Crystal Structure of Macrocyclic Tetraamine Thiocyanate Copper(II) Complex

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거대 고리 Tetraamine Thiocyanate Copper(II) 錯物의 結晶構造

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Abstract

The synthesis and characterization of [Cu(L)](NCS)$_2$ (1) (L: 2,5,9,12-tetramethyl-1,4,8, 11-tetraazacyclotetradecane) are described. Crystal structure of 1 crystallizes in the monoclinic system, space group P2$_1$/a, a=7.622(2) Å, b=17.645(2) Å, c=8.223(3) Å, β=109.99(2)°, Z=2. Least-squares refinement of 1 led to a R(R$_w$) factor of 0.087 (0.158) for 1535 observed reflections of F$_o$>4σ(F$_o$). The complex 1 has a square planar geometry with average Cu-N (secondary amines) bond distance of 2.030(4) Å. The axially disposed thiocyanate anions are not coordinated with Cu-N distances of 2.842(7) Å.

要 約

[Cu(L)](NCS)$_2$ (1) (L: 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane) 錯物을 合成하고 構造를 糾明하였다. 이 錯物은 單結晶系, 空間群 P2$_1$/a, a=7.622(2) Å, b=17.645(2) Å, c=8.223(3) Å, β=109.99(2)°, Z=2로 結晶化되었다. 이 錯物의 構造는 最小自乘法으로 精密化하였으며, 最終信賴度 R(R$_w$)값은 1535個의 回折班點에 대하여 0.087 및 0.158이었다. 이 錯物의 結晶構造는 Cu-N(二次 아민)의 平均 距離가 2.030(4) Å인 平面 四角構造를 갖는다. 軸에 놓여있는 NCS⁻ 陰이온은 Cu-N 距離가 2.842(7) Å로 結合되어 있지 않았다.

1. Introduction

Polyaza macrocyclic ligands possess cavities capable of providing a favorable environment for transition metal ions.[1] The strength of the ion binding is determined by ion size, macrocyclic cavity size and ligand conformation.[2] Typically, the 14-membered tetraamine macrocycles cyclam (1,4,8,11-tetraazacyclotetradecane) and methylcyclam incorporate metal ions into their cavities and form a stable square planar complex with several configurations.[3] Because of their important biological functions and cause of their important biological functions and some unusual properties, cyclam derivatives have been extensively studied, and structural features for biological significance are well recognized.[4-9] Recently, X-ray crystal analysis of [Cu(DTAD) (SCH$_3$)$_2$]·2H$_2$O (DTAD: 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]docosane) showed that the copper(II) ion adopts a tetragonally elongated octahedral geometry with two apical thiolate sulfur atoms.[10] We also reported the crystal structure of [Ni(L)(NCS)$_2$] (2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane),[11] in which the nickel(II) ion reveals a octahedral geometry with two apical thiocyanate nitrogen a-

toms.

We report herein the synthesis and crystal structure of the copper(II) complex of L with thiocyanate ligands.

2. Experimental Section

2-1. General

All solvents were reagent grade and purified as described elsewhere prior to use.[12] All the reagents used for the synthesis of the complex were of analytical grade. The macrocyclic ligand L was synthesized as described previously.[13] High-resolution fast atom bombardment mass spectrometry (FAB mass) were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analysis were carried out by the Korea Basic Science Institute, Seoul, Korea.

2-2. Synthesis of [Cu(L)](NCS)₂ (1)

To a methanol solution (10 m*l*) of CuCl$_2$·2H$_2$O (170 mg, 1 mmol) was added L (256 mg, 1 mmol) and then the mixture was heated at reflux for 1 hr. Solution of KSCN (194 mg, 2 mmol) in water (5 m*l*) was then added consecutively. The resulting solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Violet single crystals suitable for X-ray determinations were collected after 1 week (yield ca. 72%). Anal. Calcd for C$_{16}$H$_{32}$CuN$_6$S$_2$: C, 44.1; H, 7.4; N, 19.3. Found: C, 44.0; H, 7.3; N, 19.4%. FAB mass (CH$_2$Cl$_2$, m/z): 436.1 (M)$^+$.

2-3. X-ray Structural Determination

Data collection, cell refinement and data reduction were carried out using CAD4 software SDP.[14] The structure was solved direct methods using SHELX86.[15] Refinement was performed with SHELXL97[16] using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using riding model and fixed. Molecular graphics were prepared using ORTEP II[17] in NRCVAX.[18] Table 1 shows the ex-

Table 1. Experimental details

Crystal data	
C$_{16}$H$_{32}$CuN$_6$S$_2$	MoK$_\alpha$ radiation
M$_r$=436.14	λ=0.71069 Å
Monoclinic	Cell parameters from 25
P2$_1$/a	reflections
a=7.622(2)Å	θ=11.37-14.19°
b=17.645(2)Å	μ=1.263 mm^{-1}
c=8.223(3)Å	T=288 K
β=109.99(2)°	Violet
V=1039.3(5) Å^3	Plate
Z=2	0.33×0.26×0.13 mm
D$_x$=1.394 Mg m^{-3}	
D$_m$ not measured	

Data collection	
Enraf-Nonius CAD-4	R$_{int}$=0.0286
Diffractometer	h=$-10 \to 10$
$w/2\theta$ scans	k=0 $\to$ 24
Absorption correction:	l=0 $\to$ 11
none	3 standard reflections
7353 independent	frequency: 300 min
reflections	intensity decay: 1.1%
1804 reflections with	
F$_o \geq 3\sigma$(F$_o$)	
θ_{max}=30.0°	

Refinement	
Refinement on F	$(\Delta/\sigma)_{max}$=0.000
R(F)=0.0873	$(\Delta\rho)_{max}$=1.055 eÅ^{-3}
ωR(F)=0.1583	$(\Delta\rho)_{min}$=-0.565 eÅ^{-3}
S=1.613	Extinction correction:
3022 reflections	none
115 parameters	Scattering factors from
H atoms constrained	International Tables
$w=1/[\sigma^2(F_o^2)+(0.03000P)^2$	for Crystallography
$+0.5000P]$	(Vol. C)
where $P=(F_o^2+2F_c^2)/3$	

perimental details and final atomic coordinates are given in Table 2.

3. Results and Discussion

Fig. 1 shows an ORTEP drawing of [Cu(L)] (NCS)$_2$ (1) with the atomic numbering scheme. Interatomic bond distance and angles are listed in Table 3. In the present complex 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 1 exists on the central copper(II) ion. The

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Cu (L)](NCS)$_2$ (1)

	x	y	z	U(eq)
Cu	5000	5000	5000	43(1)
N(1)	3725(6)	5446(2)	2608(5)	44(1)
N(2)	3330(6)	4073(2)	4549(5)	46(1)
C(1)	4951(8)	6051(3)	2350(7)	54(1)
C(2)	3965(10)	6596(4)	880(7)	86(2)
C(3)	3150(8)	4891(3)	1189(6)	59(2)
C(4)	1824(9)	4318(4)	1441(7)	73(2)
C(5)	2720(10)	3708(4)	2794(7)	74(2)
C(6)	1594(14)	3043(5)	2616(11)	139(4)
C(7)	4248(8)	3530(3)	5938(7)	59(2)
S	156(3)	6396(1)	3460(3)	106(1)
N	2305(9)	5658(3)	6254(6)	60(2)
C	1573(10)	5919(4)	5308(13)	87(3)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

N-Cu-N angles of the six-membered chelate rings (94.2(2)°) are larger than those of the five-membered chelate rings (85.8(2)°). The cation of complex **1** is characterized by an essentially square planar coordination geometry around the

Table 3. Interatomic bond distances (Å) and angles (°) for [Cu(L)](NCS)$_2$ (1)

Cu-N(1)	2.031(4)	N(2)-C(7)	1.471(6)
Cu-N(1)^i	2.031(4)	C(1)-C(7)^i	1.521(7)
Cu-N(2)	2.028(4)	C(1)-C(2)	1.527(7)
Cu-N(2)^i	2.028(4)	C(3)-C(4)	1.493(8)
Cu-N	2.842(7)	C(4)-C(5)	1.532(8)
Cu-N^i	2.842(7)	C(5)-C(6)	1.431(10)
N(1)-C(1)	1.481(7)	C(7)-C(1)^i	1.521(7)
N(1)-C(3)	1.471(6)	S-C	1.750(10)
N(2)-C(5)	1.502(6)	N-C	0.912(10)
N(1)-Cu-N(2)	94.2(2)	C(5)-N(2)-C(7)	112.1(4)
N(1)-Cu-N(2)^i	85.8(2)	N(1)-C(1)-C(2)	113.8(5)
N(1)^i-Cu-N(2)	85.8(2)	N(1)-C(1)-C(7)^i	106.9(4)
N(1)^i-Cu-N(2)^i	94.2(2)	N(1)-C(3)-C(4)	111.9(4)
N(1)-Cu-N(1)^i	180.0	N(2)-C(5)-C(4)	108.1(5)
N(2)-Cu-N(2)^i	180.0	N(2)-C(5)-C(6)	115.3(6)
N-Cu-N^i	180.0	N(2)-C(7)-C(1)^i	109.6(4)
Cu-N(1)-C(1)	107.5(3)	C(7)^i-C(1)-C(2)	111.0(5)
Cu-N(1)-C(3)	115.1(3)	C(3)-C(4)-C(5)	115.0(5)
C(1)-N(1)-C(3)	113.4(4)	C(4)-C(5)-C(6)	113.5(6)
Cu-N(2)-C(5)	119.4(3)	N-C-S	178.4(9)
Cu-N(2)-C(7)	106.3(3)		

Symmetry code: (i) $-x+1$, $-y+1$, $-z+1$.

copper(II) center, formed by secondary amine nitrogens. The average Cu-N (secondary amines)
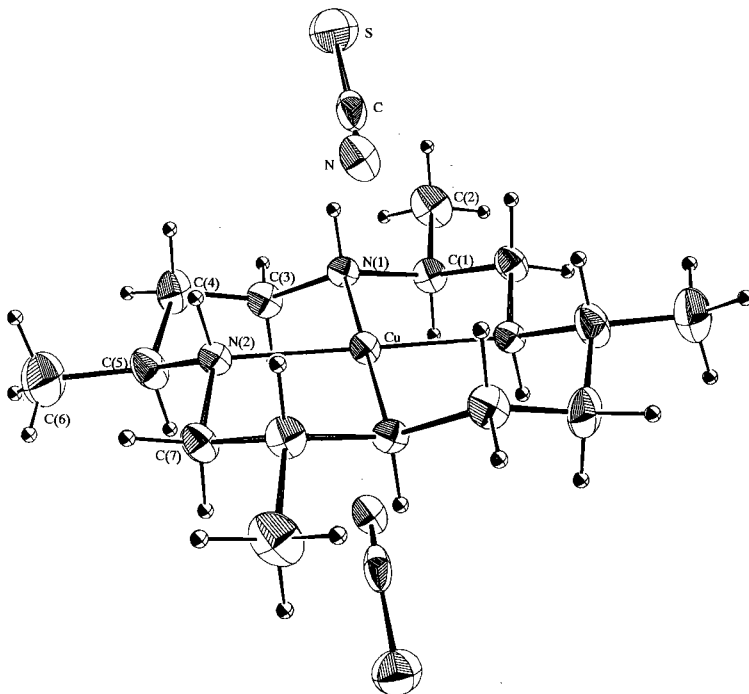

Fig. 1. An ORTEP drawing of [Cu(L)](NCS)$_2$ (1) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms are drawn as small circles of arbitrary radii.

distance of 2.030(4) Å is similar to that reported for the tetra-coordinated complex [Cu(DTAD)]I$_2$·2H$_2$O (2.029(11) Å).[19] The axial Cu-N (thiocyanate) bond distance of 2.842(7) Å is much longer than the Cu-N (secondary amine) bond distance. This indicates that the nitrogen of thiocyanate is not coordinated to the copper (II) ion. The N-C-S angle related to the thiocyanate ligand is linear within the experimental error [N-C-S angle=178.4(9)°].

Acknowledgement

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