단 신

거대고리 Ni(II) 착화합물, [Ni(L)X$_2$]의 합성(X=N$_3^-$, NCS$^-$, NCO$^-$) 및 구조(X=N$_3^-$)

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Synthesis of Macrocyclic Nickel(II) Complex, [Ni(L)X$_2$] (X=N$_3^-$, NCS$^-$, NCO$^-$) and Structure of [Ni(L)X$_2$](X=N$_3^-$)

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Since the Sargeson's pioneering work on metal ion-mediated organic syntheses in the sepulchrate compound, numerous works with macrocycles have been developed from the same group and included, among others, Lawrance and Curtis.[1,2] Suh *et al.* is one of the groups have done a lot of work in this area, and reported template synthesis of 14-membered hexaaza macrocyclic complexes of nickel (II) and copper (II) by the one pot condensation of corresponding metal ions, ethylenediamine, formaldehyde, and primary amine.[3] Studies in the solid state and in solution exhibited that the afore-mentioned nickel (II) complexes have properties similar to those of nickel (II) cyclam (1,4,8,11-tetraazacyclotetradecane, L1).[3-7] Hay *et al.* extended this synthesis to the preparation of a pendant arm macrocycle, [Ni (L)Cl$_2$](L=3,10-Bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane), by using ethanolamine as the primary amine.[6] Like many other tetraaza nickel (II) complexes, this complex has shown to exist in an equilibrium between the square planar low-spin and tetragonally distorted octahedral high-spin species in coordinating solvents such as water.[8-9] The [Ni-(L)Cl$_2$] has become the useful starting complex for the preparation of other interesting octahedral nickel (II) complexes. Ballester *et al.* have recently reported octahedral [M(L)(TCNQ)$_2$](M=Ni, Cu; TCNQ=7,7,8,8-tetracyano-p-quinodimethane) by the displacement reactions of [M(L)Cl$_2$] and LiTCNQ, and determined their crystal structures which are of interest in the field of materials chemistry.[10] Suh *et al.* have described a coordination polymer containing hexaaza nickel (II) macrocycles, in which each macrocyclic nickel (II) ion is coordinated by two nitrile groups of the neighboring macrocycles.[11] Although nickel (II) complexes of 14-membered macrocycles have been reported, relatively fewer examples of structurally characterized octahedral nickel (II) complexes with hexaaza macrocycles are now known.

Reported herein, we describe the preparation and
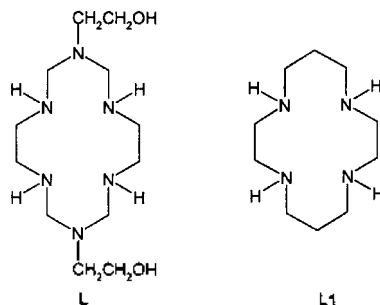
characterization of *trans*-disubstituted [Ni(L)(X)$_2$] (X=N$_3^-$, NCS$^-$, and NCO$^-$) complexes by the reaction between [Ni(L)Cl$_2$] and pseudo halides. One of these new complexes, [Ni(L)(N$_3$)$_2$] has been determined by X-ray crystallography.

EXPERIMENTAL

General Procedures. All solvents used were reagent grade and purified as described elsewhere prior to use.[12] Distilled water was used for all procedures. NiCl$_2$ · 6H$_2$O, ethylenediamine, ethanolamine, formaldehyde, NaN$_3$, KSCN, and NaOCN were purchased from Aldrich Chemical Co. and used without further purification. Infrared spectra of solid samples were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectropho-tometer between 4000 and 400 cm^{-1} as Nujol mulls on KBr discs. UV/Vis spectra were measured on a Milton Roy Spectronic 1201 recording spectrophotometer. Diffuse reflectance optical absorption spectra were measured using a Varian Cary 1C UV/Vis spectrophotometer. EA and FAB MS were carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Preparation of [Ni(L)Cl$_2$]. This was syn-thesized by a previously reported method.[6,10] It was not necessary to purify this complex for the following reactions.

Preparation of [Ni(L)(N$_3$)$_2$] · 2H$_2$O. To an aqueous solution of [Ni(L)Cl$_2$] was added NaN$_3$ in a 1:2 molar ratio.[13] The resulting solution was allowed to stand in an open beaker at ambient temperature. After several days, the diazido complex, [Ni(L)(N$_3$)$_2$] · 2H$_2$O separated out as purple plates just before the solution was dried up. This complex was indefinitely stable in the air. Found: C, 31.03; H, 7.50; N, 35.91. Calc. for C$_{12}$H$_{34}$N$_{12}$NiO$_4$: C, 30.72; H, 7.25; N, 35.84. MS (FAB): m/z=469 (calc. 469.22).

Preparation of [Ni(L)(NCS)$_2$] and [Ni(L) (NCO)$_2$]. These were prepared by a similar proce-dure above using KSCN or NaOCN instead of NaN$_3$. [Ni(L)(NCS)$_2$]; IR: 2083(s, ν_{NCS}), 2069(s, ν_{NCS}). Found: C, 36.37; H, 6.74; N, 24.23. Calc. for C$_{14}$H$_{30}$N$_8$NiO$_2$S$_2$: C, 36.15; H, 6.46; N, 24.10. [Ni(L)(NCO)$_2$]; IR: 2188(s, ν_{NCO}). Found: C, 38.61; H, 7.24; N, 25.70. Calc. for C$_{14}$H$_{30}$N$_8$NiO$_4$: C, 38.83; H, 6.93; N, 25.88.

Data Collection, Structural Determination, and Refinement for [Ni(L)(N$_3$)$_2$] · 2H$_2$O. A brief crystal data and refinement details is summarized in *Table* 1. All X-ray examination and data collection procedures were performed using an Enraf-Nonius

Table 1. Crystal Data and Structure Refinement Details for [Ni(L)(N$_3$)$_2$] · 2H$_2$O

Empirical formula	C$_{12}$H$_{34}$N$_{12}$NiO$_4$
Formula weight	469.22
Temperature (K)	153(2)
Wavelength (Å)	0.71073 (Mo Kα)
Crystal system	monoclinic
Space group	P2$_1$/c
a (Å)	9.6003(5)
b (Å)	14.2895(8)
c (Å)	7.9386(5)
β (deg)	110.045(4)
V (Å^3)	1023.07(10)
Z	2
D$_{calcd}$ (Mg/m^3)	1.523
Absorption coefficient (mm^{-1})	0.996
Final R indices [$I > 2\sigma(I)$]	R1=0.0232, wR2=0.0542 [1986 data]
R indices (all data)	R1=0.0312, wR2=0.0576

R1=$\Sigma \|F_o$-$F_c\| / \Sigma|F_o|$ and wR2 = $[\Sigma[w(F_o^2$-$F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$; w=1 / $[\sigma^2(F_o)+(0.0226P)^2+0.3853P]$, where P=$(F_o^2+2F_c^2)/3$.

CAD-4 diffractometer that was controlled by a MicroVAX II computer and control program.[14] The crystals' final cell parameters and crystal orientation matrix were determined from 25 reflections in the range $14.8 < \theta < 18.5°$. The intensity data were collected by the $\omega/2\theta$ scan technique in the region $2.3 < \theta < 27.5°$. Six standard reflections well dispersed in reciprocal space were monitored at 30 minute intervals. An absorption correction was applied based upon crystal faces with transmission factors ranging from 0.7447-0.9072. Two forms of data were collected, indices $\pm$h-k-l and $\pm$hkl, resulting in the measurement of 4964 reflections, 2353 unique [R(int)=0.0253].

Data were corrected for Lorentz and polarization factors and reduced to F_o^2 and $\sigma(F_o^2)$ using the program XCAD4.[15] Systematic absences clearly determined the centrosymmetric monoclinic space group $P2_1/c$(No. 14). The SHELXTL program package[16] was implemented to confirm the monoclinic centric space group $P2_1/c$, to apply the absorption correction, and set up the initial files. The structure was determined by direct methods by using the program XS.[17] The structure was refined with XL.[18] A single difference-Fourier map revealed the location of all of the remaining non-hydrogen atoms within the ensemble. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were placed in calculated positions and the hydroxy hydrogen's being initially located via a circular difference-Fourier about the individual oxygen atom with d(O-H)=0.84 Å and U_H set equal to 1.5 $U_{(parent)}$. Hydrogen atoms attached to nitrogen atoms were directly located from an additional difference-Fourier map along with the hydrogen atoms comprising the two water molecules present. All of the hydrogen atom positions were allowed to refine freely (U_{xyz}). Supplementary materials including full crystallographic details, atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, and hydrogen atom coordinates and anisotroic displacement parameters for [Ni(L)(N₃)₂] · 2H₂O may be obtained directly from JCK.

RESULTS AND DISCUSSION

The axial Cl⁻ ligands in [Ni(L)Cl₂] are quite labile in an aqueous solution, and the complex exists in equilibrium between yellow square-planar [Ni(L)]²⁺ and blue octahedral [Ni(L)(X)₂] species even in the presence of X(X=N₃⁻, NCS⁻, and NCO⁻). However, when the solution is almost dried up, [Ni(L)]²⁺ prefers X to Cl⁻ or H₂O ligands, eventually the octahedral [Ni(L)(X)₂] complexes have been crystallized out. Attempts to prepare uniform 1D compounds containing -(X-NiL-X-)ₙ chains from a 1:1 molar ratio of [Ni(L)-Cl₂] and X were unsuccessful. Vicente et al. reported the azido bridged 1D nickel(II) complex which is a subject of current interest.[19~20] The bridging ligands between paramagnetic nickel ions in this complex have been proved to mediate antiferromagnetic interactions through the magnetic overlap.

One of the obtained complexes, [Ni(L)(N₃)₂] · 2H₂O crystallizes in the space group $P2_1/c$ as discrete molecules of [Ni(L)(N₃)₂] and H₂O solvents. An ORTEP view and the atom labeling of the molecular unit is shown in *Fig.* 1. Selected bond distances and angles for [Ni(L)(N₃)₂] · 2H₂O are summarized in *Table* 2. The nickel ion in the macrocycle sits on an inversion center with axially bonded azido groups, and the approximate coordination geometry about the nickel ion is tetragonally elongated octahedron. The average nickel-nitrogen (macrocycle) distance of ca 2.066 Å is quite normal for a high spin nickel(II) complex and is comparable to those found in other trans-
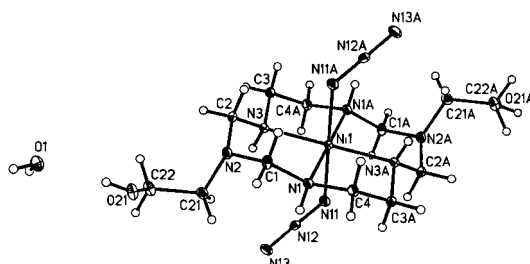

Fig. 1. ORTEP drawing of [Ni(L)(N₃)₂] · 2H₂O with numbering of the atoms.

Table 2. Selected Bond Distances(Å) and Angles(deg) for [Ni(L)(N₃)₂] · 2H₂O

Ni(1)-N(3)	2.0608(12)	Ni(1)-N(1)	2.0705(12)
Ni(1)-N(11)	2.1628(12)	N(1)-C(4)	1.4831(18)
N(1)-C(1)	1.4920(19)	C(1)-N(2)	1.4414(18)
N(2)-C(2)	1.4450(19)	N(2)-C(21)	1.4690(18)
C(21)-C(22)	1.512(2)	C(22)-O(21)	1.4278(19)
C(2)-N(3)	1.4877(18)	N(3)-C(3)	1.4785(18)
C(3)-C(4)A	1.519(2)	C(4)-C(3)A	1.519(2)
N(11)-N(12)	1.1812(16)	N(12)-N(13)	1.1710(17)
N(3)A-Ni(1)-N(3)	180.00(8)	N(3)A-Ni(1)-N(1)	86.08(5)
N(3)-Ni(1)-N(1)	93.92(5)	N(1)A-Ni(1)-N(1)	180.00(11)
N(3)-Ni(1)-N(11)	90.36(5)	N(1)-Ni(1)-N(11)	90.68(5)
N(1)-Ni(1)-N(11)A	89.32(5)	N(11)-Ni(1)-N(11)A	180.00(8)
C(4)-N(1)-C(1)	114.21(11)	C(4)-N(1)-Ni(1)	104.53(8)
C(1)-N(1)-Ni(1)	113.48(9)	N(2)-C(1)-N(1)	113.79(12)
C(1)-N(2)-C(2)	117.08(11)	C(1)-N(2)-C(21)	116.26(12)
C(2)-N(2)-C(21)	114.92(12)	N(2)-C(21)-C(22)	112.47(13)
O(21)-C(22)-C(21)	109.46(13)	N(2)-C(2)-N(3)	113.86(12)
C(3)-N(3)-C(2)	113.59(11)	C(3)-N(3)-Ni(1)	104.76(8)
C(2)-N(3)-Ni(1)	114.02(9)	N(3)-C(3)-C(4)A	108.14(12)
N(1)-C(4)-C(3)A	107.95(12)	N(12)-N(11)-Ni(1)	124.70(10)
N(13)-N(12)-N(11)	179.17(16)		

Symmetry transformations used to generate equivalent atoms: A -x,-y,-z

arranged nickel complexes of **L1** (*trans*-[Ni(L1) Y₂]; Y=Cl⁻, 2.066(1), 2.067(1); NCS⁻, 2.069(2), 2.064(2); NO₃⁻, 2.050(5), 2.060(6); H₂O, 2.072(2), 2.065(3) Å, *trans*-[Ni(L)(TCNQ)₂]; 2.053(4), 2.056 (5) Å, *catena*-(μ-N₃)[Ni(L1)](ClO₄) · H₂O; 2.060 (4), 2.073(4), 2.059(3), 2.059(4) Å.[10,20~24] Also, it is well within a general trend that the weaker nickel-nitrogen bonds (Ni-N=2.05-2.10 Å) are involved in the octahedral species than in the square planar species (Ni-N=1.88-1.91 Å).[25] The ligand skeleton of the present complex adopts the well-known *trans* *III(R,R,S,S)* conformation with two chair form six-membered and two gauche five-membered chelate rings which is believed to be the most thermodynamically favored conformation of the cyclam ring system.[26] The two *trans*-azido ligands are end bonded to the central nickel ion and are bent (N12-N11-Ni angle is 124.70(10°). As is usual in the 14-membered tetraaza macrocyclic complexes, the N-Ni-N angles of the six-membered chelate rings (93.92(5)°) are larger than those of the five-membered chelate rings (86.08(5)°).

The infrared spectra of [Ni(L)X₂](X=N₃⁻, NCS⁻, NCO⁻) contain typical bands due to axial ligands.[27]
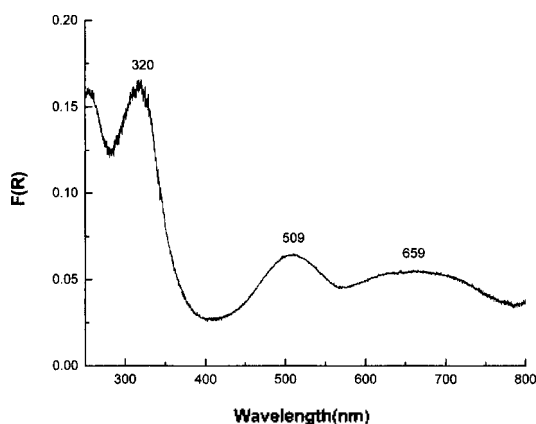
Fig. 2. Diffuse reflectance UV/Vis spectrum of [Ni(L) (N₃)₂] · 2H₂O.

Fig. 2 illustrates the diffuse reflectance UV/Vis spectrum of [Ni(L)(N₃)₂] · 2H₂O which has three absorption bands at 320 nm, 509 nm, and 659 nm, respectively. The characteristic spectrum expected for a high-spin d⁸ nickel(II) ion in a distorted octahedral environment is observed in this case. These are attributed to $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3B_{2g} + {}^3B_{1g} \rightarrow {}^3A_{2g}$ by the order of increasing

Table 3. Comparison of Spectral Band Positions (nm) of 14-Membered Macrocyclic Nickel (II) Complexes and Nickel-X (axial ligand) Bond Distances (Å)

Complexes	$^3B_{1g} \to {}^3E_g$	$\to {}^3E_g$	$\to {}^3B_{2g} + {}^3A_{2g}$	Ni-X	ref
[Ni(L)(N₃)₂] · 2H₂O[a]	320	509	659	2.1628(12)	this work
[Ni(L1)(N₃)₂][b]	d	504	690		
[Ni(L1)(NCS)₂][b]	d	494	707	2.130(2), 2.128(3)	28
				2.108(5), 2.119(6)	22,28
[Ni(L1)Cl₂][b]	343	515	678	2.49	
[Ni(L1)(H₂O)₂][c]	333	507	667	2.176(2)	21,28

[a]Diffuse reflectance spectrum at 298 K. [b]Halo-carbon grease mull spectra at 77 K. [c]Single crystal spectrum at 298 K. [d]Not observed.

wavelengths.[23,25] They are shifted to higher energies compared to those of the related nickel(II) complexes such as **L1**, which is reasonably explained by the spectrochemical series (Cl⁻ < H₂O < NCS⁻ < N₃⁻). It is a general trend that the average nickel-axial ligand distance decreases with the absorption bands showing up at wavelengths shorter on going from weaker to stronger field ligand (*Table* 3.). On the other hand, the single crystal of [Ni(L)(N₃)₂] · 2H₂O dissolved in water exhibits only a single absorption band at 446 nm ($^1B_{1g} \to {}^1B_{2g}$), indicating the dominant species in aqueous solution is square planar low-spin complex.[28] Similar spectral results were obtained for [Ni(L)(NCS)₂] and [Ni(L)(NCO)₂].

Preparation of [Ni(**L**)(N₃)₂] · 2H₂O is significant in that it permits direct structural and electronic spectral comparison between azido and other pseudohalogeno octahedral nickel(II) complexes.

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