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Macrocyclic Tetraamine Bis(isocyanato-N)nickel (II) Complex

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巨大고리 Tetraamine Bis(isocyanato-N)nickel(II) 錯物

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Abstract

The structure of bis(isocyanto-N)nickel (II) complex, [Ni(L)(NCO)$_2$] (L: 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane), is centrosymmetric and the central nickel has an axially elongated octahedral geometry with two nitrogen atoms of the isocyanate ligand.

要 約

Bis(isocyanto-N)nickel (II) 錯物 [Ni(L)(NCO)$_2$] (L: 2,5,9,12- tetramethyl-1,4,8,11-tetraazacyclotetradecane)의 構造는 中心對稱을 가지며, 對稱中心에 있는 nickel 原子는 isocyanate ligand에 있는 두 個의 窒素原子에 依하여 軸方向으로 늘어난 8面體 構造를 갖는다.

1. Introduction

The ligand cyclam (1,4,8,11-tetraazacyclotetradecane) is well recognized as exemplary among the macrocyclic polyamines in coordination chemistry.[1)] Recently, many efforts[2-5)] have been made to introduce additional ligating groups into cyclam in order to obtain new types of ligands and their nickel (II) complexes, which are often quite different from the structural and chemical properties of cyclam complexes. The number of structurally characterized compounds of macrocyclic nickel (II) complexes with the cyanate ligand is, to our knowledge, surprisingly low.[6-9)] In the present study, we describe the synthesis and crystal structure of the nickel (II) complex of 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L) with the isocyanate ligand.

2. Experimental Section

2-1. Synthesis of [Ni(L)(NCO)$_2$]

The ligand was synthesized by previously reported method.[10)] A methanol solution (20 ml) of the ligand (256 mg, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (238 mg, 1 mmol) was heated at reflux for 1 h. NaNCO (130 mg, 2 mmol) was then added to the solution. 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 light violet crystals precipitated.

2-2. X-ray Structural Determination

The details of the crystal data, data collection and the structure refinement are given in Table 1. Programs used are: SDP[11] for data collection, SDP for cell refinement, XRAYACS[12] for data reduction, SHELXS86[13] for structure solution, SHELXL97[14] for structure refinement, and ORTEP[15] in NRCVAX[16] for molecular graphics. When the absorption correction (T_{max}/T_{min}= 0.525) by φ-scan method was applied to the intensities, the worse result, which might be attributed to the too weak φ-data, was obtained. So all calculations were performed with the intensity data before the absorption correction. H atoms on C and N atoms were included at riding positions with C-H and N-H fixed at 0.95 Å and $1.2U_{eq}$ of the parent C and N atoms, and methyl H atoms were constrained to calculated positions with free rotation and isotropic displacement parameters equal to $1.5U_{eq}$ of the parent C atom. Atomic coordinates and bond distances and angles are listed in Tables 2 and 3. The anisotropic displacement parameters for the non-H atoms and hydrogen coordinates and their isotropic displacement parameters are available from authors.

Table 1. Experimental details

Crystal data	
$C_{16}H_{32}N_6NiO_2$	Mo K_α Radiation
M_r=399.19	λ=0.71069 Å
Triclinic	Cell parameters from 24 reflections
$P1$	θ=11.811-15.165°
a=8.0379(16) Å	μ=1.030 mm^{-1}
b=9.0542(18) Å	T=291 K
c=7.340(3) Å	Plate
α=92.04(2)	0.40×0.23×0.13 mm
β=99.022(19)°	Light violet
γ=111,776(16)	
V=481.2(2) $Å^3$	
Z=1	
D_x=1.337 Mg m^{-3}	
D_m not measured	
Data collection	
Enraf-Nonius CAD-4 Diffractometer $w/2\theta$ scans	R_{int}=0.0261
Absorption correction: none	h=-10 → 10
2540 independent reflections	k=0 → 12
1841 reflections with $F_o \geq 3\sigma$ (Fo)	l=-9 → 9
	3 standard reflections
	frequency: 240 min
	intensity decay: -0.43%
Refinement	
Refinement on F	$(\Delta/\sigma)_{max}$=0.000
R(F)=0.0821	$(\Delta\sigma)_{max}$=1.119 e $Å^{-3}$
ϖR(F)=0.1591	$(\Delta\sigma)_{max}$=-0.905 e $Å^{-3}$
S=1.406	Extinction correction: none
2540 reflections	Scattering factors from International Tables for Crystallography (Vol. C)
115 parameters	
H atoms constrained	
$w=1/[\sigma^2(F_o^2)+(0.03P)^2+0.5P]$	
where $P=(F_o^2+2F_c^2)/3$	

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2$×10^3) for [Ni(L)$(NCO)_2$]

	x	y	z	U(eq)
Ni	0	0	0	39(1)
N(1)	2385(5)	1699(5)	1762(7)	48(1)
N(2)	27(6)	1367(5)	-2215(7)	50(1)
C(1)	2603(8)	3355(7)	1615(10)	63(2)
C(2)	2530(9)	3770(8)	-361(11)	76(2)
C(3)	627(10)	3095(8)	-1704(11)	82(2)
C(4)	564(16)	4066(12)	-3310(15)	148(5)
C(5)	-1792(8)	572(7)	-3531(9)	58(2)
C(6)	-2373(7)	-1217(7)	-3666(8)	55(2)
C(7)	-4215(9)	-2080(9)	-5106(10)	80(2)
C(8)	-2749(7)	1421(7)	1238(9)	53(2)
N(3)	-1655(6)	912(6)	1157(7)	54(1)
O	-3855(7)	1979(7)	1324(10)	118(2)

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

3. Results and Discussion

In the structure of [Ni(L)$(NCO)_2$] shown in Fig. 1, two alternating five- and six-membered chelate rings are in the gauche and chair form with most stable trans-III conformation. An inversion center of the complex exists on the central nickel (II) ion. The N-Ni-N angles of the six-membered chelate rings [94.9(2)°] are larger than those of the five-membered chelate rings [85.1(2)°] (see Table 3). The structure of complex reveals a six-coordinated octahedral geometry with bonds to the four secondary amines of the macrocycle and to the two axial isocyanate ligands. The average Ni-N (secondary amines) distance of 2.081(3) Å is longer than

Table 3. Bond lengths (Å) and angles (°) for [Ni(L)(NCO)$_2$]

Ni-N(2)	2.077(5)	Ni-N(1)	2.085(4)	Ni-N(3)	2.100(5)
N(1)-C(1)	1.454(7)	N(1)-C(6)^a	1.480(7)	N(2)-C(3)	1.464(8)
N(2)-C(5)	1.472(7)	C(1)-C(2)	1.505(9)	C(2)-C(3)	1.522(9)
C(3)-C(4)	1.499(10)	C(5)-C(6)	1.503(8)	C(6)-C(7)	1.532(7)
C(8)-N(3)	1.145(6)	C(8)-O	1.185(7)		

N(2)-Ni-N(1)	94.89(18)	N(2)-Ni-N(1)^a	85.11(18)
N(2)-Ni-N(3)^a	86.97(19)	N(1)-Ni-N(3)^a	89.02(17)
N(2)-Ni-N(3)	93.03(19)	N(1)-Ni-N(3)	90.98(17)
C(1)-N(1)-C(6)^a	114.8(5)	C(1)-N(1)-Ni	114.8(3)
C(6)^a-N(1)-Ni	105.4(3)	C(3)-N(2)-C(5)	115.9(4)
C(3)-N(2)-Ni	116.2(4)	C(5)-N(2)-Ni	105.8(4)
N(1)-C(1)-C(2)	112.8(5)	C(1)-C(2)-C(3)	115.8(6)
C(4)-C(3)-N(2)	115.9(7)	C(4)-C(3)-C(2)	110.7(7)
N(2)-C(3)-C(2)	110.6(5)	N(2)-C(5)-C(6)	110.0(4)
N(1)a-C(6)-C(5)	108.6(5)	N(1)a-C(6)-C(7)	113.7(5)
C(5)-C(6)-C(7)	111.4(5)	N(3)-C(8)-O	178.6(7)
C(8)-N(3)-Ni	159.7(5)		

Symmetry transformations used to generate equivalent atoms: a) -x, -y, -z.

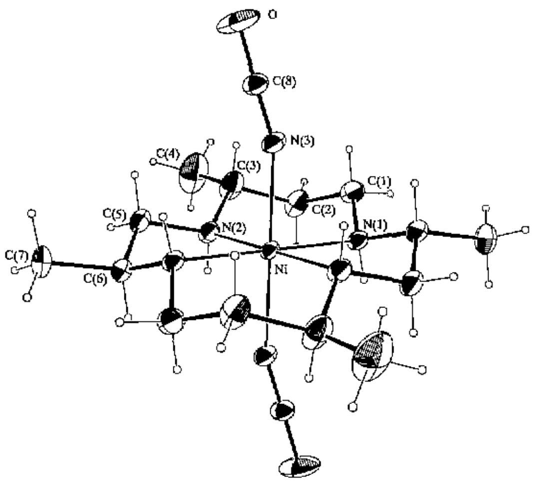

Fig. 1. The molecular structure of [Ni(L)(NCO)$_2$] with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H-atoms are drawn as small spheres of arbitrary radii.

that in corresponding square-planar complex [1.948(4) Å][17] but normal for the six-coordinated complex of this type.[5] However, the four Ni-N distances in NiN$_4$ plane are shorter than the axial Ni-N(3) (isocyanate) distance of 2.100(5) Å, indicating an axially elongated octahedral geometry. The axial Ni-N(3) linkage is not perfectly perpendicular to NiN$_4$ plane with N(1)-Ni-N(3) and N(2)-Ni-N(3) angles ranging from 87.0(2) to 93.0(2)°. The Ni-N(3)-C(8) and N(3)-C(8)-O angles related to the isocyanate ligand are 159.7(5) and 178.6(7)°, respectively.

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