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Nickel(II) Complex with 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane

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3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane를 갖는 Nickel(II) 錯物

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Abstract

The complex of $[Ni(L)](ClO_4)_2$ (L=3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane), $C_{14}H_{32}Cl_2N_4NiO_8$, has a NiN_4 square planar geometry and adopts a thermodynamically most stable trans-III conformation.

要 約

$[Ni(L)](ClO_4)_2$ (L=3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane), $C_{14}H_{32}Cl_2N_4NiO_8$, 錯物은 NiN_4平面4角構造를 가지며 熱力學的으로 가장 安定한 trans-III 構造를 하고 있다.

1. Introduction

Macrocyclic polyamines with C-alkyl substituents of the macrocylic ring and their metal complexes have attracted considerable attention because of their structural and chemical properties, which are often quite different from those of the unalkylated macrocyclic lignads.[1-8] Several factors influence the chemical properties and structures of metal complexes of macrocylic ligand. These factors are the metal ion, ring size, degree of unsaturation and types and number of substituents on the macrocyclic ring. Recently, Mochizuki *et al.*[8] reported that trans-[Ni(cyclam)$(OH_2)_2$]$Cl_2 \cdot 4H_2O$ (cylcam=1,4,8,11-tetraazacyclotetradecane) has the octahedral geometry and longer Ni-N(secondary amine) bond distances (2.065 and 2.072 Å) when compared with that of square-planar [Ni(DTAD)]$Cl_2 \cdot 2H_2O$ (DTAD=3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,$O^{1.18}$,$O^{7.12}$]docosane (1.941 and 1.954 Å).[2]

In this paper, we report the synthesis and crystal structure of $[Ni(L)](ClO_4)_2$ (L=3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane).

2. Experimental Section

The ligand L was prepared according to literature method.[9] A methanol solution (20 ml) of L (256 mg, 1 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (366 mg, 1 mol) was heated at reflux for 2 h. The solution was then evaporated to dryness and the resulting solid dissolved in acetonitrile/water (1:1, 10 ml). When this mixture was allowed to stand for a few days, a quantity of yellow crystals pre-

Table 1. Experimental details

Crystal data	
Chemical formula	$C_{14}H_{32}C_{l2}N_4NiO_8$
Chemical formula weight	514.05
Cell setting	Monoclinic
Space group	$P2_1/n$
a (Å)	10.4943 (15)
b (Å)	13.5164 (14)
c (Å)	8.167 (2)
β (°)	110.18 (2)
V (Å^3)	1087.3 (4)
Z	2
D (Mg m^{-3})	1.57
Radiation type	Mo Kα
Wave length (Å)	0.71069
No. of reflectins for cell parameters	25
θ range (°)	10.48~13.98
μ (mm^{-1})	1.186
Temperataure (K)	288
Crystal form	rectangular rod
Crystal size (mm)	0.46×0.17×0.1
Crystal color	yellow
Data collection	
Diffractometer	Enraf-Nonius CAD4
Data collection method	ω-2θ scan
Absorption correction	None
No. of measured reflections	2123
No. of independent reflections	2123
No. of observed reflections	1070
Criterion for observed reflections	$F_o>4\sigma(F_o)$
R_{int}	0.00
θ_{max}	25.96
Range of h, k, l	-12→h→12, 0→k→16, 0→l→10
No. of standard reflections	3
Frequency of standard reflections (min)	240
Intensity decay (%)	0.83
Refinement	
Refinement on	F
R	0.0620
ωR	0.1229
S	1.252
No. of reflections used in refinement	1070
No. of parameters used	133
H-atom treatment	riding model and fixed all $\omega=1/[\sigma2(F_o^2)+(0.03P)^2+0.50P]$ where $P=(F_o^2+2F_c^2)/3$
Weighting scheme	
$(\triangle/\sigma)_{max}$	0.000
$\triangle\rho_{max}$ (eÅ^{-3})	0.494
$\triangle\rho_{min}$ (eÅ^{-3})	-0.713
Extinction method	none
Source of atomic scattering factors	SHELXL93

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

	x	y	z	Ueq
Ni	0.0000	0.0000	0.0000	0.0588(4)
N1	0.1739(4)	-0.0683(3)	0.0337(5)	0.0341(11)
N2	0.1014(4)	0.0889(3)	0.1831(5)	0.0387(12)
C1	0.2845(5)	-0.0063(5)	0.1504(7)	0.0426(14)
C2	0.4158(6)	-0.0626(5)	0.2386(8)	0.071(2)
C3	0.2280(6)	0.0383(4)	0.2783(7)	0.046(2)
C4	0.0424(6)	0.1332(5)	0.3049(7)	0.061(2)
C5	0.0957(7)	-0.1836(5)	-0.2097(8)	0.067(2)
C6	0.2053(6)	-0.1132(5)	-0.1162(7)	0.051(2)
C7	0.2325(7)	-0.0337(6)	-0.2250(8)	0.079(3)
Cl	0.0236(2)	0.75525(12)	0.2616(2)	0.0480(4)
O1	0.0227(4)	0.6870(3)	0.3915(6)	0.0715(14)
O2	0.1528(6)	0.7533(4)	0.2427(7)	0.099(2)
O3	-0.0646(6)	0.7272(5)	0.1116(7)	0.116(2)
O4	0.0120(6)	0.8507(4)	0.3083(7)	0.095(2)

cipitated; yield 370 mg (72%). Analysis found: C 32.5, H 6.2, N 10.8%. Analysis calculated for [Ni($C_{14}H_{32}N_4$)](ClO_4)$_2$: C 32.7, H 6.3, N 10.9 %.

Data collection, cell refinement and data reduction were carried out using CAD-4 software SDP.[10] The structure was solved by direct methods using SHELX86.[11] Refinement was performed with SHELXL93[12] using anisotropic displacement parameters for all non-H atoms. H-atoms were included at calculated positions using riding model and fixed. Molecular graphics were prepared using ORTEPII[13] in NRCVAX.[14] Table 1 shows the experimental details and final atomic coordinates are given in Table 2.

3. Results and Discussion

The bond distances and angles for [Ni(L)](ClO_4)$_2$ are listed in Table 3 and the molecular strucure of the title compound is illustrated in Fig. 1.

The nickel atom on an inversion center is bound in square planar fashion of which four nitrogen atoms from macrocyclic ligand occupy the equatorial sites. The average bond distance of 1.953(3) Å between nickel and secondary amines (N(1) and N(2)), which is similar to those observed in other nickel(II) macrocyclic tetraaza complexes,[2,15] indicates a low-spin NiN_4 environ-

Table 3. Geometric parameters (Å, °)

Ni	N2	1.927(4)	Ni	N1	1.978(4)
N1	C1	1.481(6)	N1	C6	1.501(6)
N2	C3	1.457(6)	N2	C4	1.469(6)
C1	C3	1.494(7)	C1	C2	1.521(7)
C4	$C5^{i}$	1.546(8)	C5	C6	1.485(8)
C6	C7	1.483(8)	Cl	O3	1.312(5)
Cl	04	1.362(5)	Cl	O1	1.408(4)
Cl	02	1.417(5)			

N2	Ni	$N1^{(i)}$	93.0(2)	N2	Ni	N1	87.0(2)
N1	Ni	N1	180.0(3)	C1	N1	C6	114.2(4)
C1	N1	Ni	107.8(3)	C6	N1	Ni	121.8(3)
C3	N2	C4	110.5(4)	C3	N2	Ni	106.2(3)
C4	N2	Ni	122.0(4)	N1	C1	C3	105.4(4)
N1	C1	C2	113.8(5)	C3	C1	C2	112.6(5)
N2	C3	C1	109.0(4)	N2	C4	$C5^{(i)}$	112.4(5)
C6	C5	$C4^{(i)}$	113.7(6)	C7	C6	C5	115.5(5)
C7	C6	N1	109.7(5)	C5	C6	N1	109.2(5)
O3	Cl	O4	115.6(4)	O3	Cl	O1	109.2(3)
O4	Cl	O1	112.6(3)	O3	Cl	O2	106.7(4)
O4	Cl	O2	103.3(3)	O1	Cl	O2	109.0(3)

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

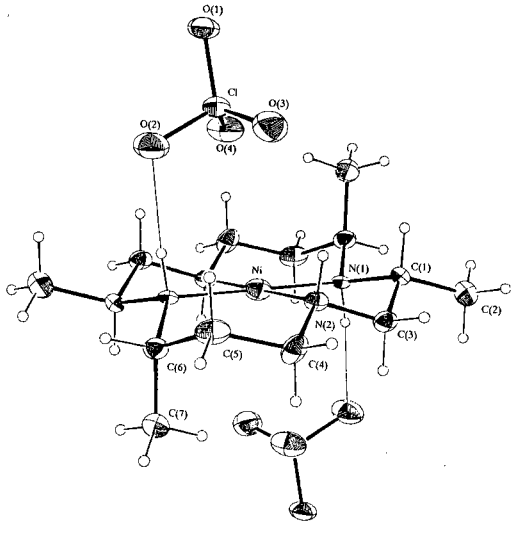

Fig. 1. ORTEP (Johnson, 1976) drawing of the title molecule showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. The hydrogen bonds between cation and anion are shown as thin lines.

ment in this complex. The N-Ni-N angles of the six-membered chelate rings (93.0(2)°) are larger than those of the five-membered chelate rings (87.0(2)°). Four methyl groups on both five- and six-membered chelate rings are anti with respect to the NiN_4 plane. N(1) atom in the cation is hydrogen bonded to O(2) atom in the perchlorate ion [N(1)...$O(2^{i})$ 3.007(7) Å and N(1)-HN1...$O(2^{i})$ 175.9(4) Å; symmetry code: (i) x,-1+y,z].

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