Korean J. Crystallography
Vol.8, No.2, pp.119~123, 1997

Preparation and Structure of $[Ni(L)]I_2$ (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)

Ki-Young Choi, Dong-Won Kim[a], Moon-Jib Kim[b], Huhn-Jun Kim[c], Chang-Hee Lee[c], Yong-Che Kim[c], Baek-Seok Seong[c], Jeong-Soo Lee[c], Hae-Seop Shim[c], Yi-Kyung Kim[c], Jin-Ho Lee[c] and Il-Hwan Suh[d]

Department of Chemistry, Mokwon University, Taejon 301-729, Korea
[a]Department of Chemistry, Chungbuk National University, Cheongju 360-763, Korea
[b]Department of Physics, Soonchunhyang University, Asan 336-600, Korea
[c]Neutron Physics Department, Korea Atomic Energy Resarch Institute, Taejon 305-600, Korea
[d]Department of Physics, Chungnam National University, Taejon 305-764, Korea

$[Ni(L)]I_2$ (L : 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) 化合物의 合成 및 構造

崔琪泳 · 金東洹[a] · 金文執[b] · 金憲俊[c] · 李彰熙[c] · 金容彩[c] · 成百石[c] · 李正秀[c]
沈海燮[c] · 金以經[c] · 李珍昊[c] · 徐日煥[d]

牧園大學校 化學科, 忠北大學校 化學科[a], 順天鄕大學校 物理學科[b],
韓國原子力研究所 中性子物理室[c], 忠南大學校 物理學科[d]

Abstract

The complex $[Ni(L)]I_2$(**1**) (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been prepared and characterized by X-ray diffraction methods. The complex **1** crystallized in the orthorhombic system, space group Pcab with cell parameters a=13.293(1) Å, b=28.550(7) Å, c=10.804(1) Å, Z=8. Least-squares refinement of **1** led to a R (Rw) factor of 0.043 (0.046) for 1851 observed reflections of $Fo>3\sigma$ (Fo). The crystal structure of 1 has a slightly distorted square-planar geometry and adopts the *trans*-III conformation.

要 約

$[Ni(L)]I_2$ (**1**) (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) 化合物을 合成하고 構造를 X-線 回折法으로 糾明하였다. 이 化合物은 直方晶系, 空間群 Pcab, a=13.293(1) Å, b=28.550(7) Å, c=10.804(1) Å, Z=8로 結晶化되었다. 이 化合物의 構造는 最小 自乘法으로 精密化하였으며, 最終 信賴度 R(Rw)값은 1851個의 回折斑點에 對하여 0.043 및 0.046이었다. 이 化合物의 結晶構造는 若干 일그러진 平面 四角構造와 *trans*-III 形態를 갖는다.

1. Introduction

The 14-membered tetraamine macrocycle cyclam (1,4,8,11-tetraazacyclotetradecane) is one of the best studied macrocyclic ligands in coordination chemistry, inorganic and biomimetic, and catalysis.[1] Since the physical and chemical properties of the metal complexes are closely related to the structural features of the corresponding macrocyclic ligands, numerous efforts in this area have been directed toward the synthesis of new types of cyclam analogs. Among the previously reported scope of cyclam analogs, relatively few examples are known which pos-

sess additional C-alkyl groups of the macrocyclic ring.[2] Recently, the nontemplate condensation reaction of methyl vinyl ketone, 1,2-diaminopropane, and perchloric acid followed by reduction with $NaBH_4$, resulting 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) which contains four *anti* methyl groups on the macrocyclic ring has been described.[3] Of much interest with this ligand is the effect on structures of metal complexes, oxidation states of the inserted metal ions, and stabilities of metal complexes.

In this paper, we report the synthesis and crystal structure of $[Ni(L)]I_2$(**1**) (L: 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane) complex.

2. Experimental Section

All solvents were reagent grade and purified according to the literature.[4] Distilled water was used for all reactions. Reagent grade $NiCl_2 \cdot 6H_2O$, methyl vinyl ketone, 1,2-diaminopropane, perchloric acid, and NaBH4 were purchased from Aldrich. All other chemicals were reagent grade and used without further purification.

High-resolution fast atom bombardment mass spectrometry (FAB MS) was 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.

Preparation of Ligand (L). The ligand L was prepared according to the previously published procedures.[3] Anal. Calcd for $C_{14}H_{32}N_4$: C, 65.6; H, 12.6; N, 21.9. Found: C, 65.7; H, 12.6; N, 21.7%. FAB MS (CH_2Cl_2, m/z): 256.4 $(M)^+$.

Preparation of $[Ni(L)]I_2$(1). A methanol solution (20 ml) of L (256 mg, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (238 mg, 1 mmol) was heated at reflux for 1 hr. The solution was cooled to room temperature. Excess KI was added to the solution and then the solution was placed in a refrigerator for crystallization. The brown crystals were filtered off, washed with diethyl ether and dried in vacuo (yield: 302 mg, 53%). Anal. Calcd for $NiC_{14}H_{32}N_4I_2$: C, 29.6; H, 5.7; N, 9.9. Found: C, 29.7; H, 5.6; N, 9.8%. FAB MS (CH_2Cl_2, m/z): 568.9 $(M)^+$.

X-ray Structural Determination. A brown crystal of **1** ($0.17 \times 0.17 \times 0.17$ mm^3) was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα (λ=0.71069 Å) radiation. Unit cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections with 2θ range of 22.76 to 25.36°. An asymmetric unit of intensity data were collected in the ω-2θ scan mode to a maximum 2θ of 50.4°. A total of 3676 unique reflections were measured, of which 1851 with ($F_o > 3\sigma(F_o)$) were used in the structural analysis. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by use of

Table 1. Crystallographic Data for $[Ni(L)]I_2$ (1)

Formula	$NiC_{14}H_{32}N_4I_2$
Formula weight	568.95
Crystal system	Orthorhombic
Space group	Pcab
a (Å)	13.293(1)
b (Å)	28.550(7)
c (Å)	10.804(1)
V (Å3)	4100.3(11)
Z	8
F (000)	2224
Dc (Mg m^{-3})	1.843
Diffractometer	Enraf-Nonius CAD4
λ (Mo Kα) (Å)	0.71069
μ (mm^{-1})	3.93
2θ range (°)	50.4
Data collection method	ω/2θ
Scan width	0.8+0.34 tanθ
h, *k*, *l* range	0 15, 0 34, 0 12
No. of unique reflections	3676
No. of observed reflections [$F_o > 3\sigma(F_o)$]	1851
R[a]	0.043
Rw[b]	0.046
GoF[c]	0.55

[a]$R = \Sigma(F_o - F_c)/\Sigma(F_o)$, [b]$Rw = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o^2)]^{1/2}$, [c]$GoF = [\Sigma w(F_o - F_c)^2/(\text{no. of rflns} - \text{no. of params})]^{1/2}$.

Table 2. Atomic Coordinates and Biso for [Ni(L)]I_2 (1)

	x	y	z	Biso
Ni	0.50453(12)	0.62570(5)	0.14761(15)	2.29(6)
N(1)	0.6006(7)	0.6092(4)	0.0210(10)	3.0(5)
N(2)	0.4370(7)	0.6610(4)	0.0184(10)	2.8(4)
N(3)	0.4057(8)	0.6445(4)	0.2680(10)	2.8(4)
N(4)	0.5668(7)	0.5893(4)	0.2799(9)	2.5(4)
I(1)	0.27139(7)	0.56205(3)	0.07430(10)	4.19(4)
I(2)	0.72099(7)	0.68723(3)	0.36766(10)	4.59(5)
C(1)	0.5467(10)	0.6103(5)	-0.0986(12)	3.6(6)
C(2)	0.4898(9)	0.6552(4)	-0.1036(12)	3.2(6)
C(3)	0.4179(13)	0.6578(7)	-0.2132(16)	5.6(9)
C(4)	0.4071(12)	0.7098(5)	0.0469(13)	4.0(7)
C(5)	0.4996(15)	0.7386(5)	0.0775(15)	5.5(9)
C(6)	0.3284(12)	0.7089(5)	0.1483(14)	4.8(8)
C(7)	0.3672(11)	0.6930(5)	0.2705(15)	4.4(7)
C(8)	0.4392(10)	0.6312(5)	0.3939(12)	3.5(6)
C(9)	0.4906(10)	0.5845(5)	0.3832(12)	3.7(6)
C(10)	0.5377(12)	0.5688(6)	0.5036(13)	4.6(8)
C(11)	0.6222(10)	0.5463(5)	0.2500(13)	3.1(6)
C(12)	0.5516(11)	0.5069(5)	0.2098(14)	3.9(7)
C(13)	0.7021(9)	0.5564(5)	0.1569(16)	4.1(7)
C(14)	0.6643(10)	0.5664(5)	0.0250(13)	3.6(6)

heavy atom methods. All remaining non-hydrogen atoms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier synthesis using NRCVAX.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at calculated positions and refined isotropically at the final cycle. The refinement gave R (Rw)=0.043 (0.046) and $(\triangle/\sigma)_{max}$ was 0.000. The maximum residual electron density was 0.66 eA^{-3}. Crystallographic data and refinement details are summarized in Table 1. Atomic coordinates and bond distances and angles for **1** are listed in Table 2 and 3.

Results and Discussion

An ORTEP drawing of [Ni(L)]I_2(**1**) with the atomic numbering scheme is shown in Figure 1. The structure of the complex **1** consists of the

Table 3. Bond Distances (Å) and Angles (deg) for [Ni(L)]I_2 (1)

Ni-N(1)	1.929(10)	N(4)-C(11)	1.469(17)
Ni-N(2)	1.941(10)	C(1)-C(2)	1.490(19)
Ni-N(3)	1.925(10)	C(2)-C(3)	1.523(21)
Ni-N(4)	1.951(10)	C(4)-C(5)	1.517(24)
N(1)-C(1)	1.478(18)	C(4)-C(6)	1.515(22)
N(1)-C(14)	1.487(17)	C(6)-C(7)	1.488(22)
N(2)-C(2)	1.502(17)	C(8)-C(9)	1.501(20)
N(2)-C(4)	1.482(18)	C(9)-C(10)	1.511(20)
N(3)-C(7)	1.479(18)	C(11)-C(12)	1.528(19)
N(3)-C(8)	1.480(18)	C(11)-C(13)	1.491(21)
N(4)-C(9)	1.513(17)	C(13)-C(14)	1.538(22)
Ni-I(1)	3.679(2)	Ni-I(2)	4.125(2)
N(1)-Ni-N(2)	85.6(4)	N(1)-C(1)-C(2)	107.2(11)
N(1)-Ni-N(3)	177.0(5)	N(2)-C(2)-C(1)	107.4(10)
N(1)-Ni-N(4)	96.3(4)	N(2)-C(2)-C(3)	112.6(11)
N(2)-Ni-N(3)	91.5(4)	C(1)-C(2)-C(3)	112.9(12)
N(2)-Ni-N(4)	177.5(4)	N(2)-C(4)-C(5)	109.7(12)
N(3)-Ni-N(4)	86.7(5)	N(2)-C(4)-C(6)	108.6(11)
Ni-N(1)-C(1)	107.1(8)	C(5)-C(4)-C(6)	114.3(13)
Ni-N(1)-C(14)	123.8(8)	C(4)-C(6)-C(7)	114.1(13)
C(1)-N(1)-C(14)	108.6(10)	N(3)-C(7)-C(6)	112.8(11)
Ni-N(2)-C(2)	111.0(7)	N(3)-C(8)-C(9)	107.1(10)
Ni-N(2)-C(4)	117.5(8)	N(4)-C(9)-C(8)	106.3(10)
C(2)-N(2)-C(4)	114.2(10)	N(4)-C(9)-C(10)	112.6(11)
Ni-N(3)-C(7)	120.6(9)	C(8)-C(9)-C(10)	112.7(12)
Ni-N(3)-C(8)	110.1(8)	N(4)-C(11)-C(12)	111.7(10)
C(7)-N(3)-C(8)	109.2(10)	N(4)-C(11)-C(13)	110.2(10)
Ni-N(4)-C(9)	107.8(7)	C(12)-C(11)-C(13)	112.9(12)
Ni-N(4)-C(11)	119.8(8)	C(11)-C(13)-C(14)	115.3(10)
C(9)-N(4)-C(11)	115.0(10)	N(1)-C(14)-C(13)	111.5(11)
I(1)-Ni-I(2)	157.2(1)		

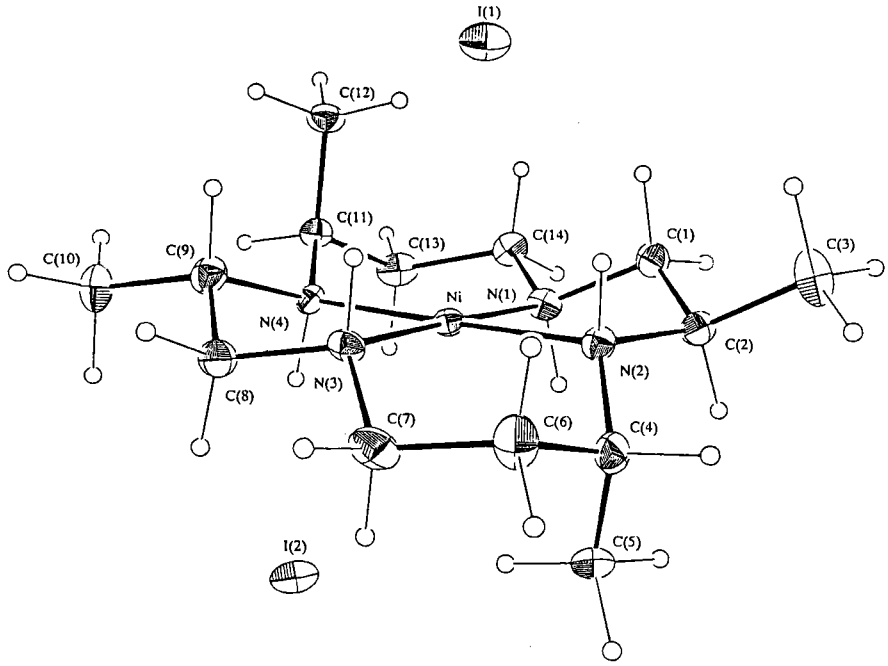

Fig. 1. An ORTEP drawing of [Ni(L)]I_2 (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. For clarity, H atoms are drawn as small circles.

complex cation and two iodide anions. The coordination of the nickel ion is a slightly distorted square-plane with four nitrogens of the macrocycle. The basal plane is slightly distorted [deviations N(1) 0.008(14), N(2) -0.028(13), N(3) 0.009(13), and N(4) -0.026(13) Å from the least-squares plane through these basal donor atoms], while the nickel (II) ion is 0.001(2) Å apart from this plane. Two iodide ions are located 3.679(2) and 4.125(2) Å from the nickel ion. The average bond distance of 1.937(10) Å between the nickel ion and secondary amine nitrogens (N(1), N(2), N(3), N(4)) is similar to those observed in other nickel(II) saturated tetraaza complexes, indicating a low-spin nickel(II)-N_4 environment in this complex.[2a, 6] However, the Ni-N bond distance is considerably shorter than those in high-spin octahedral complexes.[2f, 7] As expected in complexes of cyclam-like ligands, the N-Ni-N bite angles of the six-membered chelate rings (96.3(4) and 91.5(4) Å) are larger than those of the five-membered chelate rings (85.6(4) and 86.7(5) Å). The methyl groups on the five- and six-membered chelate rings are *anti* with respect to the N_4 plane. The complex **1** adopts a thermodynamically most stable *trans*-III conformation with the hydrogens on the nitrogen atoms N(1), N(4), and N(2), N(3) lain below and above the microcyclic plane, respectively.

Acknowledgement

This work was supported by the Basic Science Research Institute Program, Ministry of Education of Korea, 1997, Project No. BSRI-97-3435.

References

1) (a) *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum Press: New York, 1979. (b) Addison, A. W.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 1225. (c) Kunitake, T.; Ishikawa, Y.; Shimoumura, M. *J. Am. Chem. Soc.* **1986**, *108*, 327. (d) Bond,

A. M.; Khalita, M. A. *Inorg. Chem.* **1987**, *26*, 413. (e) Oshio, H. *Inorg. Chem.* **1993**, *32*, 4123. (f) Fujita, E.; Haff, J.; Sanzenbacher, R.; Elias, H. *Inorg. Chem.* **1994**, *33*, 4627.

2) (a) Choi, K. Y.; Kim, J. C.; Jensen, W, P.; Suh, I.-H.; Choi, S.-S. *Acta Cryst.* **1996**, *C52*, 2166. (b) Choi, K. Y.; Oh, M.-R.; Suh, I.-H. *Chem. Lett.* **1997**, 141. (c) Choi, K. Y.; Suh, I.-H.; Kim, J. C. *Polyhedron*, **1997**, *16*, 1783. (d) Choi, K. Y. *Polyhedron*, **1997**, *16*, 2073. (e) Choi, K. Y.; Suh, I.-H. *Polyhedron*, **1997**, *16*, 2393. (f) Choi, K. Y.; Suh, I.-H.; Choi, S. N. *Polyhedron*, in press.

3) Kolinski, R. A.; Korybut-Daszkiewicz, B.; Kubaj, Z.; Mrozinski, J. *Inorg. Chim. Acta* **1982**, *57*, 269.

4) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemical*; 2nd Ed.; Pergamon Press: New York, 1985.

5) Gabe, E. J.; Page, Y. L.; Charland, J. P.; Lee, F. L; White, P. S. *J. Appl. Cryst.* **1989**, *22*, 384.

6) (a) Abb`a, F.; De Santis, F.; Fabbrizzi, L.; Licchelli, M.; Manotti Lanfredi, M. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. Chem.* **1994**, *33*, 1366. (b) Fabbrizzi, L.; Manotti Lanfredi, A.; Taglietti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991**, 3263. (c) Henrik, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1.

7) (a) Shionoya, M.; Kimura, E.; Iitaka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 9237. (b) Kimura, E.; Kotake, Y.; Koike, T.; Shionoya, M.; Shiro, M. *Inorg. Chem.* **1990**, 29, 4991. (c) Kimura, E.; Haruta, M.; Koike, T.; Shionoya, M.; Takenouchi, K.; Iitaka, Y. *Inorg. Chem.* **1993**, *32*, 2779.