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Crystal Structure of Macrocyclic Chlorotetraamine Zinc(II) Complex

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巨大고리 Chlorotetraamine Zinc(II) 錯物의 結晶構造

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Abstract

The complex $[Zn(L)Cl](H_2O)(ClO_4)$ (**1**) (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane) has been prepared and characterized by X-ray crystallography. **1** crystallizes in the monoclinic space group $P2_1/c$, with a=8.883(1), b=19.319(9), c=15.124(2) Å, β=101.65(1)°, V=2542.0(13) Å^3, Z=4, $R_1(wR_2)$ for 4457 observed reflections of [$I>2\sigma(I)$] was 0.0640(0.1557). The coordination geometry around the zinc atom is a distorted square-pyramid with four nitrogen atoms of the macrocycle occupying the basal sites ($Zn\text{-}N_{av}$=2.131(2) Å) and a chloride atom at the axial position with the Zn-Cl distance of 2.316(2) Å.

要 約

$[Zn(L)Cl](H_2O)(ClO_4)$ (**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 單斜晶系, 空間群 $P2_1/c$, a=8.883(1), b=19.319(9), c=15.124(2) Å, β=101.65(1)°, V=2542.0(13) Å^3, Z=4로 決定化되었다. 이 錯物의 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度 $R_1(wR_2)$ 값은 4457個의 回折斑點에 대하여 0.0640 및 0.1557 이었다. 中心 zinc 原字는 巨大 고리 리간드로 부터 4個의 窒素 原子 ($Zn\text{-}N_{av}$=2.131(2) Å)와 軸方向 位置의 鹽素 原字 (Zn-Cl=2.316(2) Å)로 結合된 若干 일그러진 사각뿔 構造를 갖는다.

1. Introduction

Zinc(II) complexes of macrocyclic polyamines have been of great interest due to their relevance to inorganic,[1] biological,[2-4] as well as analytical chemistry.[5-7] Recently, a number of zinc(II) complexes of C-alkyl substituted macrocycle have been synthesized and characterized.[8-12] The coordination environments around the zinc atoms in these complexes are known to be square-pyramidal or octahedral with bonds to water[8-10] or thiocyanate ligands.[11] In a previous paper, we reported the synthesis and X-ray crystal structure of $[Zn(L)(NCO)]^+[(Cl)_{0.5}(NCO)_{0.5}]^-3H_2O$ (L=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane), in which the zinc(II) ion adopts a distorted square-pyramidal geometry.[13] The reaction of $[Zn(L)(H_2O)_2]Cl_2$[10] with an excess of sodium perchlorate was expected to produce a square-planar or elongated octahedral geometry. However, the only product isolated from the reaction mixture was a distorted square-pyramidal geometry. In this paper, we report the synthesis and crystal structure of $[Zn(L)Cl](H_2O)(ClO_4)$ (**1**).

2. Experimental

Materials and Physical Measurements. All the reagents used for the preparation of the complex were of reagent grade and were used without further purification. The macrocyclic ligand L and complex $[Zn(L)(H_2O)_2]Cl_2$ were prepared as described previously.[10] IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. High-resolution fast atom bombardment mass spectrometry (FAB mass) was performed with a Jeol JMS-HA 100A/100A instrument. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology, Taejon, Korea.

Preparation of $[Zn(L)Cl](H_2O)(ClO_4)$ (1). To a methanol solution (20 ml) of $[Zn(L)(H_2O)_2]Cl_2$ (337 mg, 0.5 mmol) was added an excess $NaClO_4$ and the mixture refluxed for 6 h. The solution was filtered and the filtrate was evaporated to dryness. The product was dissolved in water/acetonitrile (1:1, 10 ml). When this mixture was allowed to stand for a few days, light yellow crystals were precipitated. These were collected, washed with diethyl ether, and dried in air (195 mg, 73% yield). Found: C, 43.21; H, 7.61; N, 10.16. Calc. for $C_{20}H_{42}Cl_2ZnN_4O_5$: C, 43.29; H, 7.63; N, 10.10%. IR (KBr, cm^{-1}): 3434, 3151, 2930, 2012, 1591, 1452, 1393, 1315, 1273, 1150, 1125, 1109, 1011, 959, 904, 801, 631, 551. FAB mass (CH_2Cl_2, m/z): 555 (M^+).

X-ray Crystallography. A rectangular rod crystal was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections and refined by least-squares methods. Intensities were collected with graphite-monochromated

Table 1. Crystal Data and Structure Refinement for 1

Color/shape	Light yellow/block
Empirical formula	$C_{20}H_{42}Cl_2N_4O_5Zn$
Formula weight	554.85
Temperature	289(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a=8.883(1) Å α=90°
	b=19.319(9) Å β=101.65(1)°
	c=15.124(2) Å γ= 90°
Volume	2542.0(13) Å^3
Z	4
Density (calculated)	1.450 Mg/m^3
Absorption coefficient	1.214 mm^{-1}
Diffractometer	Enraf-Nonius CAD4
Radiation/wavelength	MoKα (graphite monochrom.)/0.71073 Å
F(000)	1176
Crystal size	0.26×0.26×0.17 mm
θ range for data collection	2.11 to 24.97°
Index ranges	$-10\le h\le 10$, $0\le k\le 22$, $0\le l\le 17$
Reflection collected/unique	4637/4457 (R_{int}=0.0257)
Absorption correction (φ-scan)	T_{max}=0.825, T_{min}=0.740
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4457/0/286
Goodness-of-fit on F^2	1.028
Final R indices [$I>2\sigma(I)$]	R_1[a]=0.0640, wR_2[b]=0.1557
R indices (all data)	R_1[a]=0.1064, wR_2[b]=0.1775
Weight	$w=1/[\sigma^2(F_o^2)+(0.0915P)^2+3.0215P]$
	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.989 and -0.7261 eÅ^{-3}

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2=[\Sigma[w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

Mo-Kα radiation (λ=0.71073 Å), by the ω-2θ scan technique. Lorentz and polarization correction was applied, and intensity data were corrected for absorption effects. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 1. The structure was solved by heavy atom method and refined by full-matrix least-squares methods with the SHELXL97 computer program.[14,15] All hydrogen-atom positions were computed and refined with an overall isotropic factor in a riding model.

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

	x	*y*	*z*	*U*(eq)
Zn	3117(1)	4227(1)	7861(1)	31(1)
O(1)	-1302(7)	2344(4)	5950(5)	118(3)
O(2)	-790(20)	3539(10)	5708(10)	117(2)
O(2')	-660(30)	3539(15)	6144(16)	117(2)
O(3)	50(20)	2842(9)	5040(15)	117(2)
O(3')	1170(14)	2673(6)	5722(10)	117(2)
O(4)	1001(14)	2763(7)	6683(10)	117(2)
O(4')	370(20)	3077(10)	6946(15)	117(2)
Ow(1)	6635(9)	3967(5)	10322(5)	137(3)
Cl(1)	4914(2)	5086(1)	8346(1)	52(1)
Cl(2)	-213(2)	2863(1)	5960(1)	55(1)
N(1)	3833(5)	3428(2)	8805(3)	35(1)
N(2)	3971(5)	3531(2)	6982(3)	31(1)
N(3)	1704(5)	4688(2)	6707(3)	32(1)
N(4)	1342(5)	4622(2)	8496(3)	32(1)
C(1)	4376(7)	2829(3)	8349(4)	37(1)
C(2)	5500(8)	2376(3)	8992(4)	54(2)
C(3)	6049(9)	1756(4)	8504(5)	64(2)
C(4)	6723(8)	2001(4)	7714(6)	65(2)
C(5)	5589(8)	2450(3)	7081(5)	51(2)
C(6)	5093(7)	3073(3)	7567(4)	37(1)
C(7)	5972(7)	4217(4)	6415(5)	54(2)
C(8)	4481(7)	3814(3)	6171(4)	40(1)
C(9)	3166(7)	4227(3)	5599(4)	39(1)
C(10)	2634(7)	4875(3)	6031(4)	38(1)
C(11)	944(6)	5281(3)	7073(4)	32(1)
C(12)	-219(7)	5665(3)	6370(4)	44(2)
C(13)	-1011(7)	6241(3)	6793(5)	48(2)
C(14)	-1777(7)	5968(3)	7519(5)	50(2)
C(15)	-662(7)	5562(3)	8223(4)	46(2)
C(16)	174(6)	4997(3)	7819(4)	33(1)
C(17)	715(7)	4185(3)	9163(4)	44(2)
C(18)	-515(10)	3702(4)	8708(6)	85(3)
C(19)	2037(8)	3828(4)	9794(4)	50(2)
C(20)	2781(8)	3220(4)	9405(5)	55(2)

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

Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

An ORTEP drawing of $[Zn(L)Cl](H_2O)(ClO_4)$ (**1**) with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The crystal structure consists of a $[Zn(L)Cl]^+$ cation, a disordered perchlorate anion, and one water molecule. The ligand skeleton of the present compound takes the most stable *trans*-III configuration with two chair six-membered and two gauche five-membered chelate rings. The zinc atom is coordinated to four secondary amines of the macrocycle and to chloride anion. The coordination geometry around the zinc atom is a distorted square-pyramid with the metal center lying out of the N_4 plane, by 0.476(2) Å toward the axial chlorine atom. The average Zn-N bond distance of 2.131(2) Å is slightly longer than that found in octahedral com-

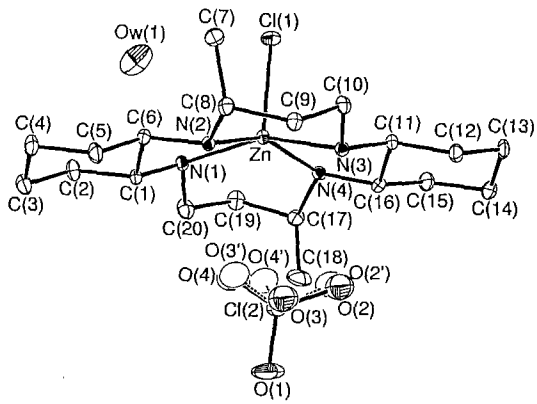

Fig. 1. An ORTEP drawing of 1 with the atomic numbering scheme.

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

Zn-N(1)	2.112(5)	Zn-N(2)	2.136(4)
Zn-N(3)	2.128(4)	Zn-N(4)	2.146(5)
Zn-Cl(1)	2.316(2)		
N(1)-Zn-N(2)	82.2(2)	N(1)-Zn-N(3)	155.1(2)
N(1)-Zn-N(4)	96.1(2)	N(2)-Zn-N(3)	88.7(2)
N(2)-Zn-N(4)	152.7(2)	N(3)-Zn-N(4)	81.6(2)
N(1)-Zn-Cl(1)	102.5(1)	N(2)-Zn-Cl(1)	109.9(1)
N(3)-Zn-Cl(1)	102.4(1)	N(4)-Zn-Cl(1)	97.2(1)

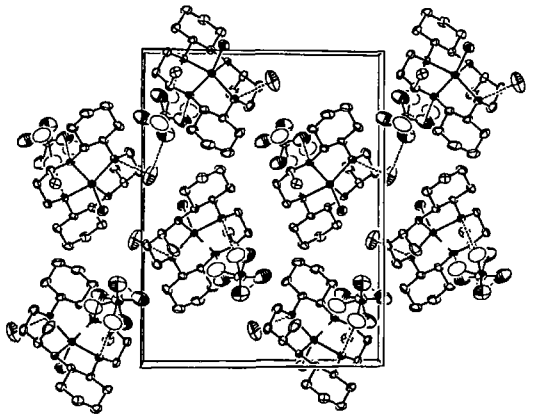

Fig. 2. Crystal packing of 1, showing the hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity. The c-axis is vertical and b-axis horizontal.

Table 4. Hydrogen Bonding Parameters for 1

D-H···A	H···A (Å)	D···A (Å)	D-H···A (°)
N(1)-H(1)···O(w1)	2.237(5)	3.200(9)	169.5(4)
N(2)-H(2)···O(3')	2.321(13)	3.264(13)	161.2(4)
N(2)-H(2)···O(4)	2.057(12)	2.980(13)	156.2(5)
N(2)-H(2)···O(4')	2.531(18)	3.311(19)	136.5(5)
N(3)-H(3)···O(2)	2.306(17)	3.282(17)	174.7(5)
N(3)-H(3)···O(2')	2.101(19)	3.062(19)	166.9(8)

plex $[Zn(L)(H_2O)_2]Cl_2$ (2.099(1) Å).[10] However, the trans-basal angles (N(1)-Zn-N(3)=155.1(2)° and N(2)-Zn-N(4)=152.7(2)°) are similar to those observed in $[Zn(L)(NCS)][NCS]$[11] and $[Zn(DTCT)Cl](ClO_4)$ (DTCT=5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane),[12] indicating the distorted square-pyramidal geometry. The axial Zn-Cl(1) bond distance of 2.316(2) Å is *ca.* 0.2 Å longer than equatorial Zn-N (secondary amines). The axial Zn-Cl(1) linkage is not perfectly perpendicular to ZnN_4 plane with the four N-Zn-Cl(1) angles ranging from 97.2(1) and 109.9(1)°. The nitrogen atoms of the macrocycle form the hydrogen bonds involving the water molecule and perchlorate oxygens (Fig. 2 and Table 4).

4. Supplementary Material

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

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