

Crystal Structure of Macrocyclic Azidotetraamine Zinc(II) Complex

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The Zn(II)-containing carbonic anhydrase (CA) has stimulated much effort into the syntheses of simple model complexes that are designed to mimic the coordination environment of the active site.¹⁻⁴ The Zn(II) in CA is coordinated to three histidine imidazols and a water molecule in a distorted tetrahedral geometry, which is considered to expand to five in a transient manner or by anion inhibitor binding.⁵⁻⁷ Recently, X-ray crystal analysis of the SCN⁻ binding to CA showed the Zn(II) ion in an ill-defined five-coordinate complex with SCN⁻ and a water bound.⁸ Kimura *et al.* discovered that a tetrahedral Zn(II)-OH₂ triamine complex with 1,5,9-triazacyclododecane(L²) is a good model for the active center of CA.⁹ In this complex the pK_a of the coordinated water molecule is close to that of CA, and the generated L²-Zn(II)-OH species acts as nucleophile in CA-catalyzing reaction, such as in hydrolysis of activated ester. Additional study on the crystal structure of the SCN⁻ binding to Zn(II) complex of L² showed a trigonal bipyramidal geometry with an equatorial and an apical Zn(II)-NCS bonds.¹⁰ We also reported the crystal structure of [Zn(L¹)(NCS)][NCS],¹¹ in which the Zn(II) ion reveals a square pyramidal geometry with an apical thiocyanate nitrogen atom.

We report herein the preparation and crystal structure of the Zn(II) complex of L¹ with azide ligands.

Experimental

General. All solvents were reagent grade and purified as described elsewhere prior to use.¹² All the reagents used for the preparation of the complex were of analytical (Aldrich Chemical Co.) grade. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. High-resolution fast atom bombardment mass spectrometry (FAB MS) was performed using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were performed by Korea Research Institute of Chemical Technology, Taejeon, Korea.

Preparation of [Zn(L¹)(N₃)](N₃)·3H₂O (1). A solution of [Zn(L¹)(H₂O)₂][Cl₂]¹³ (254 mg, 0.5 mmol) in methanol (20 mL) was added NaN₃ (65 mg, 1 mmol) and the mixture refluxed for 1 hr. The solution was allowed to cool to room temperature and was then filtered. The filtrate was evaporated to dryness. The product dissolved in acetonitrile/water (1:1, 10 mL). After the solution was allowed to stand at room temperature over a period of several days, a quantity of colorless crystals formed. These were filtered off, washed with diethyl ether and desiccated until dry (184 mg, 68%). Anal. Calcd for ZnC₂₀H₄₆N₁₀O₃: C, 44.48; H, 8.59; N, 25.94%.

Found: C, 44.32; H, 8.51; N, 25.78%. IR (KBr, cm⁻¹): 3147 (νNH), 2055 (νN=N), 2005 (νN=N), 1470, 1448, 1373, 1336, 1306, 1274, 1172, 1100, 1060, 992, 948, 898, 790, 635. FAB MS: m/z 540.0 (M)⁺, 443.9 (M-N₃-3H₂O)⁺.

Crystal structure determination. A colorless single crystal of size 0.53×0.20×0.17 mm³ was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069 Å). Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections with θ range of 11.37 to 15.04°. An asymmetric unit of intensity data were collected in the ω-2θ scan mode to a maximum 2θ of 50°. Three standard reflections (13 - 1 - 3, 13 4 - 1, 17 - 1 - 1) were measured every 240 minutes, and the intensities of the standards remained constant within 0.7% throughout data collection. Of the 4650 unique reflections measured, 3024 were considered observed (F_o > 4σ(F_o)) and used in subsequent structural analysis. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by use of direct method.¹⁴ All remaining non-hydrogen a-

Table 1. Crystallographic data for [Zn(L¹)(N₃)](N₃)·3H₂O (1)

Formula	ZnC ₂₀ H ₄₆ N ₁₀ O ₃
Formula weight	540.04
Crystal system	monoclinic
Space group	P2 ₁ /n
a (Å)	26.768(3)
b (Å)	9.400(1)
c (Å)	10.523(5)
β (°)	91.53(2)
V (Å ³)	2646.7(12)
Z	4
Crystal size (mm)	0.53×0.20×0.17
D _c (g cm ⁻³)	1.355
F (000)	1160
T (K)	293
Diffractometer	Enraf-Nonius CAD4
λ (Mo-Kα) (Å)	0.71069
μ (mm ⁻¹)	0.969
h, k, l range	-31 31, 0 11, 0 12
No. of unique reflections	4650
No. of observed reflections	3024
[F _o > 4σ(F _o)]	
R ^a	0.037
R _w ^b	0.075
GoF ^c	1.112

^aR = Σ|F_o - |F_c||/ΣF_o. ^bR_w = [Σ{w(F_o² - F_c²)²}/Σ{w(F_o²)²}]^{1/2}. ^cGoF = [Σw(F_o² - F_c²)²/(no. of rflns-no. params)]^{1/2}.

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toms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at calculated positions ($d_{C-H}=1.08 \text{ \AA}$) with a fixed U value of 0.05 \AA^2 .¹⁵ Refinement converged with $R(R_w)=0.037(0.075)$ for 2747 observed reflections and (Δ/σ) was -0.274 . The greatest residual density was 0.546 e \AA^{-3} . Crystallographic data and refinement details are presented in Table 1.

Results and Discussion

Figure 1 shows an ORTEP drawing of **1** with the atomic numbering scheme. Selected interatomic bond distances and angles are listed in Table 2. The Zn(II) ion is a five-coordinate, distorted square-pyramidal geometry with bonds to the four nitrogen atoms of macrocycle and to the axial nitrogen atom of the azido group. The average bond distance of $2.126(4) \text{ \AA}$, between zinc and secondary amine nitrogens, which is comparable to those found in $[\text{Zn}(\text{L}^1)(\text{NCS})][\text{NCS}]$ ($2.124(10) \text{ \AA}$)¹¹ and $[\text{Zn}(\text{L}^3)\text{Cl}][\text{ClO}_4]$ ($\text{L}^3=5,12\text{-dimethyl-1,4,8,11-tetraazacyclotetradecane}$) ($2.121(9) \text{ \AA}$).¹⁵ The trans-basal angles $[\text{N}(1)\text{-Zn-N}(3) 153.9(2)^\circ$ and $\text{N}(2)\text{-Zn-N}(4) 157.2(2)^\circ]$ are similar to those expected for square-pyramidal Zn(II) complexes.^{11,16} The basal plane is slightly distorted [deviation $\text{N}(1) 0.031(2)$, $\text{N}(2) -0.033(2)$, $\text{N}(3) 0.033(2)$, and $\text{N}(4) -0.032(2) \text{ \AA}$ from the least-squares plane], while the Zn(II) ion is $0.447(2) \text{ \AA}$ apart from this plane, shifted toward the

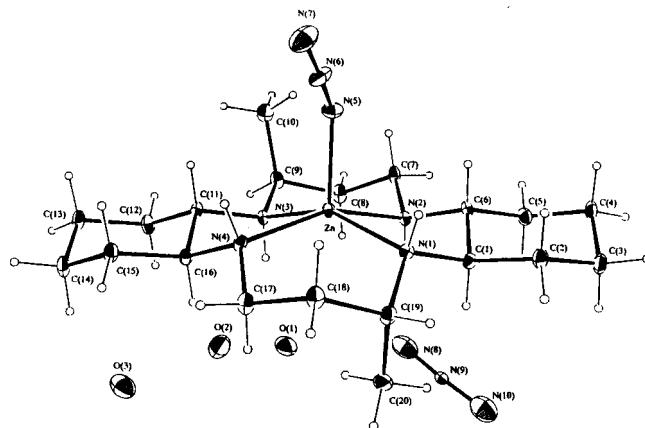


Figure 1. ORTEP drawing of **1** with the atomic numbering scheme.

apical position occupied by the N(5) atom of the azido group. The axial Zn-N(5) bond is not perfectly perpendicular to ZnN_4 plane with the four N-Zn-N(5) angles ranging from $101.1(2)$ to $104.9(2)^\circ$. The axial Zn-N(5) bond distance of $1.996(5) \text{ \AA}$ is *ca.* 0.1 \AA shorter than equatorial Zn-N (secondary amines). The Zn-N(5)-N(6) angle of $130.9(5)^\circ$ is similar to that observed in $[\text{Ni}(\text{L}^4)(\text{N}_3)][\text{ClO}_4]$ ($\text{L}^4=1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclododecane}$) (Ni-N-N $135.7(7)^\circ$).¹⁷ The $\text{Zn}\cdots\text{N}(8)$ distance of $4.165(6) \text{ \AA}$ and $\text{Zn}\cdots\text{N}(10)$ distance of $5.570(8) \text{ \AA}$ indicate that the N(8) and N(10) atoms are not in-

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Zn}(\text{L}^1)(\text{N}_3)][\text{N}_3] \cdot 3\text{H}_2\text{O}$ (**1**)

Zn-N(1)	2.143(4)	N(9)-N(10)	1.139(7)
Zn-N(2)	2.111(4)	N(1)-C(1)	1.503(6)
Zn-N(3)	2.128(4)	N(1)-C(19)	1.490(6)
Zn-N(4)	2.121(4)	N(2)-C(6)	1.492(6)
Zn-N(5)	1.996(5)	N(2)-C(7)	1.462(6)
Zn \cdots N(8)	4.165(6)	N(3)-C(9)	1.509(6)
Zn \cdots N(10)	5.570(8)	N(3)-C(11)	1.485(6)
N(5)-N(6)	1.125(6)	N(4)-C(16)	1.479(6)
N(6)-N(7)	1.153(7)	N(4)-C(17)	1.509(6)
N(8)-N(9)	1.056(7)		
N(1)-Zn-N(2)	82.3(2)	Zn-N(4)-C(17)	119.1(3)
N(1)-Zn-N(3)	153.9(2)	C(16)-N(4)-C(17)	112.4(4)
N(1)-Zn-N(4)	95.4(2)	Zn-N(5)-N(6)	130.9(5)
N(1)-Zn-N(5)	101.1(2)	N(1)-C(1)-C(2)	111.5(4)
N(2)-Zn-N(3)	90.3(1)	N(1)-C(1)-C(6)	109.2(4)
N(2)-Zn-N(4)	157.2(2)	N(1)-C(19)-C(18)	108.8(4)
N(2)-Zn-N(5)	101.2(2)	N(1)-C(19)-C(20)	111.7(5)
N(3)-Zn-N(4)	81.9(1)	N(2)-C(6)-C(1)	106.7(4)
N(3)-Zn-N(5)	104.9(2)	N(2)-C(6)-C(5)	114.5(4)
N(4)-Zn-N(5)	101.5(2)	N(2)-C(7)-C(8)	110.9(4)
Zn-N(2)-C(1)	108.1(3)	N(3)-C(9)-C(8)	109.0(4)
Zn-N(2)-C(19)	118.7(3)	N(3)-C(9)-C(10)	112.5(4)
C(1)-N(1)-C(19)	115.0(4)	N(3)-C(11)-C(12)	113.6(4)
Zn-N(2)-C(6)	104.5(3)	N(3)-C(11)-C(16)	107.8(4)
Zn-N(2)-C(7)	110.8(3)	N(4)-C(16)-C(11)	109.3(4)
C(6)-N(2)-C(7)	115.4(4)	N(4)-C(16)-C(15)	113.0(4)
Zn-N(3)-C(9)	118.0(3)	N(4)-C(17)-C(18)	112.9(4)
Zn-N(3)-C(11)	106.1(3)	N(5)-N(6)-N(7)	177.2(7)
C(9)-N(3)-C(11)	115.0(4)	N(8)-N(9)-N(10)	174.4(8)
Zn-N(4)-C(16)	109.8(3)		

involved in coordination. The nonbonded azide ion forms hydrogen bonds $N(8) \cdots H-O(1)$ 2.603(9) Å, $N(10) \cdots H-O(1)$ 2.705(9) Å, and $N(10) \cdots H-O(3)$ 2.718(11) Å (symmetry code $i: 0.5-x, -0.5+y, 1.5-z$). The N-Zn-N angles of six-membered chelate rings of **1** are larger than those of the five-membered chelate rings. The complex **1** also adopts a thermodynamically most stable *trans*-III conformation in the solid state. The IR spectrum of **1** shows two strong peaks of $\nu_{N=N}$ at 2055 and 2005 cm^{-1} , which are assigned to the nonbonded shorter N=N distance of 1.056(7) Å and the axial N=N distance of 1.125(6) Å, respectively. This is also expected by comparison with FAB mass spectra of $[Zn(L^1)(N_3)]^+$ (m/z 443.9).

Conclusion

The complex $[Zn(L^1)(N_3)][N_3] \cdot 3H_2O$ (**1**) has been prepared and characterized by X-ray crystallography. The coordination of the zinc atom is a distorted square-pyramid with four nitrogens of the macrocycle occupying the basal sites [$Zn-N_{bc}$ = 2.126(4) Å] and a terminal azide ligand at the apical position with a Zn-N distance of 1.996(5) Å.

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Supporting Information Available. Tables of crystallographic details, atomic coordinates, interatomic distances and angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for **1** (26 page) are available. Supplementary materials are available from K.-Y. Choi.

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A New Cesium-Selective Ionophore Bearing Two Convergent Kemp's Triacid Functions

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The developments of cesium-specific ionophores are very important in view of the application for the nuclear waste treatment.¹ Although many intriguing ionophores for the recognition of alkali metal cations have been developed, relatively little attention has been paid for the cesium-selective ionophores.² Recently, Ungaro *et al.* have reported that the 1,3-dialkoxycalix[4]-crown-6 in the 1,3-alternate conformation exhibited a binding preference for cesium ion.^{3,4} Asfari *et al.* performed cesium removal experiments from nuclear waste water by using supported liquid membranes

containing various structures of calix-bis-crown compounds.¹

Cleft-shaped compounds have been widely studied in the field of supramolecular chemistry because of their unique structural and ion-binding properties as molecular recognition devices.⁵ Kemp's triacid moiety is one of the most interesting structural motifs for this purpose, owing to its convergent *syn* lone pairs of carboxylate as well as U-shaped relationship between carboxylate functions, and has been extensively used by Rebek *et al.* for the construction of many unique host systems.⁶ One of them is a simple mole-