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Preparation and Structure of $[Cu(L)]I_2 \cdot 2H_2O$ (L: 3,14-Dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane)

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$[Cu(L)]I_2 \cdot 2H_2O$(L: 3,14-Dimethyl-2,6,13,17-tetraazatricyclo [14,4,$0^{1.18}$,$0^{7.12}$]docosane) 錯物의 合成 및 構造

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Abstract

The complex $[Cu(L)]I_2 \cdot 2H_2O$ (1) (L: 3,14-Dimethyl-2,6,13,17-tetraazatricyclo [14,4,$0^{1.18}$, $0^{7.12}$]docosane) has been prepared and structurally characterized. The complex (1) crystallizes in the triclinic system, space group P1, a=8.400(1) Å, b=8.986(3) Å, c=9.156(1) Å, α=82.42(1)°, β=73.61(1)°, λ=81.04(2)°, Z=1, R for 1926 observed reflections of $[F_o>4\sigma(F_o)]$, measured at 288K, was 0.042. The tetracoordination around Cu atom of complex (1) is square plane and the average bond distance of Cu-N is 2.029(11) Å. Both six-membered chelate rings adopts a chair conformation and the five-membered ring are gauche with the *sec*-NH centers having the RRSS configuration.

要 約

$[Cu(L)]I_2 \cdot 2H_2O$(1) (L: 3,14-Dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$] docosane) 錯物을 合成하고 構造를 糾明하였다. 이 錯物은 三斜晶系, 空間群 P1, a=8.400(1) Å, b=8.986(3) Å, c=9.156(1) Å, α=82.42(1)°, β=73.61(1)°, λ=81.04(2)°, Z=1로 結晶化 되었으며, 最終 信賴度 R값은 288K에서 1926個 回折班點에 대하여 0.042이었다. 이 錯物의 結晶構造는 平面 四角構造를 갖고 Cu-N의 평균距里는 2.029(11) Å이었다. 이 錯物의 六圓고리와 五圓고리는 RRSS 배열을 갖는 二次 NH와 함께 각각 의자 形態와 고우시 形態를 갖는다.

1. Introduction

Macrocyclic polyamine complexes of the copper (II) ions have been of great interest due to their importance as an essential metalloenzyme active site.[1] Cyclam (1,4,8,11-tetraazacyclotetradecane) is well recognized as an example among the macrocyclic polyamines in coordination chemistry.[2] Recently, it has been reported that the modified cyclam complexes show considerable changes in physical and chemical properties, and structures and catalytic efficiency.[3-9] Among the previously reported scope of cyclam analogs, few examples which possess additional groups at the carbon atoms of dimethylene linkages are known. We recently reported the preparation and X-ray structure of $[Cu(L)(H_2O)_2]Cl_2$ (L: 3, 14-Dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$, $0^{7.12}$]docosane).[10] It showed that this complex has the tetragonally elongated octahedral geometry

Table 1. Crystal Data and Structural Refinement for $[Cu(L)]I_2 \cdot 2H_2O$ (1)

Crystal data	
Chemical formula	$C_{20}H_{44}CuI_2N_4O_2$
Chemical formula weight	689.95
Space group	P1
a (Å)	8.400(1)
b (Å)	8.986(3)
c (Å)	9.156(1)
α (°)	82.42(1)
β (°)	73.61(1)
γ(°)	81.04(2)
V (Å^3)	652.1(3)
Z	1
F (000)	343
Dm (g · m^{-3})	1.756
Radiation type (λ)	Mo Kα (0.71069Å)
Cell dimensions based on 25 reflections	$11.40° \leq \theta \leq 14.17°$
μ (mm^{-1})	3.203
Crystal form	block
Crystal size (mm)	0.23×0.17×0.10
Crystal color	dark brown
Data collection	
Diffractometer	Enraf-Nonius CAD4
Data collection method	ω-2θ scan
Absorption correction	None
No. of measured reflections	2725
No. of independent reflections	2710
No. of observed reflections	1926
Criterion for observed reflections	$F_o > 4\sigma(F_o)$
R_{int}	0.00
θ_{max} (°)	26
Range of *h*, *k*, *l*	-9→h→10, -10→k→11, 0→l→11
No. of standard reflections	3
Frequency of standard reflections (min)	300
Intensity decay (%)	1.2
Refinement	
Refinement on	F
R	0.0421
ωR	0.1118
S	0.849
No. of reflections used in refinement	2710
No. of parameters used	262
$(\Delta/\sigma)_{max}$	0.363
$\Delta\rho_{max}$ (eÅ^{-3})	1.103
$\Delta\rho_{min}$(eÅ^{-3})	-0.882
Extinction method	none

and longer Cu-O (water molecule) bond distance (2.649(2) Å).

In the present study, we report the preparation and crystal structure of $[Cu(L)]I_2 \cdot 2H_2O$ (**1**).

2. Experimental Section

Materials. All solvents were reagent grade and purified according to the literature.[11] All chemicals used in syntheses were of reagent

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $[Cu(L)]I_2 \cdot 2H_2O$ (1)

	x	y	z	U (eq)
Cu	3575(3)	-1444(3)	-1243(3)	40(1)
N(1)	3100(15)	905(12)	-1975(15)	36(3)
N(2)	5532(13)	-1444(14)	-3037(16)	39(3)
N(3)	3958(14)	-3603(11)	-608(14)	29(2)
N(4)	1566(15)	-1409(10)	660(16)	34(3)
C(1)	4214(15)	1061(11)	-3377(12)	17(2)
C(2)	4420(3)	2789(17)	-3840(2)	56(5)
C(3)	5640(2)	2995(19)	-5560(2)	56(5)
C(4)	7397(18)	1919(19)	-5605(16)	57(5)
C(5)	7050(2)	310(2)	-5100(2)	47(4)
C(6)	5848(18)	172(13)	-3584(15)	30(3)
C(7)	7130(2)	-2507(17)	-2910(2)	52(4)
C(8)	6650(2)	-4006(18)	-2490(3)	63(5)
C(9)	5724(19)	-4530(19)	-804(17)	55(5)
C(10)	6670(2)	-4160(2)	340(2)	57(5)
C(11)	2840(2)	-4050(2)	1183(18)	60(5)
C(12)	2530(2)	-5586(18)	1530(2)	47(4)
C(13)	1350(3)	-5790(2)	2980(2)	67(6)
C(14)	-180(3)	-4883(15)	3140(3)	91(8)
C(15)	-30(3)	-3210(19)	2710(2)	57(5)
C(16)	1213(18)	-2908(19)	1070(2)	53(5)
C(17)	142(16)	-335(18)	470(2)	50(4)
C(18)	460(2)	1323(14)	39(18)	41(4)
C(19)	1420(2)	1629(13)	-1610(2)	46(4)
C(20)	610(3)	1410(2)	-2690(3)	64(5)
I(1)	1733(1)	-3221(1)	-3370(1)	73(1)
I(2)	5452(1)	282(1)	850(1)	69(1)
O(w1)	1709(13)	-179(15)	3535(13)	77(3)
O(w2)	5220(6)	-2880(2)	-6050(5)	340(2)

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

grade and were used without further purification. The macrocyclic ligand L and complex $[Cu(L)(H_2O)_2]Cl_2$ were prepared as described previously.[12,10]

Analytical Methods. High-resolution fact atom bombardment mass spectrometry (FAB mass) were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were carried out by the Korea Basic Science Institute, Seoul, Korea.

Preparation of $[Cu(L)]I_2 \cdot 2H_2O$ (1). To a methanol solution (20 ml) of $[Cu(L)(H_2O)_2]Cl_2$ (507 mg, 1 mmol) was added excess of KI and the mixture refluxed for 1 hr. The solution was placed in a refrigerator for crystallization. The dark brown crystals were filtered off, washed with diethyl ether and dried in vacua (yield: 428 mg, 62%). Anal. Calcd for $CuC_{20}H_{44}N_4O_2I_2$: C, 34.8; H, 6.4; N, 8.1. Found: C, 34.9; H, 6.4; N, 8.0%. FAB mass (CH_2Cl_2, m/z): 689.9 $(M)^+$.

X-ray Structural Determination. Data collection, cell refinement and data reduction were carried out using CAD4 software SDP.[13] The structure was solved by direct methods using SHELX86.[14] Refinement was performed with SHELXL97 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 ORTEP II[16] in NRCVAX.[17] Table 1 shows the experimental details and final atomic coordinates are given in Table 2.

3. Results and Discussion

An ORTEP drawing of $[Cu(L)]I_2 \cdot 2H_2O$ (**1**) with the atomic numbering scheme is shown in Fig. 1. Bond distances and angles are listed in Table 3. The crystal structure of **1** consists of the complex cation, two iodide anions and two water molecules. The most interesting feature of this complex is the tetracoordination of the

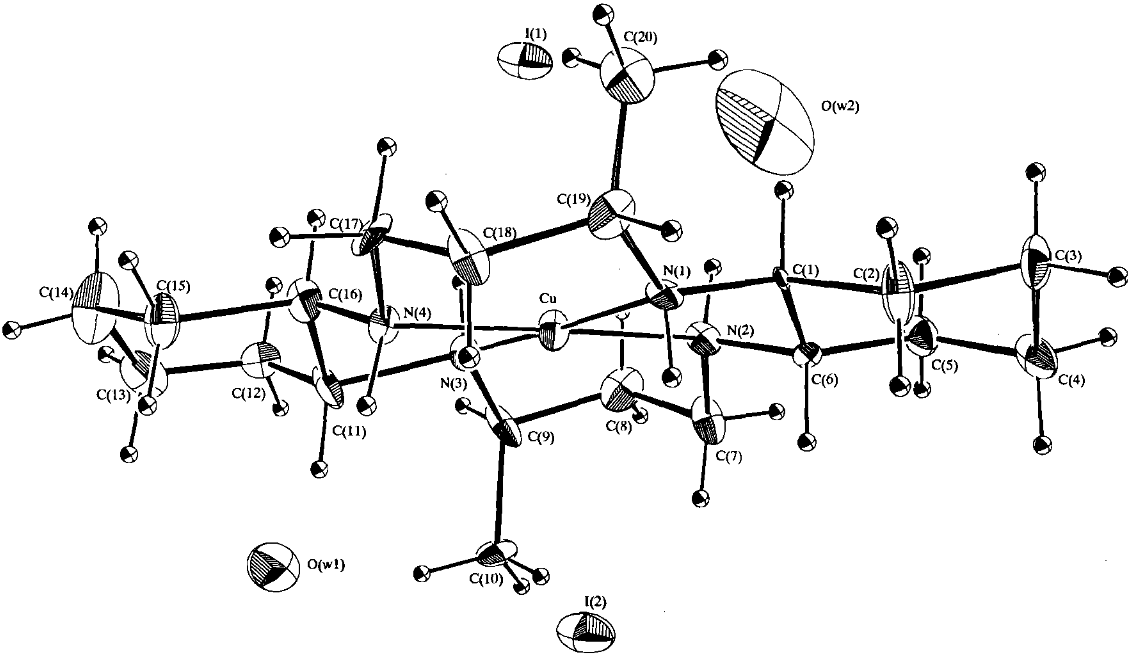

Fig. 1. An ORTEP drawing of $[Cu(L)]I_2 \cdot 2H_2O$ (1) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 40% probability level. H atoms are drawn as small circles of arbitrary radii.

Table 3. Bond Distances (Å) and Angles (°) for $[Cu(L)]I_2 \cdot 2H_2O$ (1)

Cu-N(1)	2.139(11)	C(4)-C(5)	1.500(20)
Cu-N(2)	1.969(12)	C(5)-C(6)	1.470(20)
Cu-N(3)	1.954(10)	C(7)-C(8)	1.440(20)
Cu-N(4)	2.055(13)	C(8)-C(9)	1.570(30)
N(1)-C(1)	1.364(17)	C(9)-C(10)	1.570(20)
N(1)-C(19)	1.428(19)	C(11)-C(12)	1.420(20)
N(2)-C(6)	1.511(17)	C(11)-C(16)	1.600(20)
N(2)-C(7)	1.540(20)	C(12)-C(13)	1.420(30)
N(3)-C(9)	1.559(16)	C(13)-C(14)	1.390(30)
N(3)-C(11)	1.675(18)	C(14)-C(15)	1.520(20)
N(4)-C(16)	1.403(19)	C(15)-C(16)	1.590(20)
N(4)-C(17)	1.452(19)	C(17)-C(18)	1.534(19)
C(1)-C(2)	1.577(17)	C(18)-C(19)	1.510(20)
C(1)-C(6)	1.453(19)	C(19)-C(20)	1.400(30)
C(2)-C(3)	1.620(30)	Cu-I(1)	3.468(20)
C(3)-C(4)	1.630(20)	Cu-I(2)	3.436(20)
N(1)-Cu-N(2)	84.5(5)	C(4)-C(5)-C(6)	112.3(14)
N(1)-Cu-N(3)	178.2(7)	C(1)-C(6)-C(5)	117.9(12)
N(1)-Cu-N(4)	95.0(5)	N(2)-C(6)-C(1)	106.3(9)
N(2)-Cu-N(3)	95.7(5)	N(2)-C(6)-C(5)	112.7(12)
N(2)-Cu-N(4)	178.4(8)	N(2)-C(7)-C(8)	106.8(14)
N(3)-Cu-N(4)	84.9(4)	C(7)-C(8)-C(9)	121.4(18)
C(1)-N(1)-C(19)	124.5(11)	N(3)-C(9)-C(8)	102.3(11)
Cu-N(1)-C(1)	103.5(8)	N(3)-C(9)-C(10)	113.2(14)
Cu-N(1)-C(19)	118.8(8)	N(3)-C(11)-C(12)	115.3(15)
C(6)-N(2)-C(7)	113.2(11)	N(3)-C(11)-C(16)	95.5(10)
Cu-N(2)-C(6)	108.8(8)	C(8)-C(9)-C(10)	110.3(16)
Cu-N(2)-C(7)	117.6(10)	C(11)-C(12)-C(13)	110.8(16)
C(9)-N(3)-C(11)	106.9(10)	C(12)-C(11)-C(16)	113.2(16)
Cu-N(3)-C(9)	124.1(10)	C(12)-C(13)-C(14)	115.2(18)
Cu-N(3)-C(11)	112.2(9)	C(13)-C(14)-C(15)	113.9(17)
C(16)-N(4)-C(17)	114.3(11)	C(14)-C(15)-C(16)	111.7(16)
Cu-N(4)-C(16)	106.7(9)	N(4)-C(16)-C(11)	112.0(13)
Cu-N(4)-C(17)	113.7(11)	N(4)-C(16)-C(15)	115.2(14)
N(1)-C(1)-C(2)	109.2(10)	N(4)-C(17)-C(18)	116.4(11)
N(1)-C(1)-C(6)	117.4(10)	C(11)-C(16)-C(15)	102.2(13)
C(1)-C(2)-C(3)	109.4(13)	C(17)-C(18)-C(19)	112.9(13)
C(2)-C(1)-C(6)	110.0(11)	C(18)-C(19)-C(20)	115.4(16)
C(2)-C(3)-C(4)	108.2(14)	N(1)-C(19)-C(18)	114.4(14)
C(3)-C(4)-C(5)	109.1(12)	N(1)-C(19)-C(20)	110.9(15)

copper atom, probably due to the steric constrains with two methyl groups and cyclohexane rings of the ligand. The basal plane is slightly distorted [deviations N(1) -0.029(1), N(2) 0.030 (1), N(3) -0.031(1) and N(4) 0.028(1) Å from the least-squares plane through these basal donor atoms] with copper (II) ion displaced 0.003 (1) Å toward the apical position. Two iodide ions are located 3.468(2) and 3.436(2) Å from the copper (II) ion. The four Cu-N (secondary amines) bond distances are 2.139(11), 1.969(12), 1.954(10) and 2.055(13) Å. The N-Cu-N angles of the six-membered chelate rings (95.0(5) and 95.7(5)°) are larger than those of the five-membered chelate rings (84.5(5) and 84.9(4)°) The same tetracoordinate structure is observed for those of 14-membered tetraaza macrocyclic ligands.18,19 The ligand skeleton of **1** contains two cyclohexane rings and two gauche five-membered and two chair six-membered chelate rings with the *sec*-NH centers having the RRSS configuration. The N(4) atom in the cation is hydrogen bonded to O(w1) atom in the water molecule [N(4)···O(w1) 3.026(3) Å].

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