

단 신

Di-N-acetamide Tetraaza 거대고리 Zinc(II) 착물의 합성 및 결정구조

崔琪泳* · 李漢亨 · 徐日煥
공주대학교 자연과학대학 분화재보존학과
충남대학교 자연과학대학 물리학과
(2001. 1. 3 접수)

Synthesis and Crystal Structure of Zinc(II) Complex of a Di-N-acetamide Tetraaza Macrocycle

Ki-Young Choi*, Han-Hyoung Kim, and Il-Hwan Suh[†]

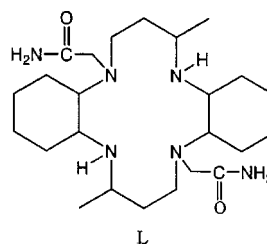
Department of Cultural Heritage Conservation Science, Kongju National University, Kongju 314-701, Korea

[†]Department of Physics, Chungnam National University, Taejeon 305-764, Korea

(Received January 3, 2001)

There has been considerable interest in the synthesis of tetraaza macrocyclic ligands having N-pendant functional groups because of high selectivity for particular metal ions.¹⁻⁴ The DOTHP(1,4,7,10-tetrakis(2-hydroxypropyl)-1,4,7,10-cyclododecane) ligand has shown considerable selectivity for the large Cd(II) ion over the small Zn(II) ion in thermodynamic studies.¹ It is the selectivity for large metal ions over Zn(II) ion in biomedical applications that appears to be the most important thing to achieve in many situations. Morrow *et al.*⁵ have reported on the complexing properties of a cyclen (1,4,7,10-tetraazacyclododecane)-based ligand containing N-propionamide donor groups, whose lanthanide complexes may be of potential use in the cutting of RNA at specific sites. This ligand forms six-membered chelate rings on complex formation, so that it is not well suited to complexing large metal ions such as lanthanides. Additional study on the metal ion complexing properties of DOTAM (1,4,7,10-tetrakis(acetamido)-1,4,7,10-cyclododecane) derivatives were also reported by Hancock *et al.*⁶ They concluded that the DOTAM derivatives proved successful for selectively removing toxic metal ions such as Cd(II) and Pb(II), and the crystal structures of [M(DOTAM)](ClO₄)₂ · 3H₂O (M=Cd²⁺, Zn²⁺) described as a six-coordinate with secondary coordination of the other

two oxygen donors. Recently, we have been interested in the synthesis of the partially N-functionalized tetraaza macrocycles because the structural and chemical properties of their metal complexes differ considerably from those of unsubstituted analogs.⁷⁻¹¹ Choi *et al.*¹² have previously reported on the synthesis and crystal structure of 2,13-bis(acetamido)-5,16-dimethyl-2,6,13,17-tetraazatri-cyclo[14.4.0^{1,15},0^{7,13}]docosane(I.), which contains six donor atoms capable of forming coordination bonds with metal ions. To further investigate the effect of the nature of functional N-pendant arms on the coordination behaviors, we have synthesized and characterized the zinc(II) complex of L.



EXPERIMENTAL SECTION

Materials and physical methods. All chemicals used in syntheses were of reagent grade and were used with-

out further purification. The macrocycle (**L**) was prepared according to the literature method.¹² IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Elemental analyses and FAB mass spectra were performed by the Korea Basic Science Institute, Taejeon, Korea.

Synthesis of [ZnL]Cl₂ · 3H₂O (1**).** A methanol solution (20 mL) of ZnCl₂ (68 mg, 0.5 mmol) and **L** (225 mg, 0.5 mmol) was heated at reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until colorless crystals formed. The product was filtered and recrystallized from a hot water-acetonitrile (1:1, 10 mL) mixture. Yield: 215 mg (67%). Anal. Calcd for C₂₃H₃₂Cl₂N₆O₄Zn: C, 44.97; H, 8.18; N, 13.11. Found: C, 44.90; H, 8.07; N, 13.23%. IR (KBr, cm⁻¹): 3144 (ν_{NH}), 1657 (ν_{C=O}). FAB mass (CII₂Cl₂, *m/z*): 640 (M)⁺.

X-ray crystallography. Intensity data for **1** were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation in the ω-2θ scan mode. Accurate cell parameters and an orientation matrix were determined by least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. All data were corrected for empirical absorption. The structure was solved direct methods¹³ and refined¹⁴ on *F*² by full-matrix least squares with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Crystal parameters and details of the data collections and refinement are summarized in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Table 1. Crystal data and structure refinement for **1**

Empirical formula	C ₂₃ H ₃₂ Cl ₂ N ₆ O ₄ Zn
Formula weight	640.99
Temperature	289 K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 11.173(1) Å <i>α</i> = 90° <i>b</i> = 17.758(1) Å <i>β</i> = 107.9(1)° <i>c</i> = 9.266(2) Å <i>γ</i> = 90°
Volume	1749.5(3) Å ³
<i>Z</i>	2
Density (calculated)	1.217 Mg/m ³
Absorption coefficient	0.892 mm ⁻¹
<i>F</i> (000)	684
Crystal size	0.30 × 0.26 × 0.26 mm
θ range for data collection	2.23 to 24.97°
Limiting indices	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 21, -11 ≤ <i>l</i> ≤ 10
Reflection collected/unique	3227/3063 (<i>R</i> _{int} = 0.0538)
Absorption correction	Empirical (<i>ψ</i> -scan)
Max. and min. transmission	0.839 and 0.744
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3063/0/196
Goodness-of-fit on <i>F</i> ²	1.063
Final <i>R</i> indices [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0788, <i>wR</i> ₂ ^b = 0.2105
<i>R</i> indices (all data)	<i>R</i> ₁ ^a = 0.1169, <i>wR</i> ₂ ^b = 0.2362
Weight	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.1258 <i>P</i>) ² + 5.9354 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Largest diff. peak and hole	0.928 and -1.110 eÅ ⁻³

^a*R*₁ = Σ||*F*_o|| - ||*F*_c|| / Σ||*F*_o||.

^b*wR*₂ = [Σ[w(*F*_o² - *F*_c²)² / (Σ[w(*F*_o²)²])] ^{1/2}.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Zn	0	0	0	22(1)
O(1)	-506(4)	925(2)	-1595(5)	29(1)
N(1)	-940(5)	629(3)	1274(6)	25(1)
N(2)	1657(5)	459(3)	1549(6)	21(1)
N(3)	-1989(7)	1300(3)	-3733(7)	47(2)
C(1)	16(6)	967(4)	2583(7)	25(1)
C(2)	-476(7)	1666(4)	3160(9)	41(2)
C(3)	518(9)	2062(5)	-4431(9)	50(2)
C(4)	1635(8)	2271(4)	3920(9)	49(2)
C(5)	2188(7)	1573(4)	3381(8)	40(2)
C(6)	1180(6)	1156(3)	2112(7)	26(1)
C(7)	2567(6)	656(4)	704(8)	30(2)
C(8)	-2982(6)	0(4)	88(8)	36(2)
C(9)	-2068(6)	293(4)	1586(8)	32(2)
C(10)	-1719(7)	-300(5)	2825(9)	46(2)
C(11)	-2230(6)	80(3)	-2789(7)	29(2)
C(12)	-1494(6)	811(4)	-2627(7)	26(1)
Cl(1)	5582(3)	2043(2)	1500(3)	68(1)
Cl(2)	5708(6)	860(4)	-4019(7)	186(2)
Ow(1)	-2476(6)	2908(4)	-5403(7)	62(2)
Ow(2)	5303(6)	-627(3)	3560(7)	62(2)
Ow(3)	4071(7)	3180(4)	2941(8)	73(2)

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

RESULTS AND DISCUSSION

An ORTEP diagram of 1 with the atomic labelling scheme is shown in Fig. 1, and the selected bond lengths and angles are presented in Table 3. The macrocyclic ligand of the present compound takes the most stable *trans*-III configuration. An inversion center exists on the

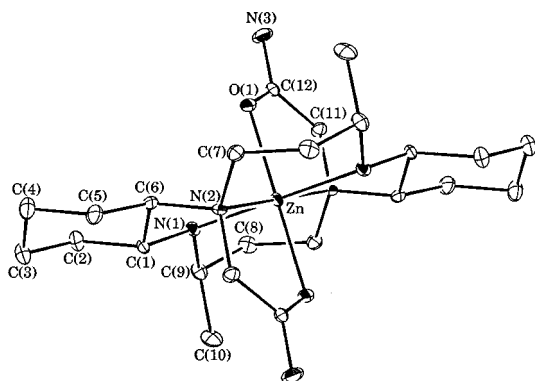


Fig. 1. An ORTEP drawing (30% probability ellipsoids) of 1 with the atomic numbering scheme. The chloride anions and water molecules are omitted for clarity.

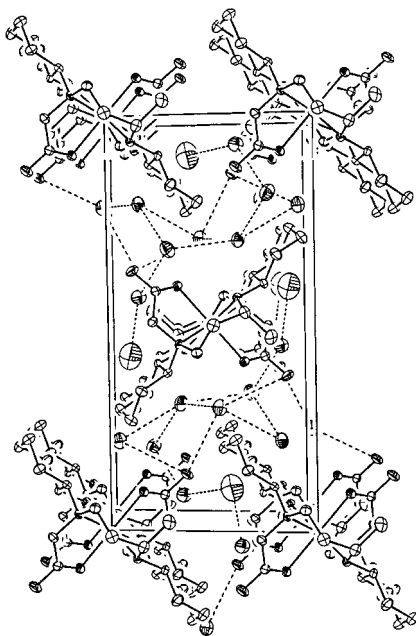
central zinc(II) ion. The complex cation $[\text{ZnL}]^{2+}$ shows that the two acetamide groups are attached to the less sterically hindered nitrogen atoms of the macrocyclic ligand. The complex 1 has a tetragonally elongated octahedral structure, with a coordination sphere consisting of pair of symmetry related secondary amines, tertiary amines, and acetamide oxygen atoms. The Zn atom and the four nitrogen atoms [N(1), N(2), N(1'), N(2')] are exactly on the same plane. The average Zn-N distance of 2.125(4) Å is comparable to *N*-functionalized octahedral complexes $[\text{Zn}(\text{L}^1)] \cdot 10\text{H}_2\text{O}$ (2.133(3) Å; L^1 -2,13-bis(2-carboxymethyl)-5,16-dimethyl-2,6,13,17-tetraazatriacyclo[14.4.0^{1,18}.0^{7,12}]docosane)⁷ and $[\text{Zn}(\text{L}^2)]\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ (2.122(12) Å; L^2 -2,13-bis(2-pyridylmethyl)-5,16-dimethyl-2,6,13,17-tetraazatriacyclo[14.4.0^{1,18}.0^{7,12}]docosane).⁸ The axial Zn-O(1) distance of 2.165(4) Å is slightly longer than the equatorial Zn-N bond distances, indicating the axially elongated octahedral geometry. The axial Zn-O(1) linkage is not perpendicular to the ZnN_2 plane with N(2)-Zn-O(1) and N(1)-Zn-O(1) angles of 99.2(2) and 84.9(2)°, respectively. The Zn-O(1)-C(12) angle related to the acetamide group is 112.9(4)°. The N(2)-Zn-O(1) bond angle

Table 3. Selected bond lengths (Å) and angles (°) for **1**^a

Zn-N(1)	2.123(5)	Zn-N(2)	2.126(5)
Zn-O(1)	2.165(4)	O(1)-C(12)	1.235(8)
N(3)-C(12)	1.327(9)	C(11)-C(12)	1.519(9)
N(1)-Zn-N(2)	84.2(2)	N(1)-Zn-N(2) ⁱ	95.8(2)
N(1)-Zn-O(1)	84.9(2)	N(1)-Zn-O(1)	95.1(2)
N(2)-Zn-O(1)	99.2(2)	N(2)-Zn-O(1)	80.8(2)
Zn-O(1)-C(12)	112.9(4)	O(1)-C(12)-N(3)	123.5(6)
O(1)-C(12)-C(11)	122.9(6)	N(3)-C(12)-C(11)	113.5(6)

^aSymmetry code: (i) -x, -y, -z.Table 4. Hydrogen-bonding parameters for **1**^a

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(3)-H(N3A)...Ow(1)	0.929(6)	2.527(7)	3.213(9)	130.9(4)
Ow(1)-Ow(1B)...Cl(1) ⁱ	1.030(6)	2.188(3)	3.190(7)	163.6(4)
Ow(2)-Ow(2A)...Cl(2) ⁱⁱ	0.953(6)	2.021(6)	2.835(9)	142.2(4)
Ow(2)-Ow(2B)...Ow(3) ⁱⁱⁱ	0.956(6)	1.800(7)	2.742(9)	167.9(4)
Ow(3)-Ow(3A)...Cl(1)	0.966(7)	2.215(3)	3.177(8)	174.4(4)
Ow(3)-Ow(3B)...Cl(1) ^{iv}	0.960(7)	2.355(3)	3.234(8)	151.9(4)

^aSymmetry codes: (i) x-1, -y+1/2, z-1/2; (ii) -x+1, -y, -z-1; (iii) -x+1, y-1/2, -z-1/2; (iv) x, -y+1/2, z+1/2.Fig. 2. Packing diagram of **1**, showing the hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

on the five-membered chelate ring is expected for the bite-angle of this type of the macrocyclic ligand. The other angle N(1)-Zn-O(1) may be due to the steric hin-

drance involving the methyl group C(10). Interestingly, the molecules are interconnected to give a two-dimensional network through weak hydrogen-bonding interactions involving the acetamide nitrogen atom, lattice water molecules, and chloride ions (Fig. 2 and Table 4).

This work was supported by Grant (No. 2001-1-12200-008-2) from the Basic Research Program of the Korea Science and Engineering Foundation.

Supplementary material. Atomic coordinates, bond lengths and angles and thermal parameters for **1** are available from author K.-Y. Choi on request.

REFERENCES

1. Thom, V. J.; Shaikjee, M. S.; Michael, J. P.; Howard, A. S.; Hancock, R. D. *Inorg. Chem.* **1986**, *25*, 3879.
2. Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
3. Pittet, P.-A.; Laurence, G. S.; Lincoln, S. F.; Turonek, M. L.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1991**, 1205.
4. Hancock, R. D.; Shaikjee, M. S.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1988**, *154*, 229.
5. Morrow, J. R.; Amin, S.; Lake, C. H.; Churchill, M. R. *Inorg. Chem.* **1993**, *32*, 4566.
6. Maumela, H.; Hancock, R. D.; Carlton, I.; Reibenspies,

- J. H.; Wainwright, K. P. *J. Am. Chem. Soc.* **1995**, *117*, 6698.
7. Choi, K.-Y. *J. Chem. Crystallogr.* **1999**, *29*, 1015.
8. Choi, K.-Y.; Chun, K.-M.; Suh, I.-H. *Polyhedron* **1999**, *18*, 2811.
9. Choi, K.-Y.; Suh, I.-H.; Kim, J.-G.; Park, Y.-S.; Jeong, S.-I.; Kim, I.-K.; Hong, C.-P.; Choi, S.-N. *Polyhedron* **1999**, *18*, 3013.
10. Choi, K.-Y.; Suh, I.-H. *Inorg. Chim. Acta* **2000**, *299*, 128.
11. Choi, K.-Y.; Park, Y.-S.; Kim, J.-G.; Suh, I.-H.; Kim, C. S. *Kor. J. Crystallogr.* **1999**, *10*, 33.
12. Choi, K.-Y.; Lee, H.-H.; Park, B. B.; Kim, J. H.; Kim, J.; Kim, M. W.; Ryu, J. W.; Suh, M.; Suh, I.-H. *Polyhedron*, in press.
13. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
14. Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
-