compounds **H₂L**, **NiL** and **CuL** are shown in Figure 1, covering the 15000-40000 cm⁻¹ region. In compound **H₂L**, the very intense absorption band at 31200 cm⁻¹ reveals a shift to higher energy upon the introduction of the substituent groups at the 7,16-positions. This seems to show that the steric hin-

drance effect by the substituent group gives strain to compound **H₂L** and the delocalization of the conjugated system in compound **H₂L** faintly decreases.
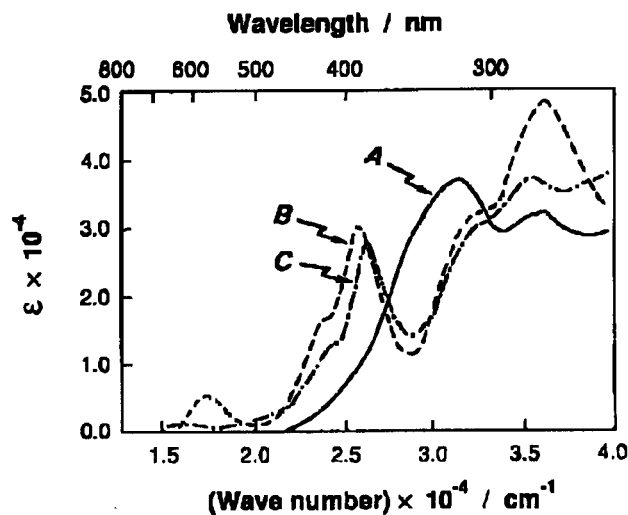
Figure 1. Electronic spectra for tetraaza[14]annulene and its complexes at room temperature in chloroform. A, **H₂L**; B, **NiL**; C, **CuL**.

In complexes, the general spectral features for complex **NiL** is analogous to that for complex **7Ni** which has no substituent group at the 7,16-positions. The general feature of the spectrum for complex **CuL** is also similar to that for complex **7Cu** in analogy with the nickel(II) complex. This suggests that the delocalization of a conjugated system in the complexes **NiL** and **CuL** is nearly similar to that for complexes **7Ni** and **7Cu**, respectively. The absorption bands appearing in the energy greater than 23000 cm⁻¹ are attributable to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal to ligand, because the molar extinction coefficients of the bands are much larger than those commonly assigned to ligand-field transitions [8-11]. The nickel(II) and copper(II) complexes possess a weak absorption band at 15500 and 16900 cm⁻¹, respectively, which is attributed to ligand-field transitions because of having the analogous molar extinction coefficients for the bands usually assigned to d $\rightarrow$ d* transitions [10,11]. This spectral behavior is compatible with that observed for the square-planar coordination of nickel(II) and copper(II) complexes [10,11]. The ligand-field, $\pi \rightarrow \pi^*$ and CT transitions for compounds **H₂L**, **NiL** and **CuL** are compiled in Table 1. Accordingly, it is thought that the tetraaza[14]-annulene skeleton of compound **H₂L** is sparingly distorted upon the substitution reaction at the 7,16-positions, but that of complexes **NiL** and **CuL** is little distorted for the sake of protecting the skeleton with metal coordination.

Table 1

Electronic Absorption Bands for Crown Tetraaza[14]annulene
and its Complexes [a]

Compound	Transition energy in cm^{-1} (ε)
H$_2$L	28700 sh (29000), 31200 (36600), 35600 (31700)
NiL	16900 (5660), 23400 sh (16500), 25600 (29900), 31300 sh (28800), 36100 (48100)
CuL	15500 (1180), 23900 sh (12400), 26000 (26800), 32300 sh (30000), 35500 (36800)

[a] Measured in chloroform at room temperature.

NMR Spectra.

On account of the diamagnetism nickel(II) complex NiL gives well-resolved ^{1}H nmr spectra. The ^{1}H nmr data and their assignments for compounds H$_2$L and NiL are listed in Table 2. The signals for the olefinic protons at the 7,16-positions are extinguished upon the substitution reaction at these positions. The methyl proton signals at the 6,8,15,17-positions show upfield shifts by 0.15 ppm on the substitution reaction at the 7,16-positions. This seems to indicate that the methyl groups are within the shielding zone which is produced by the magnetic anisotropy of the benzene ring in the substituent groups of the 7,16-positions. The aromatic proton signals in the tetraaza[14]annulene skeleton hardly shift upon the substitution reaction, because the aromatic protons are not within the shielding and deshielding zone of the substituted benzene rings. The amine proton signals exhibit downfield shifts by 1.4 ppm on the substitution reaction. The downfield shift is dependent on the deshielding effect of the benzene ring and carbonyl group in the substituent groups of the 7,16-positions. The amine proton signal disappears upon the nickel(II)-coordination. The aromatic proton signals in the tetraaza[14]annulene skeleton reveals upfield shifts by

0.42 ppm on the formation of the nickel(II) complex. The upfield shift is ascribed to the shielding effect that is derived from the magnetic anisotropy of chelating rings formed. The methylene protons in the crown ether groups couple with each other and the signal is split into a multiplet.

Aggregation.

The ^{1}H nmr spectra for compounds H$_2$L and NiL were measured in various solvents, but the spectra scarcely change and broad nmr signals do not appear. Consequently, these spectra are assigned to monomeric compounds [12]. We have already reported self-aggregation of crown tetraaza[14]annulene, that is, 2,3,11,12-bis(1',-4',7',10',13'-pentaoxatridecamethylene)-5,14-dihydro-7,-16-diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine which brings about dimerization of crown phthalocyanine type [4a]. It is quite interesting to note that the present crown tetraaza[14]annulene does not aggregate on the contrary to adopting state of aggregation on the previous crown tetraaza[l4]annulene. It can therefore be presumed that the present crown tetraaza[14]annulene and its complexes are difficult to set off self-aggregation through the steric hindrance which is based upon the introduction of the substituent groups at the 7,16-positions.

Cation Complexation.

We investigated the stoichiometry of complexation for a variety of alkali metal salts with crown tetraaza[14]annulene H$_2$L and its complexes NiL and CuL with ultraviolet and visible spectra in chloroform-methanol (4:1 vol/vol). Addition of Li$^+$ and Na$^+$ to compounds H$_2$L, NiL and CuL in chloroform-methanol solution does not form any appreciable changes in the visible spectra of the compounds. Nevertheless, marked changes are observed, when K$^+$ and Cs$^+$ ions are added to the solution of compounds H$_2$L, NiL and CuL. An example of the above spectral change is shown in Figure 2. It is found that increasing addition of K$^+$ and Cs$^+$ ions causes (a) reduction in intensity, (b) broadening and (c) blue shift (~ 4nm) of the intense band in the 320-400 nm range. These pro-

Table 2

^{1}H NMR Data for Crown Tetraaza[14]annulene and its Nickel(II) Complex [a]

Compound	Methyl (6,8,15,17-CH$_3$)	Crown (-OCH$_2$CH$_2$O-)	(Aromatic)	Macrocycle (Aromatic)	Amine (N-H)
H$_2$L	1.98(s)	3.77 (m)	7.58 (m)	7.03 (s)	14.04 (br, s)
NiL	1.92(s)	3.78(m)	7.63(m)	6.61(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, m = multiplet; br = broad.
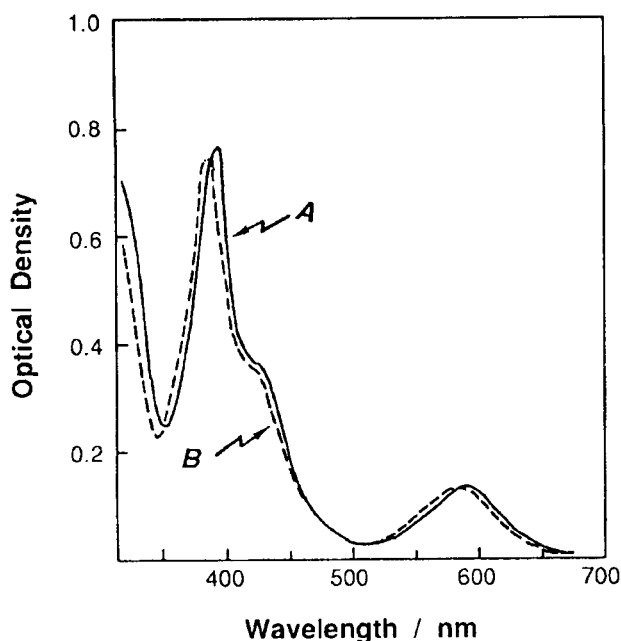
Figure 2. Electronic spectra for crown tetraaza[14]annulene nickel(II) complex (**NiL**) (5 x 10^{-4} mol/l) at room temperature in chloroform-methanol (4:1 vol/vol). **A**, in the absence of any cations; **B**, in the presence of CsNCs (5 x 10^{-3} mol/l).

nounced spectral changes indicate that in the blended solvent used compounds **H₂L**, **NiL** and **CuL** form 1:2 (host-guest) complexes with Li^+ and Na^+ ions and 2:2 complexes with K^+ and Cs^+ ions. The experimentally observed reduction in intensity, broadening and blue shift of the intense band in the K^+ and Cs^+ ion complexation studies are analogues to those for the formulation of a dimer in porphyrin and/or phthalocyanine system [1d,2e]. These remarkable spectral changes are much smaller in magnitude than those observed for the previous crown tetraaza-[14]annulene and its complexes [4a]. The reason for the spectral changes is as follows. The present crown tetra-aza[14]annulene and its complexes are hard to give rise to dimerization because of the steric hindrance caused by the substituent groups of the 7,16-positions and the methyl groups of the 6,8,15,17-positions and because of depressing the rotation for rigidity of the carbonyl bond joining the crown ether groups.

The choice of **CuL** presents an esr probe to study the cation complexation by these macrocyclic compounds. The esr spectrum for addition of Na^+ ions to **CuL** is similar to that observed for cation-free **CuL**, as shown in Figure 3 (upper trace). A possible reason is that the introduction of Na^+ ions into crown ether cavities prevents any likely aggregation of **CuL** due to strong repulsion among the two macrocycles induced by two Na^+ ions on each complex. Interesting changes in the esr spectrum of **CuL** is observed on addition of K^+ ions, as shown in Figure 3 (lower trace). The four parallel lines of the Cu(II) (I = 3/2)

are broken and the set is split into seven lines that are not appreciably resolved. Further, strong perpendicular transitions are observed in the g ≈ 2 range. Support for the existence of a dimer complex stems from the appearance of a half-field spectrum of equal spacing of 100 G [1d,2f,4a]. These indicate that sandwiching two K^+ ion crown ether moieties, this complex becomes a dimer type. This result is consistent with the corresponding electronic spectral behavior.
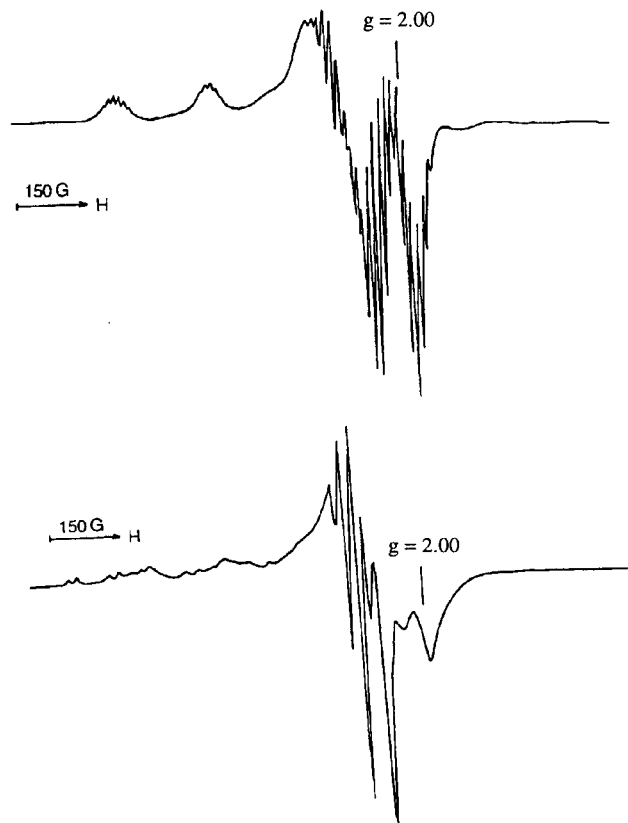

Figure 3. Esr spectra for crown tetraaza[14]annulene copper(II) complex (**CuL**) (8 x 10^{-4} mol/l) at 77 K in chloroform-methanol (4:1 vol/vol): **Upper trace**, in the absence of any cations; **Lower trace**, in the presence of CH₃COOK (8 x 10^{-3} mol/l).

EXPERIMENTAL

Melting points were observed on a Yanaco MP-500D micro melting point apparatus (hot-plate type). The mass spectra (FD) for compounds **H₂L**, **NiL** and **CuL** were carried out with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Infrared spectra in the 400-4000 cm^{-1} region were recorded on a Hitachi 260-30 spectrophotometer at room temperature as potassium bromide pellets. Electronic spectra covering the 12500-40000 cm^{-1} range were obtained with a Shimadzu UV 200S double beam spectrophotometer for chloroform and chloroform-methanol solutions at room temperature. Elemental analyses were determined with a Yanaco CHN corder MT3. ¹H nmr spectra were taken using a JEOL JNM-FX 60 spectrometer in chloroform-d at room temperature. Chemical shifts are given

in ppm relative to TMS as an internal reference standard. The esr spectra were recorded on a JEOL JES-RE2X X-band spectrometer equipped with a 100 kHz field modulation unit. The spectrum of **CuL** were measured in chloroform-methanol (4:1 vol/vol) at 77 K, the concentration being maintained at 8 x 10^{-4} mol/l. Manganese ion diffused thermally into magnesium oxide was used to gain the standard reference signals for the measurements.

Synthesis of the Macrocycle and its Complexes.

Catechol Diacetate (**1**).

This was prepared after the method of Smid et al. [5] from catechol (73.33 g) and acetic anhydride (126 ml). The crude product was recrystallized from n-heptane to give compound **1** as colorless needles. The yield was 104.90 g (81%) (lit [5] mp 63-64°), mp 61.3-62.5°; ir: ν C=O 1760, ν C-O-C 1208, 1035 cm^{-1}; ^{1}H nmr (chloroform-d): 2.29 (s, 6H, -CH$_3$), 7.21 (s, 4H, aromatic) ppm.

Anal. Calcd. for C$_{10}$H$_{10}$O$_4$: C, 61.85; H, 5.19. Found: C, 61.75; H, 5.20.

3,4-Dihydroxyacetophenone (**2**).

Compound **2** was prepared from compound **1** (24.40 g) and anhydrous aluminium chloride (33.62 g) in nitrobenzene (100 ml) after Smid et al. [5]. The crude product was purified by recrystallization from benzene to afford 9.82 g (51%) of fine pale yellow crystals (lit [5] mp 121-123°), mp 117.3-119.7°; ir: ν O-H 3375, ν C=O 1668 cm^{-1}; ^{1}H nmr (chloroform-d): 2.47 (s, 3H, -CH$_3$), 6.91 (m, 1H, aromatic), 7.26 (m, 2H, aromatic), 8.50 (s, 2H, O-H) ppm.

Anal. Calcd. for C$_8$H$_8$O$_3$: C, 63.15; H, 5.30. Found: C, 63.13; H, 5.33.

1,11-Dichloro-3,6,9-trioxaundecane (**3**).

The synthetic procedure for compound **3** has been described previously [4a].

2,3-(4'-Acetobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (**4**).

This compound was prepared by using the method of Smid et al. [5] from compound **2** (11.40 g), compound **3** (17.44 g) and sodium hydroxide (6.53 g) dissolved in water (13.3 ml) in 1-butanol (159 ml) under a nitrogen atmosphere. The oily substance was extracted with n-heptane to yield the crude product. Recrystallization from n-heptane afforded the pure product **4** as white flaky crystals. The yield was 10.68 g (46%) (lit [5] mp 96-97°), mp 92.5-96.4°; ir: ν C-H 2920, 2870, ν C=O 1660, ν C-O-C 1282, 1132 cm^{-1}; ^{1}H nmr (chloroform-d): 2.55 (s, 3H, -CH$_3$), 3.68-4.26 (m, 16H, -OCH$_2$CH$_2$O-), 6.90 (m, 1H, aromatic), 7.46 (m, 2H, aromatic) ppm.

Anal. Calcd. for C$_{16}$H$_{22}$O$_6$: C, 61.92; H, 7.15. Found: C, 61.88; H, 7.14.

2,3-(4'-Carboxybenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (**5**).

This was prepared from compound **4** (7.00 g), bromine (14.57 g) and sodium hydroxide (14.67 g) dissolved in water (100 ml) after Smid et al. [6]. The crude product was recrystallized from ethanol to give 5.28 g (75%) of white flaky crystals (lit [6] mp 180°), mp 187.7-189.1°; ir: ν O-H 2700-2500 (br), ν C-H 2910, 2860, ν C=O 1680, ν C-O-C 1279, 1139 cm^{-1}; ^{1}H nmr (dimethyl

sulfoxide-d$_6$): 3.62-4.02 (m, 16H, -OCH$_2$CH$_2$O-), 7.01 (m, 1H, aromatic), 7.54 (m, 2H, aromatic), 12.40 (s, 1H, O-H) ppm.

Anal. Calcd. for C$_{15}$H$_{20}$O$_7$: C, 57.69; H, 6.45. Found: C, 57.66; H, 6.39.

2,3-(4'-Chloroformylbenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (**6**).

A modification of the procedure of Smid et al. [6] was used to prepare this compound. A mixture of compound **5** (2.00 g) and thionyl chloride (50 ml) was heated under reflux for 4 hours with stirring and being protected from the moisture, and followed by removal of excess thionyl chloride under vaccum. A small amount of benzene was added and the solution was evaporated to dryness. The latter procedure was repeated three times. The residual product was vacuum dried to yield 2.02 g (95%) of fine ivory crystals, mp 61.3- 63.2°; ir: ν C-H 2920, 2860, ν C=O 1745, 1712, ν C-O-C 1275, 1135, ν C-Cl 682 cm^{-1}; ^{1}H nmr (chloroform-d): 3.75-4.24 (m, 16H, -OCH$_2$CH$_2$O-), 6.95 (m, 1H, aromatic), 7.58 (m, 2H, aromatic) ppm.

5,14-Dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (**7L**), (6,8,15,17-Tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (**7Ni**) and (6,8,-15,17-Tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)copper(II) (**7Cu**).

The preparative procedure for compounds **7L, 7Ni** and **7Cu** have been reported previously [12].

(7,16-Bis((3',4'-(1'',4'',7'',10'',13''-pentaoxatridecamethylene))-benzoyl)-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (**NiL**).

A mixture of complex **7Ni** (0.46 g) and compound **6** (1.52 g) in dry toluene (600 ml) containing triethylamine (5.08 g) was kept under reflux for one week with stirring and being protected from the moisture. Allowed to stand at room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness under diminished pressure. The resulting solid was chromatographed on activated aluminium oxide (200 mesh, Wako Pure Chemical Industries, Ltd.) and eluted with chloroform. The third effluent was collected, evaporated to dryness in vacuo and vacuum dried to obtain fine dark green crystals **NiL**. The yield was 0.68 g (60%), mp 140.9-149.7° dec; ir: ν C-H 2920, 2870, ν C=O 1643, ν C=C and C=N 1535, 1512, ν C-O-C 1268, 1138 cm^{-1}; ms: (FD) m/z 988 (M$^+$, ^{58}Ni).

Anal. Calcd. for C$_{52}$H$_{58}$N$_4$O$_{12}$Ni: C, 63.10; H, 5.91; N, 5.66. Found: C, 62.75; H, 5.95; N, 5.55.

7,16-Bis((3',4'-(1'',4'',7'',10'',13''-pentaoxatridecamethylene))-benzoyl)-5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,-8,11]tetraazacyclotetradecine (**H$_2$L**).

A mixture of compound **7L** (0.35 g) and compound **6** (1.29 g) was dissolved in dry toluene (700 ml) containing triethylamine (3.99 g) under argon atmosphere and heated under gentle reflux for six days with stirring and being protected from the 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. The resulting solid was chromatographed on activated aluminium oxide using dichloromethane as an eluent. The second fraction was collected, evaporated to dryness in vacuo and vacuum dried to give compound **H$_2$L** as fine yellow crystals. The yield was 0.35 g

(37%), mp 81.6-87.1° dec; ir: ν C-H 2905, 2860, ν C=O 1640 (br), ν C=C and C=N 1550, 1505, ν C-O-C 1260, 1130 cm^{-1}; ms: (FD) m/z 932 (M$^+$).

Anal. Calcd. for $C_{52}H_{60}N_4O_{12}$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.65; H, 6.73; N, 5.88.

(7,16-Bis((3',4'-(1'',4'',7'',10'',13''-pentaoxatridecamethylene))benzoyl)-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)copper(II) (**CuL**).

A mixture of complex **7Cu** (0.45 g) and compound **6** (1.50 g) in dry toluene (600 ml) containing triethylamine (4.36 g) was held under reflux for four days with stirring and being protected from the moisture. After being permitted to stand at room temperature, triethylamine hydrochloride was taken off by filtration. The filtrate was freed of solvent under diminished pressure. The resulting solid was chromatographed over activated aluminium oxide eluted with dichloromethane. The third effluent from the column was vaporized to dryness under reduced pressure. The resulting product was chromatograhed on activated aluminium oxide using dichloromethane-benzene (1:1 vol/vol) as an eluent again. The second fraction was collected, evapo-rated to dryness *in vacuo* and vacuum dried to obtain 0.48 g (44%) of fine dark green crystals **CuL**, mp 104.9-112.3° dec; ir: ν C-H 2930, 2866, ν C=O 1641, ν C=C and C=N 1529, 1510, ν C-O-C 1263, 1127 cm^{-1}; ms: (FD) m/z 993 (M$^+$, ^{63}Cu).

Anal. Calcd. for $C_{52}H_{58}N_4O_{12}Cu$: C, 62.80; H, 5.88; N, 5.63. Found: C, 63.06; H, 6.02; N, 5.27.

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