Studies on Reactions of a Nickel Complex of a New Completely Conjugated Macrocyclic Ligand

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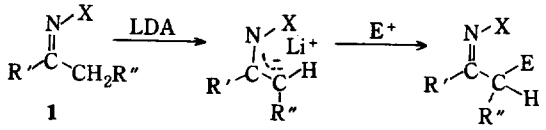
The macrocyclic nickel complex of the molecular formula $[Ni(C_{32}H_{26}N_4)]$ has been synthesized from the template condensation reaction between 1-benzoylacetone and *o*-phenylenediamine in the presence of nickel acetate. Protonation and deuterium exchange reactions of the demetallated macrocyclic ligand and the nickel complex have been carried out. The infrared, electronic and proton magnetic resonance spectral data of both compounds are compared and discussed; protonation of the macrocyclic ligand take place at the nitrogen atoms and all the amine protons undergo very rapid deuterium exchange while the methine protons undergo very slow exchange. On the other hand, protonation of the nickel complex occurs at the nitrogen atoms and only amine protons undergo rapid deuterium exchange. Protonation and deprotonation of the nickel complexes proceed reversibly.

Introduction

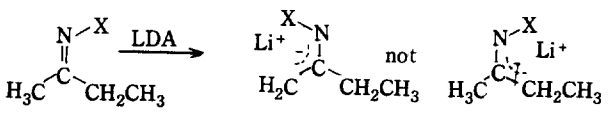
Macrocyclic polypyrrolic ligands and their transition metal complexes are nucleophiles capable of undergoing reaction with electrophiles at several sites such as nitrogen, meso-carbon and metal. In general, electrophile substitution and protonation of the unsaturated tetraaza macrocyclic ligands occur much more easily at nitrogen than at meso-carbon in the absence of activating substituents.[1] Thus, the reaction at nitrogen is preferred in the consequence of two -N= atoms in the macrocyclic skeleton, which confer on the macrocyclic ring properties related to those of pyridine. N-alkylation of the nitrogen donor atoms have been observed for porphyrins and related macrocycles.[2] However, it has been also shown that octa-alkylporphyrin may undergo the electrophilic substitution reaction at meso-carbon center.[1,3]. The "masked enolates," **1**, are known to exhibit a marked thermodynamic preference for the *syn* configuration at the C-N partial double bond.[4-8]



1

X = NR_2, OR, alkyl or aryl
R' = H or alkyl, R" = alkyl
E = electrophile
LDA = lithium diisopropylamide

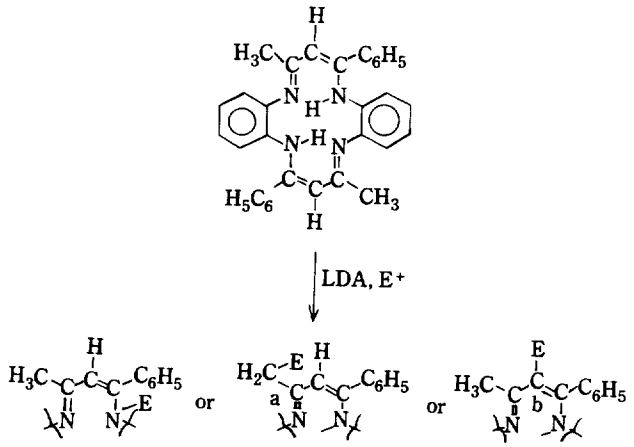
Sometimes steric hindrance by bulky substituents attached to the nitrogen atom may result in the formation of **2** type isomers exclusively.[9,10]



2 **3**

Thus, there are three active sites including nitrogen atom and two kinds of carbon centers (*a* and *b*) in the macrocyclic ligand shown below.

When a metal is incorporated to a macrocycle, the nucleophilicity of the nitrogen is reduced due to the involvement of the lone pair electrons on -N=atoms in complex formation. Like the macrocyclic ligands, the electrophilic reactions of the



transition metal complexes may occur at one of the three sites of the macrocyclic, i.e. nitrogen, meso-carbon or methyl-carbon atom. Methylation of palladium octaethylporphyrin yielded the meso-methyl palladium porphyrin[11]. Formylation and protonation of $[Ni(AT)]^+$ and $[Cu(AT)]^+$ (AT: 11, 13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienato ligand) showed the reactive site to be the methine carbon atom[12,13]. On the other hand, the methylation of a copper corrole has been shown to take place at the nitrogen atom[14].

In our laboratory the macrocyclic nickel complex of the molecular formula $Ni(C_{32}H_{26}N_4)$ has been synthesized from the template condensation reaction between 1-benzoylacetone and *o*-phenylenediamine in the presence of nickel acetate[15]. We now report the protonation and deuterium exchange reactions of the dematallated macrocyclic ligand and the nickel complex. The infrared, electronic and proton magnetic resonance spectra and deuterium exchange reaction of the reaction products are compared and discussed.

Experimental

Materials. Nickel acetate tetrahydrate ($NiAc_2.4H_2O$) was purchased from Aldrich Chemical Co., Inc. Hydrogen chloride gas of extra pure quality was available from Yakuri Pure Chemicals Co., Ltd. All other chemicals were reagent-grade quality and were used without further purification. Lithium diisopropylamide (LDA) was freshly prepared from the reaction of *n*-BuLi with diisopropylamine in THF under

nitrogen atmosphere before every reaction. All reagent-grade solvents were dried by distillation over appropriate drying agents under nitrogen prior to use.

Instruments. Infrared spectra covering 400-4000 cm^{-1} range were taken on an Analect FX-6160 FT-IR spectrometer. Proton NMR spectra were measured on a Varian T-60A spectrometer in $CDCl_3$. Fourier-mode proton NMR spectra were collected on a Bruker AM-200SY spectrometer in certain cases. Chemical shifts on the proton NMR spectra are reported relative to tetramethylsilane as an internal strandard. Electronic absorption spectra of the solutions of the complexes were recorded on a Beckman DU-40 spectrophotometer. Melting points were obtained on a Electrothermal apparatus. Analytical thin layer chromatography was performed on silica gel coated glass plates (Merck 60F-254). Basic alumina (Brockman activity I) was used for column chromatography. Electrical conductivity was measured using YSI Model 31 conductivity bridge. Elemental analyses were performed by the analytical chemistry laboratory of KAIST.

Synthesis 6,15-Dimethyl-8,17-diphenyldibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinatonickel (II), 1. A solution of 1-benzoylacetone (16.20g) and *o*-phenylenediamine (10.80g) in methanol (150 m*l*) was heated to reflux for 4 hours. To the above solution was added 12.45g of $NiAc_2\ 4H_2O$. Reflux was continued for additional 25 hours and the solution was cooled to room temperature. Green crystalline product was filtered, washed with methanol and dried *in vacuo*. However, the product was found to contain some by-product on a TLC plate. The main product of the present interest was separated through a column of basic alumina employing 1:1 mixture of benzene and hexane as an eluent. Upon solvent removal, green crystals were obtained, washed with methanol and dried *in vacuo*. Yield 30%.

M.P. > 300°C, Rf = 0.48
Anal. Calcd. for $Ni(C_{32}H_{26}N_4)$: C, 73.10; H, 4.95; N, 10.66
Found: C, 73.2; H, 4.99; N, 10.3.

5,9,14,18-Tetrahydro-6,15-dimethyl-8,17-diphenyldibenzo[b,i] [1,4,8,11]tetraazacyclotetradecinium dichloride, 2. Anhydrous hydrogen chloride gas was bubbled through a solution of the nickel complex, **1**, in absolute ethanol (20 m*l*) for 25 min. The initial green color of the solution rapidly turned red-brown and diethyl ether (40 m*l*) was added to help precipitation. Bright yellow precipitate was collected after the solution sat overnight. It was washed with diethyl ether and dried *in vacuo*. Yield 53%.

m.p. 225-228°C
Anal. Calcd. for $[C_{32}H_{30}N_4]Cl_2 \cdot 2H_2O$: C, 66.55; H, 6.23; N, 9.70. Found: C, 66.50; H, 5.45; N, 9.28.

5, 14-Dihydro-6, 15-dimethyl-8, 17-diphenyldibenzo [b,i] [1,4,8,11]tetraazacyclotetradecine, 3. To a boiling solution of **2** (0.90g) in absolute ethanol (20 m*l*) was added 15 drops of triethylamine. The resulting mixture was heated to reflux for 30 min. After the solution was cooled to room temperature, an orange crystalline product was obtained upon filtration; it was washed with absolute ethanol and dried *in vacuo*. Yield 81%. Protonation of this product with conc. HCl gives the above protonated ligand.

m.p. 242-244°C
Anal. Calcd. for $C_{32}H_{28}N_4 \cdot \frac{1}{2}H_2O$: C, 80.50; H, 6.07; N, 11.74
Found: C, 80.9; H, 5.96; N, 11.6.

5,14-Dihydro-6,15-dimethyl-8,17-diphenyldibenzo [b,i] [1,4,8,11]tetraazacyclotetradecinenickel (II) perchlorate, 4. To a boiling solution of **1** (0.21g) in acetone was added 0.10 m*l* of 60% $HClO_4$. After 20 minutes' reflux of the resulting mixture, pale green crystals were obtained. The product was filtered, washed with acetone and dried *in vacuo*.

m.p. > 300°C
Anal. Calcd. for $[Ni(C_{32}H_{28}N_4)](ClO_4)_2$: C, 52.91; H, 3.86; N, 7.71. Found: C, 52.7; H, 4.03; N, 7.42.

Attempted methylation and acetylation of neutral ligand. To a solution of **3** (0.22g) in 1,4-dioxane (20 m*l*) was added 3 m*l* of CH_3I and the resulting mixture was brought to reflux. Pale yellow solid was precipitated after 3 hours' reflux. The product was filtered, washed with diethyl ether. Another attempt for electrophilic reactions of the macrocyclic ligand has been made using electrophiles (CH_3I, $CH_3\overset{O}{\overset{\|}{C}}Cl$) in the presence of LDA. The reaction resulted in the formation of mixture.

Results and Discussion

Synthesis. The template reaction of $NiAc_2 \cdot 4H_2O$ with 1-benzoylacetone and *o*-phenylenediamine yields green colored product of the formulation $Ni(C_{32}H_{26}N_4)$, **1**. The product was purified using a basic alumina column to remove some by-products as described in the experimental section. Although the exact structure of this nickel complex should be determined by X-ray crystallography, we can safely conclude the complex is 6,15-dimethyl-8,17-diphenyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecinatonickel (II) instead of 6,17-dimethyl-8,15-diphenyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecinatonickel (II) due to the severe steric hindrance of the latter. When **1** is treated with anhydrous hydrogen chloride, nickel is stripped from the macrocyclic complex. The formulation of this protonated ligand is found to be the following; 5,9,14,18-tetrahydro-6,15-dimethyl-8,17-diphenyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecinium dichloride, **2**. Neutralization of the protonated ligand with triethylamine gives the macrocyclic ligand of this work; 5,14-dihydro-6,15-dimethyl-8,17-diphenyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecine, **3**. The protonation and neutralization reactions of this ligand system occur reversibly.

The infrared spectrum of the nickel complex with dianionic macrocyclic ligand, $C_{32}H_{26}N_4^{2-}$, has certain features that enable us to distinguish between the coordinated and the free ligand. The useful change is in the C=N stretching mode. Upon coordination of nitrogen to a metal atom, decrease both in the frequency and in the intensity of these modes is expected[16,17]. The absorption band for C=N stretching mode which appears at 1613 cm^{-1} with very strong intensity in the free ligand is shifted to the lower frequency region at 1579 cm^{-1} with weak intensity. The same trend is observed for the similar type of tetramethyl-substituted macrocyclic ligand, 5,14-dihydro-6,8,15,17-tetramethyldibenzo [b,i] [1,4,8,11] tetraazacyclotetradecine ($C_{22}H_{24}N_4$), **5**[17]. The C=N stretching mode for the nickel complex, $Ni(C_{22}H_{22}N_4)$, appears at 1560 cm^{-1} with medium intensity whereas that for the free ligand appears at 1630 cm^{-1} with strong intensity. The C=N absorption band in the protonated ligand is not observable since it is masked by the absorption band of water molecule in the crystal lattice.

Proton nmr spectral data for the dimethyldiphenyl-substituted macrocyclic ligand of this work and its nickel complex

Table 1. Proton NMR Spectral Data[a]

Compound	Solvent	methyl -CH_3	methine H-C=	aromatic	amine N-H
$Ni(C_{32}H_{26}N_4)$	$CDCl_3$	2.21(s)	5.02(s)	5.56-5.96(m), 6.62-6.86(m)} d, 7.32(s)[e]	
$C_{32}H_{28}N_4$[b]	$CDCl_3$	2.30(s)	5.14(s)	6.10-7.94(m)	12.73(br)
$Ni(C_{22}H_{22}N_4)$	$CDCl_3$	2.07(s)	4.82(s)	6.28-6.82(m)	
$C_{22}H_{24}N_4$[c]	$CDCl_3$	2.11(s)	4.83(s)	6.61-7.09(m)	12.63(br)

a) Chemical shifts in ppm for TMS. S-singlet, m-multiphet, br-broad, b) $C_{32}H_{28}N_4$; dimethyldiphenyl-substituted ligand c) $C_{22}H_{24}N_4$; tetramethyl-substituted ligand d) Chemical Shift for benzenoid rings e) Chemical shift for phenyl substituents

are compared with those for tetramethyl-substituted macrocyclic ligand and its nickel complex in Table 1. The methine proton peak of **3** is shifted to downfield by **ca** 0.3 ppm relative to that of **5**. As the extent of down-field shift by cyclization is larger than that for **5**, conjugation throughout the macrocyclic skeleton of the macrocyclic ligand of this work seems to be more extensive than observed in **5**. The signal for protons attached to nitrogen is broad due to coupling with nitrogen nucleus (I = 1).

Upon formation of the nickel complex, methine peak of this work is shifted to upfield by 0.12 ppm. This may be attributed to the reduction of the ring current by incorporation of nickel (II)[18]. The proton nmr spectrum of the nickel complex can not be taken in CD_3CN, since the acetonitriles coordinate on the axial position to yield 6-coordinate paramagnetic nickel complex. Magnetic moment measured by NMR technique[19] is 2.57 B.M., indicating diamagnetic square planar nickel complex and paramagnetic octahedral complex are in equilibrium in solution.

Protonation and Deuterium Exchange Reaction. The protonation reactions of the neutral macrocyclic ligand and the nickel complex have been carried out as the simplest electrophilic reaction. The reaction scheme is shown in Figure 1. The reaction of the macrocyclic ligand with two equivalents of either HCl of $HClO_4$ yields bright yellow solid of the formulation $[C_{32}H_{30}N_4]X_2 \cdot nH_2O$ ($X = Cl^-$, ClO_4^-). Electrical conductivity of **2** is 280 $cm^2ohm^{-1}mol^{-1}$ in acetone, indicating the protonated ligand is a 1:2 electrolyte. The proton nmr spectrum in DMSO-d_6 shows the peak at 1.93 ppm for methyl protons and the peak at 5.07 ppm for methine protons. The methyl and methine proton peaks of the protonated ligand are in the upfield region compared with that of the neutral ligand. This indicates these proton peaks are not deshielded on protonation as observed for porphyrins and dipyrromethenes[20,21]. There are two sharp peaks with same intensity for amine protons of the protonated ligand. The one on the upfield region (11.25 ppm) can be assigned to the amine proton near to the methyl groups and the other (11.97 ppm) to the amine proton near to the phenyl groups due to the different electronic effect between methyl and phenyl groups. The reason of amine peak being at more upfield position in the protonated than in the neutral ligand may be explained as follows. The protonation of the neutral ligand may cause the reduction in the π-electron numbers by two, thus the ring current of the protonated macrocycle has been changed so that the N-H resonance is shifted to upfield region. The intensity of each amine peak is also same as that of the methine

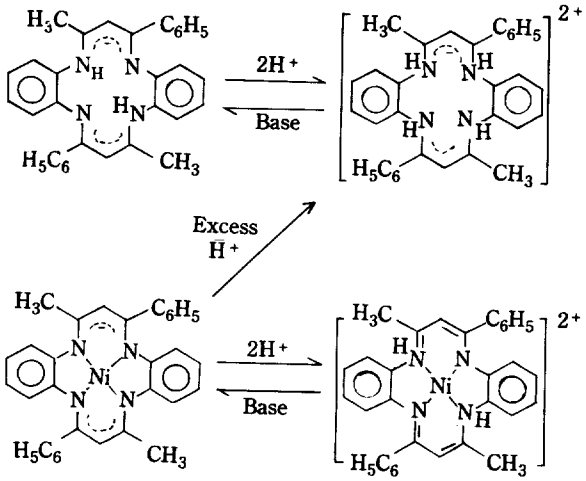


Figure 1. The reaction scheme for protonation.

peak, which tells two nitrogens and the methine carbon have the same number of protons attached to themselves (2:2:2). Thus, protonation of the neutral ligand must have occurred at the nitrogen atoms rather than at the methine carbon atoms. Deuterium exchange reaction of the protonated ligand in DMSO-d_6 with D_2O-CF_3COOD was examined by direct proton counting on the complete deuteration at all four amine positions (<10 min.) and very slow exchange of the methine protons (5 days). The reaction of the nickel complex, **1**, with two equivalents of 60% $HClO_4$ in acetone give pale green protonated nickel complex, $[Ni(C_{32}H_{28}N_4)](ClO_4)_2$, **4**. The infrared spectrum of the compound shows the N-H absorption band at 3210 cm^{-1} and C=N stretching mode at 1644 cm^{-1}. The absorption due to the perchlorate ion is observed at 1091 cm^{-1}. The proton nmr spectrum in $CDCl_3$-CF_3COOH (pH 2) shows the methyl peak at 2.27 ppm (singlet), the methine peak at 4.75 ppm (singlet), the N-H peak at 9.52 ppm (broad) and the peaks for benzene rings in the range of 6.32-7.25 ppm (multiplet). The peak for the proton of trifluoroacetic acid is also observed at 11.6 ppm. In order to confirm the N-H peak (9.52 ppm), the proton nmr spectrum has been taken in $CDCl_3$-CF_3COOD and both peaks at 9.52 ppm and 11.6 ppm disappeared. Besides the above observation, the intensity ratio of the methine peak to the methyl peak remains same on protonation. Therefore, the protonation of **1** must have taken place at the nitrogen atoms and the protons on nitrogen atoms undergo the deuterium exchange reaction as observed in the neutral ligand. However, the methine proton of the protonated nickel complex does not undergo the deuterium exchange reaction like the porphyrin complex[22]. The proton nmr spectra of **1**, the protonated nickel complex both in $CDCl_3$-CF_3COOH and in $CDCl_3$-CF_3COOD are shown in Figure 2. The electrical conductivity of the protonated nickel complex in acetone-$HClO_4$ (pH 2) is 289 $cm^2ohm^{-1}mol^{-1}$, which corresponds to the value of 1:2 electrolyte. The protonated nickel complex is easily deprotonated in common organic solvents even without addition of a base. The proton nmr spectrum of the deprotonated complex is identical to that of the original nickel complex. When the nickel complex, **1**, is treated with excess of acid, demetallation takes place very rapidly to give the protonated ligand.

Attempted Methylation of Neutral Ligand. Electro-

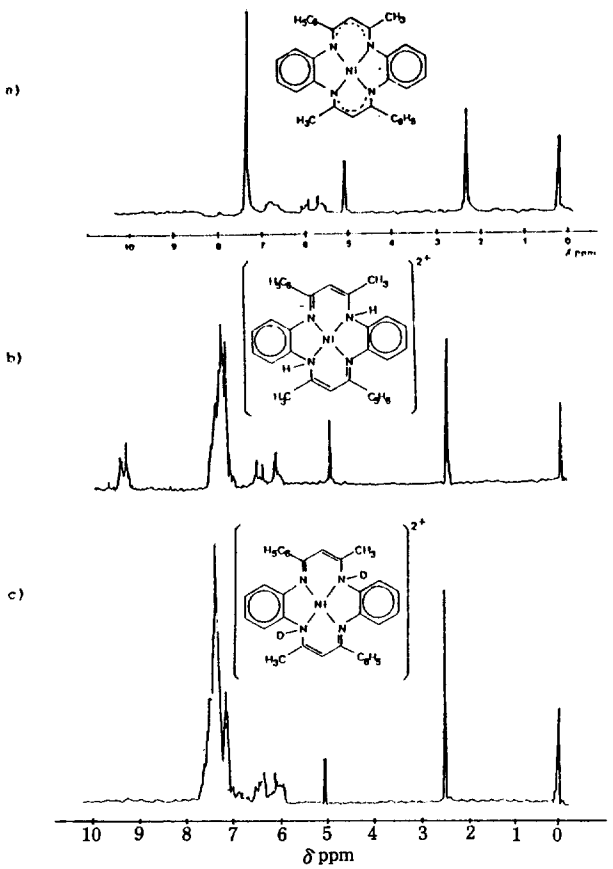


Figure 2. Proton nmr spectra of a) $Ni(C_{32}H_{26}N_4)$, b) $[Ni(C_{32}H_{28}N_4)](ClO_4)_2$ in $CDCl_3$-CF_3COOH and c) $[Ni(C_{32}H_{28}N_4)](ClO_4)_2$ in $CDCl_3$-CF_3 COOD

Table 2. Electronic Spectral Data for Nickel Complexes In the Range 16,000-30,000 cm^{-1}

Compound	Absorption in cm^{-1}(ε)		
$Ni(C_{32}H_{26}N_4)$	16,600(9,300)	22,400(sh.24,000)	24,800 (40,400)
$[Ni(C_{32}H_{28}N_4)](ClO_4)_2$	15,100(3,200)	23,400(17,500)	
$Ni(C_{18}H_{14}N_4)$[a]	19,900(7,200)	21,600(7,620)	23,600 (64,400)

[a] $C_{18}H_{14}N_4$; dibenzo [b,i][1,4,8,11]tetraazacyclotetradecinato ligand[16].

philic substitution reaction of the demetallated macrocyclic ligand and the nickel complex have been attempted using methyl iodide and acetyl chloride with or without addition of a base, LDA. Both reactions lead to the formation of the mixture, which is mostly the starting material. For example, the proton nmr spectrum of the reaction product of the neutral ligand with methyl ioide shows two kinds of methyl peaks at 2.33 ppm and 2.21 ppm with different intensity (1:3) as well as two kinds of methine peaks at 5.13 ppm and 5.02 ppm (1:2). The methylation of the macrocyclic ligand doesn't seem to be impossible. Separation and full characterization of the mixture are in progress, so the paper about this will be published in the near future.

Electronic Spectra. Visible and ultraviolet spectral data for the nickel complex covering 16,000-30,000 cm^{-1} range are listed in Table 2. The absorption bands appearing in the energy region greater than 16,000 cm^{-1} with large extinction coefficients (10^3~10^4) are reasonably assigned to π-π^* transition within the ligand molecule and charge transfer transitions from metal to ligand[23]. The general features of the spectra of **1** and **4** are similar to those observed for the square planar 16π-macrocyclic systems[16,24-26].

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