

## Crystal Structure of [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (L: 2,13-bis(2-pyridylmethyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane)

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### [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (L: 2,13-bis(2-pyridylmethyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane)

#### 錯物の 結晶構造

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#### Abstract

The complex [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1) (L=2,13-bis(2-pyridylmethyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) has been synthesized and characterized by X-ray crystallography. (1) crystallizes in the triclinic, space group  $P\bar{1}$ , with  $a=10.948(2)$ ,  $b=10.948(2)$ ,  $c=14.911(4)$  Å,  $\alpha=93.73(2)$ ,  $\beta=93.77(2)$ ,  $\gamma=99.29(2)^\circ$ ,  $V=1754.8(7)$  Å<sup>3</sup>,  $Z=2$ .  $R1(wR2)$  for 5217 observed reflections of  $[I>2\sigma(I)]$  was 0.048(0.099). The coordination environment around nickel(II) ion shows a distorted octahedron with four secondary and tertiary amines of the macrocycle and two nitrogen atoms of pyridylmethyl groups.

#### 要 約

[Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1) (L=2,13-bis(2-pyridylmethyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) 錯物を 合成하고 構造를 糾明하였다. 이 錯物은 三斜晶系, 空間群  $P\bar{1}$ ,  $a=10.948(2)$ ,  $b=10.948(2)$ ,  $c=14.911(4)$  Å,  $\alpha=93.73(2)$ ,  $\beta=93.77(2)$ ,  $\gamma=99.29(2)^\circ$ ,  $V=1754.8(7)$  Å<sup>3</sup>,  $Z=2$ 로 決定化되었다. 이 錯物의 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度  $R1(wR2)$  값은 5217個의 回折斑點에 대하여 0.048 및 0.099이었다. 中心 nickel(II) 이온은 巨大고리 리간드의 二次 및 三次 아민과 pyridylmethyl 基의 두 個 窒素 原子에 의하여 結合된 若干 일그러진 六配位 八面體 構造를 갖는다.

#### 1. Introduction

Various fully N-functionalized macrocycles containing pendant arms and their metal complexes have attracted considerable attention because of their specific structures and chemical properties, which are often quite different from those of the unsubstituted macrocyclic compounds. Recently, a

number of nickel(II) and copper(II) complexes of the fully N-aminoethyl and N-pyridylmethylated cyclam (1,4,8,11-tetraazacyclotetradecane) have been synthesized.<sup>1-8)</sup> For example, [Ni<sub>2</sub>(taec)Cl<sub>2</sub>(H<sub>2</sub>O)] (taec=tetrakis(2-aminoethyl) cyclam) reveals a mixed-spin binuclear complex containing a low-spin Ni(II) on the basis of the spectral, X-ray analysis and magnetic data.<sup>1-3)</sup> To date, however, only a few par-

tially N-functionalized tetraaza macrocycles and their complexes have been isolated and structurally characterized,<sup>9-11</sup> because of steric hinderance by C-alkyl substituents on the macrocyclic ring. Thus, the partially N-pyridylmethylated macrocyclic complexes are of interest.

In this study, we report herein the synthesis and crystal structures of [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1) (L=2,13-bis(2-pyridylmethyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[14.4.0<sup>1,18</sup>,0<sup>7,12</sup>]docosane).

## 2. Experimental

### 2-1. Materials and Physical Methods

The macrocyclic ligand L was prepared as described previously.<sup>9</sup> IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Electronic spectra were obtained by using a Jasco Uvidec-610 spectrometer. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-II

magnetic susceptibility balance. The diamagnetic corrections were evaluated from Pascal's constants. Elemental analyses and FAB mass spectra were performed by the Korea Basic Science Institute, Taejeon, Korea.

### 2-2. Synthesis of [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1)

A methanol solution (20 mL) of NiCl<sub>2</sub> · 6H<sub>2</sub>O (119 mg, 0.5 mmol) and L (259 mg, 0.5 mmol) was heated to reflux for 1 hour and then cooled to room temperature. The solution was filtered and left at room temperature until the violet crystals formed. The product was filtered and recrystallized from a hot water-acetonitrile (1:1, 10 mL) mixture. Yield: 290 mg (75%). Found: C, 49.44; H, 6.42; N, 10.73. Calc. for C<sub>32</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>6</sub>NiO<sub>8</sub>: C, 49.50; H, 6.49; N, 10.82%. IR (KBr, cm<sup>-1</sup>): 3443, 3248, 2940, 2864, 1612, 1587, 1445, 1309, 1093, 1008, 900, 768, 623. Electronic spectra (H<sub>2</sub>O): λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 525 (7.5). FAB mass (CH<sub>2</sub>Cl<sub>2</sub>, m/z): 776 (M)<sup>+</sup>. μ<sub>eff</sub>: 2.88 μ<sub>B</sub> at 25 °C.

Table 1. Crystal Data and Structure Refinement for [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1)

Empirical formula	C <sub>32</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>6</sub> NiO <sub>8</sub>
Formula weight	776.39
Temperature	292 K
Wavelength	0.71069
Crystal system	Triclinic,
Space group	P $\bar{1}$
Unit cell dimensions	a=10.948(2) Å α=93.73(2) <sup>o</sup> b=10.948(2) Å β=93.77(2) <sup>o</sup> c=14.911(4) Å γ=99.29(2) <sup>o</sup>
Volume	1754.8(7) Å <sup>3</sup>
Z	2
Density (calculated)	1.469 Mg m <sup>-3</sup>
Absorption coefficient	0.764 mm <sup>-1</sup>
F(000)	820
Crystal size	0.36×0.30×0.17 mm
θ range for data collection	2.25 to 24.97 <sup>o</sup>
Index ranges	-13≤h≤12, -13≤k≤12, 0≤l≤17
Reflections collected/unique	5450/5217 (R <sub>int</sub> =0.0512)
Max. and min. transmission	0.884 and 0.769
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	5217/0/457
Goodness-of-fit on F <sup>2</sup>	1.024
Final R indices [I>2σ(I)]	R1 <sup>a</sup> =0.048, wR2 <sup>b</sup> =0.099
R indices (all data)	R1 <sup>a</sup> =0.074, wR2 <sup>b</sup> =0.104
Largest diff. peak and hole	0.659 and -0.597 eÅ <sup>-3</sup>

<sup>a</sup>R1=Σ||F<sub>o</sub>-|F<sub>c</sub>||/Σ|F<sub>o</sub>|.

<sup>b</sup>wR2=[Σ[w(F<sub>o</sub><sup>2</sup>-F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(F<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>.

**Table 2. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ni}(\text{L})](\text{ClO}_4)_2$  (1)**

	x	y	z	U(eq)
Ni(1)	5000	5000	5000	37(1)
N(1)	3144(3)	5039(4)	5314(3)	40(1)
N(2)	4908(4)	3088(4)	5094(3)	48(1)
N(3)	5222(3)	5076(4)	6532(3)	42(1)
C(1)	2850(4)	6190(4)	4908(3)	43(1)
C(2)	1581(4)	6523(5)	5111(3)	50(2)
C(3)	1363(5)	7689(5)	4677(4)	59(2)
C(4)	2340(5)	8746(5)	4950(5)	83(2)
C(5)	6380(5)	1562(5)	5262(4)	73(2)
C(6)	6118(5)	2738(5)	4831(4)	51(2)
C(7)	2324(4)	3913(4)	4882(4)	51(2)
C(8)	2662(5)	2697(5)	5190(4)	65(2)
C(9)	3777(5)	2215(5)	4792(4)	61(2)
C(10)	3594(5)	1942(5)	3766(4)	62(2)
C(11)	3026(4)	5150(5)	6291(3)	54(1)
C(12)	4095(4)	4910(4)	6869(3)	44(1)
C(13)	3967(5)	4702(5)	7767(3)	67(2)
C(14)	4955(6)	4625(7)	8339(4)	90(2)
C(15)	6126(5)	4815(5)	7996(3)	65(2)
C(16)	6183(5)	4998(4)	7112(3)	51(1)
Ni(2)	0	0	0	37(1)
N(4)	-22(4)	1862(3)	-296(3)	39(1)
N(5)	1897(4)	71(3)	-119(3)	45(1)
N(6)	-78(4)	-220(4)	-1533(3)	45(1)
C(17)	-1192(5)	2153(4)	89(3)	42(1)
C(18)	-1526(5)	3416(4)	-106(3)	51(2)
C(19)	-2685(5)	3642(5)	321(4)	54(2)
C(20)	-3739(5)	2646(5)	39(5)	79(2)
C(21)	3446(5)	-1363(5)	-253(4)	74(2)
C(22)	2266(5)	-1117(4)	170(4)	49(1)
C(23)	1086(5)	2676(4)	126(4)	54(2)
C(24)	2316(5)	2349(4)	-170(4)	61(2)
C(25)	2796(5)	1234(5)	224(4)	58(2)
C(26)	3062(5)	1407(5)	1230(4)	65(2)
C(27)	-142(5)	1975(4)	-1299(3)	56(1)
C(28)	90(4)	899(4)	-1867(3)	45(1)
C(29)	302(6)	1051(5)	-2760(4)	71(2)
C(30)	363(7)	54(6)	-3331(4)	93(2)
C(31)	176(5)	-1124(5)	-3010(3)	60(2)
C(32)	-2(4)	-1177(4)	-2112(3)	51(1)
Cl(1)	4201(2)	807(2)	7502(1)	97(1)
O(1)	5319(9)	974(8)	7930(6)	247(5)
O(2)	4004(8)	-338(8)	7075(6)	240(4)
O(3)	4310(20)	1985(14)	7048(10)	138(5)
O(3')	3910(20)	1207(14)	6698(10)	138(5)
O(4')	3765(16)	1070(20)	8299(11)	144(6)
O(4)	3032(16)	720(20)	7952(11)	144(6)
Cl(2)	-108(2)	5108(2)	7500(1)	72(1)
O(5)	-484(6)	5536(6)	6743(4)	162(2)
O(6)	-551(6)	5464(6)	8251(3)	164(3)
O(7)	1077(6)	6236(7)	7602(6)	90(2)
O(7')	911(7)	4571(8)	7761(7)	90(2)
O(8)	-1242(7)	3922(6)	7383(6)	93(2)
O(8')	414(9)	4085(7)	7201(7)	93(2)

U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### 2-3. Crystallography

All measurements were carried out with an Enraf-Nonius CAD4 diffractometer. Crystal parameters and details of the data collection and refinement are summarized in Table 1. The crystal (**1**) was mounted on the diffractometer, and used for data collections at room temperature with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71069$  Å). Accurate cell parameters and a crystal orientation matrix were determined by least-squares fit of 25 reflections. An asymmetric unit of intensity data were collected in the  $\omega$ -2 $\theta$  scan mode. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption correction ( $\phi$ -scan) was applied. The structures were solved by direct methods<sup>12)</sup> and refined<sup>13)</sup> on  $F^2$  by full-matrix least squares with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Final atomic coordinates and equivalent displacement parameters are given in Table 2.

### 3. Results and Discussion

An ORTEP diagram of **1** with the atomic labelling scheme is shown in Fig. 1 and the selected bond lengths and angles are presented in Table 3. There are two crystallographically independent [Ni(L)](ClO<sub>4</sub>)<sub>2</sub>, in each of which resides at a center of inversion. The structure of **1** consists of [Ni(L)]<sup>2+</sup> cation and two ClO<sub>4</sub><sup>-</sup> ions, which are disordered over two sites. The complex cation [Ni(L)]<sup>2+</sup> shows that the two pyridylmethyl groups are attached to the less sterically hindered nitrogen atoms of the macrocycle. The macrocyclic ligand adopts a thermodynamically the most stable *trans*-III configuration. The pyridylmethyl pendant arms and the methyl groups in a six-membered chelate ring are *anti* with respect to the plane. The coordination environment around nickel(II) ion shows a distorted octahedron with four secondary and tertiary amines of the macrocycle and two nitrogen atoms of pyridylmethyl groups. The average Ni-N bond distance (2.162(2) Å) of six Ni-N bonds is similar to that observed for the octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands.<sup>14-16)</sup> However, the average Ni(1)-N<sub>4</sub> and Ni(2)-N<sub>4</sub> bond distances of 2.108(3) and 2.102(3) Å are longer than those of the axial

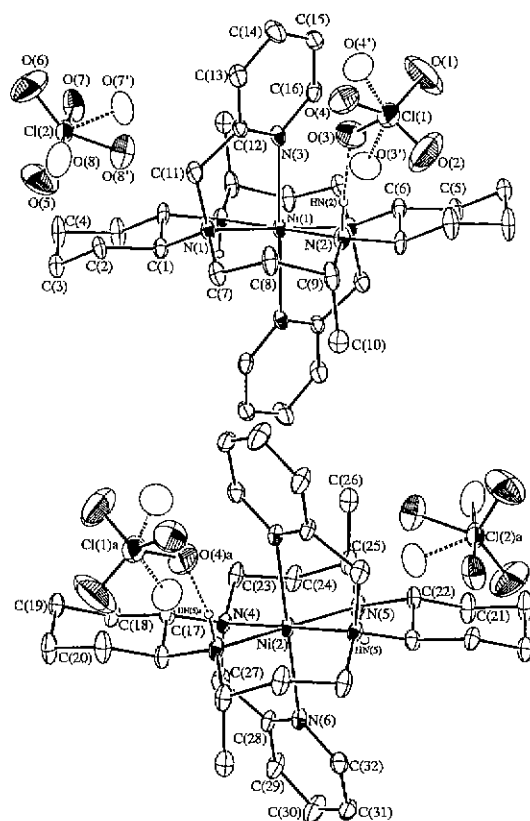


Fig. 1. An ORTEP drawing of [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (**1**) showing the atom-labelling scheme. Hydrogen bonds are indicated by dotted lines.

Ni(1)-N(3) and Ni(2)-N(6) (pyridylmethyl) (2.276(4) and 2.278(4) Å), indicating an axially elongated octahedral geometry. The N-Ni-N angles of the six-membered chelate rings are longer than those of the five-membered chelate rings. Furthermore, the axial Ni(1)-N(3) and Ni(2)-N(6) linkages are not perpendicular to the NiN<sub>4</sub> planes as the N<sub>axial</sub>-Ni-N<sub>basal</sub> angles by 79.3(1)-83.6(2)<sup>o</sup> and 80.0(1)-82.6(2), respectively. The secondary amines N(2) and N(5) are hydrogen bonded to the perchlorate oxygen atoms O(3) and O(4)<sup>i</sup> (symmetry code i: x, y, z-1) (Table 4).

The IR spectra of **1** show two vibration bands at 1587 and 1612 cm<sup>-1</sup>, which corresponds to the characteristic of  $\nu$ (C=N) and  $\nu$ (C=C) of the pendant pyridylmethyl groups.<sup>8)</sup> The maximum absorption band of **1** appears at 525 nm ( $\epsilon=7.5$  M<sup>-1</sup> cm<sup>-1</sup>) in water, which is 62 nm longer wavelength compared with that of square-planar [Ni(DTTD)](ClO<sub>4</sub>)<sub>2</sub> (DTTD=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14.4.0<sup>1,18</sup>, 0<sup>7,12</sup>]docosane) (463 nm,

**Table 3. Selected Bond Lengths (Å) and Angles (°) for [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1)**

Ni(1)-N(1)	2.121(3)	Ni(2)-N(4)	2.117(3)
Ni(1)-N(2)	2.094(4)	Ni(2)-N(5)	2.086(4)
Ni(1)-N(3)	2.276(4)	Ni(2)-N(6)	2.278(4)
N(1)-C(1)	1.504(5)	N(4)-C(17)	1.508(5)
N(1)-C(7)	1.484(6)	N(4)-C(23)	1.463(6)
N(1)-C(11)	1.470(5)	N(4)-C(27)	1.508(5)
N(2)-C(6)	1.505(5)	N(5)-C(22)	1.504(5)
N(2)-C(9)	1.463(6)	N(5)-C(25)	1.515(6)
N(3)-C(12)	1.352(5)	N(6)-C(28)	1.341(5)
N(3)-C(16)	1.335(6)	N(6)-C(32)	1.330(6)
N(1)-Ni(1)-N(2)	95.4(2)	N(4)-Ni(2)-N(5)	95.3(2)
N(1)-Ni(1)-N(2) <sup>i</sup>	84.6(2)	N(4)-Ni(2)-N(5) <sup>ii</sup>	84.7(2)
N(1)-Ni(1)-N(3)	79.3(1)	N(4)-Ni(2)-N(6)	80.0(1)
N(2)-Ni(1)-N(3)	83.6(2)	N(5)-Ni(2)-N(6)	82.6(2)
Ni(1)-N(1)-C(1)	103.3(3)	Ni(2)-N(4)-C(17)	103.5(3)
Ni(1)-N(1)-C(7)	109.6(3)	Ni(2)-N(4)-C(23)	110.6(3)
Ni(1)-N(1)-C(11)	112.3(3)	Ni(2)-N(4)-C(27)	111.2(3)
Ni(1)-N(2)-C(11)	108.3(3)	Ni(2)-N(5)-C(22)	109.0(3)
Ni(1)-N(2)-C(22)	121.1(3)	Ni(2)-N(5)-C(25)	119.7(3)
Ni(1)-N(3)-C(12)	110.1(3)	Ni(2)-N(6)-C(28)	110.1(3)
Ni(1)-N(3)-C(16)	132.4(3)	Ni(2)-N(6)-C(32)	132.4(3)

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x, -y, -z.

**Table 4. Hydrogen-Bonding Parameters (Å, °) for [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (1)**

D-H...A	D-H	H...A	D A	D-H...A
N(2)-H(N2)...O(3)	0.91(2)	2.46(3)	3.291(18)	151.4(5)
N(5)-H(N5)...O(4) <sup>i</sup>	0.91(2)	2.46(3)	3.280(20)	150.4(5)

Symmetry code: (i) x, y, z-1.

$\epsilon=73 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>17)</sup> This fact indicates that the presence of two coordinated pyridylmethyl groups affects the ligand field strength of the complex. The effective magnetic moment ( $\mu_{\text{eff}}$ ) of **1** in the solid state is  $2.88 \mu_{\text{B}}$  at room temperature, which is consistent with a  $d^8$  electron configuration in an octahedral geometry.

### Supplementary Material

Atomic coordinates, bond lengths and angles and thermal parameters are available from author K.-Y. Choi on request.

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