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단 신

거대고리 Tetraamine Diazido Nickel(II) 착물의 합성, 성질 및 X-ray 결정구조

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Synthesis, Properties, and X-ray Crystal Structure of Macrocyclic Tetraamine Diazido Nickel(II) Complex

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The coordination chemistry of C-alkyl substituted macrocyclic tetraamines has been of considerable interest in recent years.[1~13] When coordinated as a tetradentate, the spectroscopic and structural characteristics of the macrocyclic tetraamine complexes are often quite different from those of the unsubstituted macrocyclic ligands. Steric effects exerted by substituents on the ligand may influence the oxidation of the metal center. Busch *et al.*[14] reported that for complexes of C-methyl substituted cyclam (1,4,8,11-tetraazacyclotetradecane) derivatives the Ni(II)/Ni(III) redox change occurred at a more positive potential than for the cyclam analogue. This fact was ascribed to nonbonding interactions between the methyl groups on the carbon backbone and the axial ligands such as solvent molecules bound to the Ni(III) ion. More recently, an analogous effect has been described for the nickel(II) complexes of 14-membered macrocycles, in which one or two cyclohexane rings are fused to cyclam framework.[15] The azido group is one of the bridging ligands which can coordinated nickel(II) ions, giving binuclear complex in end-to-end form.[16] In this chain structure, each nickel(II) ion is coordinated by one cyclam and two azido ligands in an axially elongated octahedral arrangement. This result contrasts with the mononuclear complex of $[Ni(DTAD)(N_3)_2]$ (DTAD= 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4, $0^{1.18}$, $0^{7.12}$]docosane), in which the nickel(II) ion adopts an axially elongated octahedral geometry with two axial azido groups.[10]

In this paper we report the synthesis and characterization of $[NiL(N_3)_2]$ (1) (L=2,7,9,14-tetramethyl-1,4,8,11-tetrazacyclotetradecane). We have investigated the spectroscopic and electrochemical properties of this complex. Furthermore to understand the nature of the axial ligand the solid state X-ray crystal structure of **1** is determined and compared with their solution structure by electronic absorption spectroscopy and cyclic voltammetry.

EXPERIMENTAL

Materials. All solvents were reagent grade and purified according to the literature.[17] Distilled water was used for all reactions. Reagent grade $NiCl_2 \cdot 6H_2O$, methyl vinyl ketone, 1,2-diaminopropane, perchloric acid and $NaBH_4$ were purchased from Aldrich. All other reagents were reagent grade.

The ligand L and $[NiL(H_2O)_2]Cl_2$ were prepared according to the previously published procedures.[11,18]

Physical measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Electronic absorption spectra were obtained on a Jasco Uvidec-610 spectrophotometer. High-resolution fast atom bombardment mass spectrometry (FAB mass) were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology Taejon, Korea.

Cyclic voltammograms were obtained by using a BAS 100BW electrochemical system. All measurements were made on 0.01 M tetraethylammonium perchlorate-dichloromethane solution at 20.0±0.1 °C. A hanging mercury dropping electrode for cathodic voltammetry and a platinum disc electrode of about 2 mm diameter for anodic voltammetry were used as the working electrode. The counter electrode was a coiled platinum wire and a saturated calomel electrode was used as a reference electrode. The solution was degassed with high purity nitrogen prior to carring out the electrochemical measurements.

Preparation of $[NiL(N_3)_2]$ (1). To a methanol solution (20 ml) of $[NiL(H_2O)_2]Cl_2$ (211 mg, 0.5 mmol) was added NaN_3 (65 mg, 1.0 mmol) and the mixture was heated for 30 min on a steam bath. The solution was filtered to remove the sodium chloride. The solution was then evaporated to dryness. The resulting solid was extracted into chloroform and recrystallized by adding 10 mL of acetonitrile. The violet crystals were collected by filtration and dried *in vacuo* (yield: 142 mg, 71%). Anal. Calcd for $NiC_{14}H_{32}N_{10}$: C, 42.12; H, 8.08; N, 35.10%. Found: C, 42.28; H, 8.01; N, 35.01%. IR (KBr, cm^{-1}): 3192 (νNH), 2964, 2910, 2870, 2032 (νN_3), 1443, 1378, 1336, 1178, 1115, 1024, 988, 961, 942, 903, 836, 615. Electronic spectra ($CHCl_3$): λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 528 (10.5), 341 (18.6), and 245 (5265). FAB mass (CH_2Cl_2, m/z): 399.2 $(M)^+$.

X-ray structure analysis. Analysis on single crystal of $[NiL(N_3)]$ (1) was carried out with an Enraf-Nonius CAD4 diffractometer. A violet single crystal of size 0.26×0.20×0.13 mm^3 was mounted on the diffractometer, and used for data collections at room temperature with graphite-monochromated Mo-Kα radiation (λ=0.71069 Å). Accurate cell parameters and a crystal orientation matrix were determined from the least-squares fit of 25 reflections with θ range of 11.42 to 14.11°. An asymmetric unit of intensity data were collected in the ω-2θ scan mode to a maximum 2θ of 50.34°. Intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied. Of the 1726 unique reflections measured, 1223 were considered observed ($F_o > 4\sigma(F_o)$) and used in subsequent structural analysis. The structure was solved by direct methods[19] and successive cycles of difference Fourier map followed by full matrix least-squares refinement.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions;

Table 1. Crystallographic data for $[NiL(N_3)_2]$ (1)

Formula	$NiC_{14}H_{32}N_{10}$
Formula weight	399.18
Crystal system	Monoclinic
Space group	$P2_1/a$
a (Å)	15.572(2)
b (Å)	7.497(2)
c (Å)	11.334(1)
β (°)	133.58(1)
V(Å^3)	958.6(3)
Z	2
F (000)	386
D_c (g cm^{-3})	1.383
λ (Mo-Kα)(Å)	0.71069
μ (mm^{-1})	1.034
T(*K*)	288(2)
h, *k*, *l* range	0 18, 0 8, −13 9
2θ range (°)	50.34
No. of unique reflections	1726
No. of observed reflections $[F_o > 4\sigma\ (F_o)]$	1223
R^a	0.038
Rw^b	0.076
GoF^c	1.094

$^aR = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
$^bRw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.
$^cGoF = [\Sigma w(|F_o| - |F_c|)^2/(\text{no. of rflns} - \text{no. of params})]^{1/2}$.

those on the five- and six-membered chelate rings were allowed to ride on their parent C and N atoms with $U_{iso}(H)=1.2\ U_{eq}(C)$, while the methyl groups were treated as rotating rigid groups with $U_{iso}(H)=1.5\ U_{eq}(C)$. In the final refinement cycles a unit weight was employed. The highest and deepest peaks in the last difference map were 0.417 and −0.323 eÅ ^{3}, respectively. A summary of crystal data, data collection, and refinement for all crystallographically characterized compound are given in *Table* 1.

RESULTS AND DISCUSSION

Crystal structure of $[NiL(N_3)_2]$ (1). An ORTEP diagram of $[NiL(N_3)_2]$ (1) with atomic numbering scheme is shown in *Fig.* 1. The final atomic coordinates and interatomic bond distances and angles are listed in *Tables* 2 and 3. The ligand skeleton of the present compound takes the most stable *trans*-III conformation with two chair six-membered and two gauche five-membered chelate rings. Four methyl groups on both five- and six-membered chelate rings are *anti* with respect to the N_4 plane. An inversion center of complex **1** exists on the central nickel(II) ion. The N-Ni-N angles of the six-membered chelate rings (95.4(1)°) are larger than those (84.6(1)°) of the five-membered chelate rings. The crystal structure of **1** shows that the nickel(II) ion is coordinated by the secondary amine nitrogens of the macrocycle and that the axial positions are bonded by the two nitrogen atoms of the azido ligands, which is six-coordinated octahedral environment. The structure of **1** is similar to that found in the mononuclear complex of

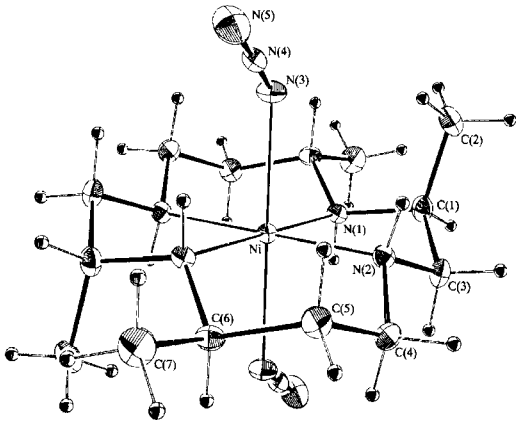

Fig. 1. ORTEP drawing of **1** showing the atom-labelling scheme and 40% probability thermal ellipsoids.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[NiL(N_3)_2]$ (1)

Atom	x	y	z	U (eq)
Ni	0	0	0	24(1)
N(1)	−1765(2)	−771(4)	−2029(3)	29(1)
N(2)	−209(3)	1647(4)	−1622(3)	29(1)
N(3)	−620(3)	2087(4)	608(4)	39(1)
N(4)	27(3)	3266(4)	1449(4)	36(1)
N(5)	691(3)	4398(5)	2326(5)	65(1)
C(1)	−2248(3)	504(5)	−3380(4)	37(1)
C(2)	−2779(3)	2181(5)	−3334(5)	48(1)
C(3)	−1231(3)	944(5)	−3251(4)	38(1)
C(4)	857(3)	1862(5)	−1355(4)	38(1)
C(5)	1915(3)	2533(5)	347(4)	39(1)
C(6)	2536(3)	1203(5)	1747(4)	34(1)
C(7)	3730(3)	1981(6)	3264(5)	54(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Interatomic bond distances (Å) and angles (°) for $[NiL(N_3)_2]$ (1)

Ni-N(1)	2.112(3)	Ni-N(2)	2.046(3)
Ni-N(3)	2.184(3)	N(3)-N(4)	1.175(4)
N(4)-N(5)	1.166(4)	N(1)-C(1)	1.495(4)
N(1)-C(6)^{i}	1.477(4)	N(2)-C(3)	1.473(4)
N(2)-C(4)	1.476(4)	C(1)-C(2)	1.525(5)
C(1)-C(3)	1.524(5)	C(4)-C(5)	1.519(5)
C(5)-C(6)	1.527(5)	C(6)-C(7)	1.532(5)
N(1)-Ni-N(1)^{i}	180.0	N(1)-Ni-N(2)	84.6(1)
N(1)-Ni-N(2)^{i}	95.4(1)	N(2)-Ni-N(2)^{i}	180.0
N(3)-Ni-N(3)^{i}	180.0	N(1)-Ni-N(3)	90.8(1)
N(1)-Ni-N(3)^{i}	89.2(1)	N(2)-Ni-N(3)	91.1(1)
N(2)-Ni-N(3)^{i}	88.9(1)	Ni-N(3)-N(4)	118.5(2)
Ni-N(1)-C(1)	107.4(2)	Ni-N(1)-C(6)^{i}	117.8(2)
Ni-N(2)-C(3)	106.0(2)	Ni-N(2)-C(4)	114.9(2)
C(1)-N(1)-(6)^{i}	116.9(3)	C(3)-N(2)-C(4)	112.7(3)
N(1)-C(1)-C(2)	113.2(3)	N(1)-C(1)-C(3)	106.5(3)
C(2)-C(1)-C(3)	111.7(3)	N(2)-C(3)-C(1)	110.6(3)
N(2)-C(4)-C(5)	112.2(3)	C(4)-C(5)-C(6)	117.3(3)
N(1)^{i}-C(6)-C(5)	109.9(3)	N(1)^{i}-C(6)-C(7)	112.3(3)
C(5)-C(6)-C(7)	109.1(3)	N(3)-N(4)-N(5)	177.8(4)

Symmetry code: (i) −x, −y, −z.

$[Ni(DTAD)(N_3)_2]$,[10] but is contrast to that observed for the binuclear complex of catena-(μ-N_3)$[Ni(cyclam)](ClO_4)\cdot H_2O$.[16] This fact may be due to the steric hinderance of the four methyl groups on the ligand. The average bond distance of 2.075(3)Å, between nickel and secondary nitrogens, which is similar to those found in *trans*-$[Ni(cyclam)(H_2O)_2]Cl_2\cdot 4H_2O$ (2.069(7)Å)[21] and $[NiL(H_2O)_2]Cl_2$ (2.074(3)Å).[11] The axial Ni-N(3) distance of 2.184(3)Å is longer than the average Ni-N distances in NiN_4 plane, indicating an axially elongated octahedral geometry. The axial Ni-N(3) bonds are bent slightly off from the perpendicular axis to the NiN_4 plane by 0.8-1.1°. The axial Ni-N(3) bond distance and Ni-N(3)-N(4) angle (118.5(2)°) are similar to the observed for $[Ni(DTAD)(N_3)_2]$.[10] Both azido groups which act monodentate ligands are slightly asymmetric [N(3)-N(4)=1.175(4) and N(4)-N(5)=1.166(4)Å] and linear within the experimental error [N(3)-N(4)-N(5) angle=177.8(4)°].

Spectra and properties. The complex **1** is soluble in water, methylene chloride, chloroform, and acetonitrile. The infrared spectra of **1** shows a strong band at 3192 cm^{-1}, which is assigned to the ν(NH) of the coordinated secondary amines. A single very strong band at 2032 cm^{-1} is associated with the azide stretching frequency. Visible spectra of **1** in $CHCl_3$ solution shows d-d bands 341 and 528 nm, indicating that the nickel(II) ion is in an octahedral environment. However, the wavelength of the d-d bands for the present compound is somewhat shorter than those found for $[NiL(H_2O)_2]Cl_2$ (352 and 534 nm).[11] This fact can be explained by the spectrochemical series ($H_2O < N_3^-$).[21]

In order to investigate the effect of the axial azido group on the redox properties of **1**, the potentials *vs.* saturated calomel electrode (SCE) for the Ni(II)/Ni(III) and Ni(II)/Ni(I) processes were measured in 0.01 M TEAP-CH_2Cl_2 solution by cyclic voltammetry (*Table* 4). The oxidation potential of **1** is quite similar to that of $[NiL(H_2O)_2]Cl_2$ in 0.01 M TEAP-CH_2Cl_2 solution.[11] However, the reduction potential is slightly more positive than that of $[NiL(H_2O)_2]Cl_2$, indicating that the complex **1** makes reduction more difficult and oxidation easier. This result can be reflected by the π-donor ability of the axial ligands as observed in the visible spectra of nickel(II) complex.

Table 4. Cyclic voltammetric data for nickel(II) complexes[a]

Complex	Potentials(V) *vs.* SCE	
	Ni(II)/Ni(III)	Ni(II)/Ni(I)
1	+0.67	−1.47
$[NiL(H_2O)_2]Cl_2$[b]	+0.66	−1.53

[a]Measured in 0.01 M TEAP-CH_2Cl_2 solution at 20.0± 0.1 °C. [b]Reference 11.

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Supporting information available. Tables of crystallographic details, atomic coordinates, interatomic distances and angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for **1** (7 pages) are available. Supplementary materials are available from K.-Y. Choi.

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