

Crystal Structure of Macrocyclic Azidotetraamine Zinc(II) Complex

Ki-Young Choi*, Dong Won Kim[†], and Il-Hwan Suh[‡]

*Department of Chemistry, Mokwon University, Taejon 301-729, Korea

[†]Department of Chemistry, Chungbuk National University, Cheongju 360-763, Korea

[‡]Department of Physics, Chungnam National University, Taejon 305-764, Korea

Received October 1, 1997

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 imidazoles 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, Taejon, 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
Formular 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}.

*Author to whom all correspondence should be addressed.

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

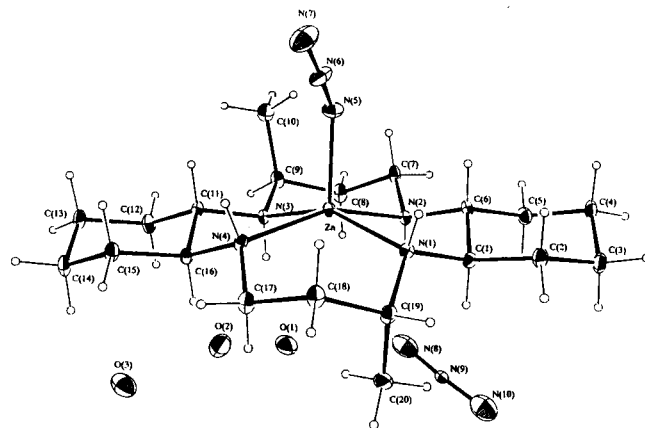


Figure 1. ORTEP drawing of **1** with the atomic numbering scheme.

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 $[\text{Ni}(\text{L}^4)(\text{N}_3)][\text{ClO}_4]$ ($\text{L}^4=1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclododecane}$) ($\text{Ni-N-N} 135.7(7)^\circ$).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 [$Zn-N_{av}$ =2.126(4)Å] and a terminal azide ligand at the apical position with a Zn-N distance of 1.996(5)Å.

Acknowledgements. The present studies were supported by the Basic Science Research Institute Program, Ministry of Korea, 1997, Project No. BSRI-97-3435 and the Research Fund of Mokwon University, 1997.

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.

References

1. Chlebowski, J. F.; Coleman, J. E. In *Metal Ions in Bio-*

- logical Systems*; Sigel, H., Ed.; Dekker: New York, 1976; Vol. 6, pp 1-40.
2. Silverman, D. N.; Lindskog, S. *Acc. Chem. Res.* **1988**, *21*, 30.
3. Kimura, E. *Prog. Inorg. Chem.* **1994**, *41*, 443.
4. Greener, B.; Moore, M. H.; Walton, P. H. *J. Chem. Soc., Chem. Commun.* **1996**, 27.
5. Pocker, Y.; Deits, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3949.
6. Pocker, Y.; Deits, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 2424.
7. Yachandra, V.; Powers, L.; Spiro, T. G. *J. Am. Chem. Soc.* **1983**, *105*, 6596.
8. Eriksson, A. E.; Kylsten, P. M.; Jones, T. A.; Liljas, A. *Proteins* **1988**, 283.
9. Kimura, E.; Shiota, T.; Koike, T.; Shiro, M.; Kodama, M. *J. Am. Chem. Soc.* **1990**, *116*, 5805.
10. Kimura, E.; Koike, T.; Shionoya, M.; Shiro, M. *Chem. Lett.* **1992**, 787.
11. Choi, K. Y.; Suh, I.-H. *Polyhedron* **1997**, *16*, 2393.
12. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: New York, 1985.
13. Choi, K. Y.; Suh, I.-H.; Kim, J. C. *Polyhedron* **1997**, *16*, 1783.
14. Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
15. Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, 1993.
16. Choi, K. Y. *Polyhedron* **1997**, *16*, 2073.
17. D'Aniello, M. J.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

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

Nam Yee Kim, Sung Woo Park[†], and Suk-Kyu Chang*

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

[†]National Institute of Scientific Investigation, Seoul 158-097, Korea

Received October 9, 1997

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-