Crystal Structure of a Zinc(II) Complex of HNE, *N*-(4-Nitro-2-hydroxy)phenylmethyl-*N*-(2-pyridylethyl)-*N*-(pyridylmethyl)amine

Hiromasa KUROSAKI, Hiroyuki YOSHIDA, Yoshihiro YAMAGUCHI, and Masafumi GOTO[†]

Graduate School of Pharmaceutical Sciences, Kumamoto University, Oe-honmachi 5-1,
Kumamoto 862 – 0973, Japan

The zinc(II) complex (**1**) with a tripodal ligand, *N*-(4-nitro-2-hydroxy)phenylmethyl-*N*-(2-pyridylethyl)-*N*-(pyridylmethyl)amine, HNE, was prepared and its structure was determined by X-ray crystallography. The crystal structure reveals that complex [Zn(NE)Cl], **1**, is a neutral mononuclear zinc(II) complex with a distorted square-pyramidal geometry.

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A number of zinc(II) complexes have been synthesized as model compounds in order to elucidate the properties of substrate or inhibitor recognition at the active centers of zinc enzymes, such as carbonic anhydrase and carboxypeptidase.¹ Previously, we synthesized a zinc(II) complex with a tripodal ligand, *N*-(mercaptoethyl)-di(2-pyridylmethyl)amine, DPASH, in order to investigate the hydrolysis reaction of sodium bis(*p*-nitrophenyl)hydrogenphosphate, BNP[−].² To investigate the influence of the pendant donor on the hydrolysis reaction of BNP[−], we synthesized a tripodal ligand, *N*-(4-nitro-2-hydroxy)phenylmethyl-*N*-(2-pyridylethyl)-*N*-(pyridylmethyl)amine, HNE, where H denotes a dissociable proton.

Here, we describe the crystal structure of a zinc(II) complex of HNE, [Zn(NE)Cl], **1** (Fig. 1).

The ligand HNE was prepared according to a published method of Fenton *et al.*³ The zinc(II) complex **1** was prepared by reacting HNE with an equimolar amount of ZnCl₂ in methanol in the presence of one equimolar amount of piperidine at room temperature. The precipitated powder was collected and dried under vacuum. Recrystallization from acetonitrile gave colorless single crystals of **1** suitable for an X-ray diffraction study. Data collections were performed at 293 K

with graphite-monochromated Mo K_{α} radiation on a Rigaku AFC7R diffractometer ($\lambda = 0.71069 \text{ \AA}$). The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 . All hydrogen atoms were located by geometrical calculations, and were not refined. All calculations were performed using the teXsan crystallographic software package.⁴ The crystal and experimental data are given in Table 1. The atomic coordinates and temperature factors for non-H atoms are given in Table 2, and selected bond lengths and bond angles are listed in Table 3. An ORTEP drawing of **1** with the atomic labeling scheme is shown in Fig. 2. The crystal structure of complex **1** consists of a neutral five-coordinate complex. The coordination geometry around the zinc(II) atom is distorted square pyramidal with $\tau = 0.22$ [$\tau = (\beta - \alpha)/60$, where $\beta = \text{Cl(1)}-\text{Zn(1)}-\text{N(1)}$, $161.77(6)^{\circ}$ and $\alpha = \text{N(2)}-\text{Zn(1)}-\text{N(3)}$, $148.50(9)^{\circ}$]; for an ideal square pyramid, τ

Fig. 1 Chemical structure of **1**.

Table 1 Crystal and experimental data

Formula: ZnClC ₂₀ H ₁₉ O ₃ N ₄
Formula weight = 464.23
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 2$
$a = 10.683(3) \text{ \AA}$ $\alpha = 101.35(4)^{\circ}$
$b = 10.976(5)$ $\beta = 97.82(3)$
$c = 8.659(3)$ $\gamma = 81.63(3)$
$V = 978.8(7) \text{ \AA}^3$
$D_{\text{calc}} = 1.575 \text{ g/cm}^3$
No. measured reflections = 4739 (unique: 4495 ($R_{\text{int}} = 0.017$))
No. reflections used in refinement of reflections = 3365
$2\theta_{\text{max}} = 55^{\circ}$ with Mo K_{α}
$R1 = 0.037$
$R_w = 0.048$
Goodness of fit = 1.46
$(\Delta/\sigma)_{\text{max}} = 0.00$
$(\Delta\rho)_{\text{max}} = 0.33 \text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.41 \text{ e\AA}^{-3}$
Measurement: Rigaku AFC7R
Program system: Rigaku teXsan
Structure determination: direct method
Refinement: full-matrix least-squares

[†] To whom correspondence should be addressed.
E-mail: gmphiwin@gpo.kumamoto-u.ac.jp

Table 2 Atomic coordinates and equivalent isotropic thermal parameters B_{eq}

atom	x	y	z	B_{eq}
Zn(1)	0.27026(3)	0.12600(3)	-0.01348(4)	2.586(7)
Cl(1)	0.29612(8)	-0.02312(7)	0.15006(9)	3.74(2)
O(1)	0.1110(2)	0.2300(2)	0.0372(2)	3.29(5)
O(2)	-0.3135(3)	0.5147(3)	-0.3691(3)	7.38(9)
O(3)	-0.1488(3)	0.5788(3)	-0.4310(3)	8.15(10)
N(1)	0.3119(2)	0.2506(2)	-0.1765(2)	2.39(5)
N(2)	0.1982(2)	0.0037(2)	-0.2172(3)	2.82(5)
N(3)	0.4267(2)	0.2152(2)	0.1155(3)	3.05(6)
N(4)	-0.1975(3)	0.5167(3)	-0.3581(3)	5.27(8)
C(1)	0.2874(3)	0.2053(3)	-0.3489(3)	2.94(7)
C(2)	0.3273(3)	0.0654(3)	-0.3939(4)	3.06(7)
C(3)	0.2285(3)	-0.0116(2)	-0.3663(3)	2.68(6)
C(4)	0.1699(3)	-0.0907(3)	-0.4904(4)	3.22(7)
C(5)	0.0779(3)	-0.1565(3)	-0.4605(4)	3.72(8)
C(6)	0.0445(3)	-0.1412(3)	-0.3090(4)	3.73(8)
C(7)	0.1069(3)	-0.0609(3)	-0.1921(3)	3.52(7)
C(8)	0.4476(3)	0.2683(3)	-0.1360(3)	2.99(7)
C(9)	0.4882(3)	0.2779(3)	0.0381(3)	2.88(6)
C(10)	0.5867(3)	0.3436(3)	0.1146(4)	4.11(8)
C(11)	0.6217(3)	0.3451(3)	0.2734(4)	4.82(9)
C(12)	0.5575(3)	0.2822(3)	0.3537(4)	4.21(8)
C(13)	0.4609(3)	0.2176(3)	0.2707(4)	3.69(8)
C(14)	0.2341(3)	0.3735(2)	-0.1275(3)	2.76(6)
C(15)	0.0933(2)	0.3684(2)	-0.1475(3)	2.45(6)
C(16)	0.0144(3)	0.4416(3)	-0.2421(3)	3.08(7)
C(17)	-0.1162(3)	0.4412(3)	-0.2563(3)	3.36(7)
C(18)	-0.1692(3)	0.3662(3)	-0.1781(4)	3.67(8)
C(19)	-0.0930(3)	0.2949(3)	-0.0821(4)	3.46(7)
C(20)	0.0409(3)	0.2946(2)	-0.0605(3)	2.69(6)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha).$$

= 0 while for an ideal trigonal pyramid, $\tau = 1$.⁵ Two pyridine nitrogen atoms, N(2) and N(3), and the tertiary amine N(1), and one chloride ion Cl(1) make the basal plane with the *p*-nitrophenolate O(1) occupying the apical position. The *trans*-basal angles of Cl(1)-Zn(1)-N(1) and N(2)-Zn(1)-N(3) are 161.77(6) and 148.50(9)°, respectively. The O(1)-Zn(1)-N(2) and O(1)-Zn(1)-N(3) angles are 98.90(9) and 109.26(9)°, respectively. The N(1), N(2), N(3), and Cl(1) lie -0.121(1), 0.121(1), 0.144(1), and -0.0140(1) Å, respectively, out of the least-squares plane through them; the Zn(1) atom is displaced 0.404(1) Å above the mean basal plane in the direction of the axial O(1). The Zn(1)-N(1), -N(2), -N(3), -O(1) and -Cl(1) bond distances are also similar to those of found in reported compounds.^{2,3} The dihedral angle between the pyridylmethyl and *p*-nitrophenylmethyl rings (N(2)-C(3)-C(4)-C(5)-C(6)-C(7)

Table 3 Selected bond distances (Å) and angles (°)

Zn(1)-Cl(1)	2.3313(8)	Zn(1)-O(1)	1.957(2)
Zn(1)-N(1)	2.274(2)	Zn(1)-N(2)	2.123(2)
Zn(1)-N(3)	2.130(2)	Cl(1)-Zn(1)-O(1)	104.37(6)
Cl(1)-Zn(1)-N(1)	161.77(6)	Cl(1)-Zn(1)-N(2)	94.22(6)
Cl(1)-Zn(1)-N(3)	92.25(7)	O(1)-Zn(1)-N(1)	93.00(8)
O(1)-Zn(1)-N(2)	98.90(9)	O(1)-Zn(1)-N(3)	109.26(9)
N(1)-Zn(1)-N(2)	88.43(8)	N(1)-Zn(1)-N(3)	76.55(8)
N(2)-Zn(1)-N(3)	148.50(9)

Fig. 2 ORTEP drawing of **1** with thermal ellipsoids drawn at the 50% probability level.

and C(15)-C(16)-C(17)-C(18)-C(19)-C(20)) is 113.81(10)°.

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