Synthesis and Molecular Structure of a Macrocyclic Chlorotetraamine Cadmium(II) Complex

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巨大고리 Chlorotetraamine Cadmium(II) 錯物의 合成과 分子 構造

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Abstract

The molecular structure of [Cd(L)Cl]Cl · 2H$_2$O (**1**) (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0$^{1.18}$,0$^{7.12}$]docosane) has been determined by X-ray diffraction. Crystallographic data for **1**: triclinic space group P$\bar{1}$, a=9.671(1), b=10.784(1), c=12.679(2) Å, α=112.31(1), β=99.49(1), γ= 93.95(1)°, V=1230.6(3) Å^3, Z=2, R=0.0779. The coordination of the cadmium atom is a distorted square-pyramid with four secondary amines of the macrocycle occupying the basal sites (Cd-N$_{av}$= 2.300(3) Å) and a terminal chlorine atom at the axial position with a Cd-Cl(1) distance of 2.463(2) Å.

要 約

X-ray 回折法을 이용하여 [Cd(L)Cl]Cl · 2H$_2$O (**1**) (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0$^{1.18}$,0$^{7.12}$]docosane) 化合物의 分子 構造가 糾明되었다. 化合物 **1**의 結晶學 資料: triclinic space group P$\bar{1}$, a=9.671(1), b=10.784(1), c=12.679(2) Å, α=112.31(1), β=99.49(1), γ=93.95(1)°, V=1230.6(3) Å^3, Z=2, R=0.0779. 中心 cadmium 原字는 巨大 고리 리간드로 부터 4個의 2次 아민 (Cd-N$_{av}$=2.300(3) Å)과 軸方向 位置의 鹽素 原字 (Cd-Cl(1)=2.463(2) Å)로 結合된 若干 일그러진 사각뿔 構造를 갖는다.

1. Introduction

Recently, it has been reported that the transition-metal (II) complexes of the modified cyclam (1,4,8,11-tetraazacyclotetradecane) show considerable changes in physical and chemical properties, structures, and catalytic efficiency.[1-5] Many metal (II) complexes of these tetraaza macrocyclic ligands undergo a square-planar and octahedral geometry in the solid state. In a previous paper, we have isolated and characterized the trans-diaqua tetraaza macrocyclic zinc (II) complex [Zn(L)(H$_2$O)$_2$]Cl$_2$ (L=3,14-dimethyl-2,6,13,17-tet-

raazatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]docosane), in which two water molecules are coordinated to the central zinc (II) ion by the formation of chelate rings with secondary amines and chlorides.[6] Further study on the crystal structure of the SCN$^-$ binding to zinc (II) complex of L showed a square pyramidal geometry with an apical thiocyanate nitrogen atom.[7] However, the corresponding chlorine-coordinated cadmium (II) complex with ligand the L has not yet been isolated. In the present work, we report the synthesis and molecular structure of [Cd(L)Cl]Cl · 2H$_2$O (**1**).

2. Experimental Section

Materials and Measurements. All chemicals and slovents used in the synthesis were of reagent-grade and were used without further purification. The macrocyclic ligand L was prepared as described previously.[8] Infrared spectra were obtained on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer with samples prepared as KBr pellets. High-resolution fast-atom bombardment mass spectrometry (FAB mass) was performed by using a Jeol JMS-HA 100A/100A instrument. Elemental analyses (C, H, N) were carried out at the Korea Research Institute of Chemical Technology, Taejon, Korea.

Synthesis of [Cd(L)Cl]Cl·2H₂O (1). To a methanol solution (20 m*l*) of L (336 mg, 1 mmol) was added CdCl₂ (183 mg, 1 mmol), and then the mixture heated at reflux for 1 h. The solution was allowed to stand at room temperature and was then filtered. The filtrate was evaporated to dryness and the resulting solid dissolved in acetonitrile/water (1 : 1, 10 m*l*). When this mixture was allowed to stand for a few days, a quantity of colorless crystals precipitated. These were filtered off, washed with diethyl ether, and dried in air (361 mg, 65% yield). IR (KBr, cm⁻¹): 3431, 3158, 2946, 1590, 1456, 1383, 1318, 1154, 1122, 1106, 1018, 956, 905, 815, 633, 552. Found: C, 43.12; H, 7.91; N, 10.17. Calc. for $C_{20}H_{44}CdCl_2N_4O_2$: C, 43.21; H, 7.98; N, 10.08%. FAB mass (CH_2Cl_2, m/z): 555 (M⁺).

X-ray Crystallography. Suitable crystals of **1** were obtained by slowly evaporating the complex solution in a mixture of acetonitrile and water. A summary of the data collection and details of the structure refinement is given in Table 1. A colorless crystal was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected with graphite-monochromated Mo-Kα radiation (λ=0.71069 Å) by the ω-2θ scan technique. The accurate unit-cell parameters and a crystal orientation matrix were determined by least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical φ-scan method. The structure was solved by direct methods and refined by

Table 1. Crystal Data and Structure Refinement for 1

Color/shape	Colorless/block
Empirical formula	$C_{20}H_{44}CdCl_2N_4O_2$
Formula weight	555.89
Temperature	293 K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a=9.967(1) Å α=112.31(1)°
	b=10.784(1) Å β=99.49(1)°
	c=12.679(2) Å γ=93.95(1)°
Volume	1230.6(3) Å³
Z	2
Density (calculated)	1.500 Mg/m³
Absorption coefficient	1.127 mm⁻¹
Diffractometer	Enraf-Nonius CAD4
Radiation/wavelength	MoKα (graphite monochrom.)/0.71069 Å
F(000)	580
Crystal size	0.30×0.28×0.23 mm
θ range for data collection	2.06 to 24.97°
Index ranges	-11≤h≤11, -12≤k≤11, 0≤l≤15
Reflection collected/ unique	4344/4137 (R_{int}=0.0633)
Absorption correction (φ-scan)	T_{max}=0.7724, T_{min}=0.0096
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4137/0/260
Goodness-of-fit on F^2	1.086
Final R indices [$I>2\sigma(I)$]	R_1^a=0.0779, wR_2^b=0.2318
R indices (all data)	R_1^a=0.0816, wR_2^b=0.2395
Weight	$w=1/[\sigma^2(F_o^2)+(0.2000P)^2 +0.0000P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.174 and -3.499 eÅ⁻³

$^aR_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|.$
$^bwR_2=[\Sigma[w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}.$

full-matrix least-squares on F^2 with anisotropic factors for all non-hydrogen atoms.[9,10] All hydrogen atoms except for the water hydrogen atoms were placed in calculated positions with isotropic displaced parameters. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 1

	x	y	z	U(eq)
Cd	126(1)	-1948(1)	-3143(1)	24(1)
Cl(1)	734(2)	-3050(2)	-5057(2)	43(1)
Cl(2)	-3973(4)	-3769(5)	-5847(4)	90(1)
N(1)	2149(6)	-1354(7)	-1776(5)	25(1)
N(2)	186(6)	-3742(6)	-2544(5)	23(1)
N(3)	-2170(5)	-1845(6)	-3288(6)	25(1)
N(4)	67(6)	332(6)	-2435(5)	23(1)
C(1)	2637(7)	-2585(8)	-1796(6)	27(2)
C(2)	3956(9)	-2426(10)	-926(9)	45(2)
C(3)	4427(9)	-3741(12)	-1045(12)	60(3)
C(4)	3310(10)	-4657(12)	-834(11)	58(3)
C(5)	1919(8)	-4887(9)	-1764(10)	44(2)
C(6)	1507(7)	-3489(8)	-1646(7)	29(2)
C(7)	-1140(8)	-4309(8)	-2314(7)	29(2)
C(8)	-1141(9)	-3735(8)	-990(6)	32(2)
C(9)	-2357(8)	-4000(10)	-2994(9)	43(2)
C(10)	-2734(7)	-2611(9)	-2655(8)	34(2)
C(11)	-2401(7)	-354(8)	-2834(7)	26(2)
C(12)	-3823(7)	-252(10)	-3449(8)	42(2)
C(13)	-4127(8)	1171(10)	-2973(9)	41(2)
C(14)	-2983(9)	2181(10)	-3011(11)	50(2)
C(15)	-1592(8)	2033(9)	-2480(8)	36(2)
C(16)	-1283(7)	536(7)	-3003(6)	21(1)
C(17)	1323(7)	1216(8)	-2388(7)	31(2)
C(18)	1539(9)	899(11)	-3628(8)	44(2)
C(19)	2584(8)	1032(8)	-1599(7)	29(2)
C(20)	3062(7)	-326(8)	-1960(7)	28(2)
Ow(1)	0	0	0	18(1)
Ow(2)	3935(8)	-3458(9)	-4319(7)	72(2)

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

3. Results and Discussion

The structure of [Cd(L)Cl]Cl · 2H₂O (**1**) with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The complex **1** consists of a [Cd(L)Cl]⁺ cation, a chloride anion, and two water molecules. The ligand
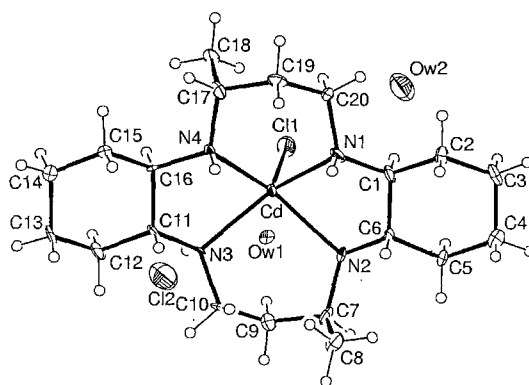
Fig. 1. An ORTEP drawing (30% probability ellipsoids) of 1 with the atomic numbering scheme.

Table 3. Selected Bond Distances (Å) and Angles (°) for 1

Cd-N(1)	2.303(6)	Cd-N(2)	2.332(5)
Cd-N(3)	2.280(5)	Cd-N(4)	2.285(6)
Cd-Cl(1)	2.463(2)		
N(1)-Cd-N(2)	76.2(2)	N(1)-Cd-N(3)	141.2(2)
N(1)-Cd-N(4)	83.9(2)	N(2)-Cd-N(3)	97.3(2)
N(2)-Cd-N(4)	141.2(2)	N(3)-Cd-N(4)	77.8(2)
N(1)-Cd-Cl(1)	106.4(2)	N(2)-Cd-Cl(1)	99.2(2)
N(3)-Cd-Cl(1)	112.4(2)	N(4)-Cd-Cl(1)	118.5(2)
Cd-N(1)-C(1)	107.6(4)	Cd-N(1)-C(20)	108.5(4)
Cd-N(2)-C(6)	109.2(4)	Cd-N(2)-C(7)	118.4(4)
Cd-N(3)-C(10)	109.1(4)	Cd-N(3)-C(11)	109.2(4)
Cd-N(4)-C(16)	106.9(4)	Cd-N(4)-C(17)	116.9(4)

skeleton of the present compound contains a *trans*-III configuration in the solid state. The N-Cd-N angles of the six-membered chelate rings of **1** are larger than those of the five-membered chelate rings. The cadmium atom is a five coordinate, distorted square-pyramidal geometry with bonds to the four secondary amines of the macrocycle and to the axial chlorine atom. The average Cd-N bond to the macrocyclic secondary amines (2.300(3) Å) is sig-

Table 4. Hydrogen Bonding Parameters (Å, °) for 1

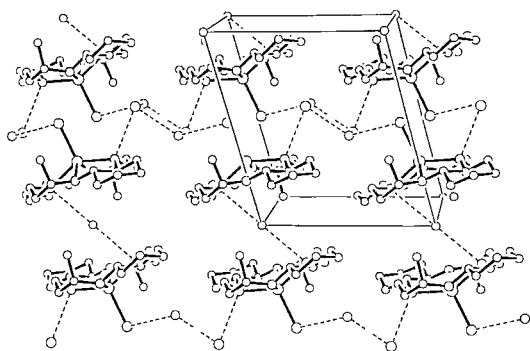| D-H···A	D···A (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)-HN(1)···Ow(1)	0.91	2.58	3.364(6)	144.9
N(3)-HN(3)···Cl(2)	0.91	2.36	3.242(8)	163.0
Ow(2)···Cl(1)			3.025(9)	
Ow(2)···Cl(2)ⁱ			3.078(10)	
Ow(2)···Cl(2)ⁱⁱ			3.282(8)	

Symmetry codes: (i) x+1, y, z; (ii) -x, -y-1, -z-1.

Fig. 2. Packing diagram of 1, showing the hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

nificantly shorter than that found in $[CdL^1][ClO_4]_2^{11)}$ (L^1=6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine) (2.418(2) Å), indicating the six-coordinated octahedral geometry. The trans-basal angles of N(1)-Cd-N(3) and N(2)-Cd-N(4) are exactly same (141.2(2)°). The cadmium atom is 0.751(3) Å displaced out of plane, in the direction of the chloride anion [Cd-Cl(1)=2.463(2) Å]. The axial cadmium-chlorine bond is not perpendicular to the square plane as the Cl_{axial}-Cd-N_{basal} angles range from 99.2(2) to 118.5(2)°. Interestingly, the secondary amines N(1) and N(3) of the macrocycle form hydrogen bonds with the water molecule Ow(1) and chloride anion Cl(2). Furthermore, the water molecule Ow(2) is linked to the chloride anions Cl(1) and Cl(2) through hydrogen bonds, which form a two-dimensional chain (Table 4 and Fig. 2).

4. Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from author K.-Y.

Choi on request.

References

1) Kimura, E., Kotake, T., Koike, T., Shionoya, M. and Shiro, M., *Inorg. Chem.*, **29**, 4991 (1990).

2) Shionoya, M., Kimura, E. and Iotaka, Y., *J. Am. Chem. Soc.*, **112**, 9237 (1990).

3) Fujita, E., Haff, J., Sanzenbacher, R. and Elias, H., *Inorg. Chem.*, **33**, 4627 (1994).

4) Choi, K.-Y., Kim, J. C., Jensen, W. P., Suh, I.-H. and Choi, S.-S., *Acta Crystallogr., Sect. C.*, **C52**, 2166 (1996).

5) Kimura, E. and Koike, T., *Adv. Inorg. Chem.*, **44**, 229 (1997).

6) Choi, K.-Y., Suh, I.-H. and Kim, J. C., *Polyhedron*, **16**, 1783 (1997).

7) Choi, K.-Y. and Suh, I.-H., *Polyhedron*, **16**, 2393 (1997).

8) Kang, S.-G., Kweon, J. K. and Jung, S.-K., *Bull. Korean Chem. Soc.*, **12**, 483 (1991).

9) Sheldrick, G. M., *Acta Crystallogr., Sect. A*, **A46**, 467 (1990).

10) Sheldrick, G. M., SHELXL-97, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).

11) Bernhardt, P. V., Comba, P., Hambley, T. W., Lawrance, G. A. and V rnagy. K., *J. Chem. Soc., Dalton Trans.*, 355 (1992).