

Synthesis and X-ray Structure of $\text{Zn}(\text{bpeae})\text{ZnCl}_3$ ($\text{bpeae} = 2\text{-}\{\text{Bis-}[2\text{-}(3,5\text{-dimethyl-pyrazol-1-yl})\text{-ethyl}]\text{amino}\}\text{ethoxy}$)

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Coordination chemistry of zinc with chelate ligands containing nitrogen and/or oxygen donors is of considerable interest as a model of enzymes such as carbonic anhydrase [NNN]¹ and thermolysin [NNO].² A variety of coordination possibilities such as the variability and flexibility of functional ligands in relevant coordination spheres for zinc could provide highly interesting reactions, structures and catalyst chemistry.³

Although transition metal complexes of the ligands, bis(pyrazol-1-yl)ethylamine (bpea),^{4,6} bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether^{5,6} and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]sulfide⁶ having commonly three-coordinated T-shape, N₃-donor ligand are known, the zinc complexes of their ligands were still limited.^{4a,4b,4d} We have focused on the design and synthesis of *N*-substituted pyrazole derivative ligand in order to gain better understandings of the controlling electronic effects and coordination numbers from the reaction of those ligands with ZnCl_2 in a structural model of trigonal-bipyramidal Cl_2ZnN_3 or ClZnN_3O complex.

Herein, we report the synthesis and structural properties of the Zn(II) complex of the bpeae as a new type of tetradentate ligand.

Experimental Section

All chemicals were all reagent-grade and all solvents were freshly distilled prior to use. The bpea was prepared as described in the literature.^{4c,5a} ¹H NMR spectra were obtained with a Varian 300-NMR Spectrometer at ambient temperature and chemical shifts were referenced to internal tetramethylsilane. Elemental analyses were performed at the Chemical Analysis Laboratory of Center for Scientific Instruments in Kyungpook National University.

2-}\{Bis-[2-(3,5-dimethyl-pyrazolyl-1-yl)-ethyl]amino}\-ethanol (bpeaeH). To the solution of bpea (7.03 g, 26.9 mmol) in acetone (70 mL) was added slowly 2-bromoethanol (5.01 mL, 67.2 mmol) and subsequently triethylamine (9.34 mL, 67.2 mmol) with stirring at room temperature. The solution was refluxed for 2 weeks and then the resulting solution was filtered, dried and extracted with dichloromethane, washed four times with brine, dried with MgSO_4 and evaporated in *vacuo* to afford a yellow oil. Yield: 5.01 g (61%). ¹H NMR (CDCl_3): δ 5.68 (s, 4-*H*-Pz), 3.76 (t, $\text{NCH}_2\text{CH}_2\text{-Pz}$, $J = 6.3, 6.3$ Hz), 3.48 (t, $\text{NCH}_2\text{CH}_2\text{OH}$, $J = 4.5, 4.8$ Hz), 2.80 (t, $\text{NCH}_2\text{CH}_2\text{-Pz}$, $J = 6.3, 6.3$ Hz), 2.62

(t, $\text{NCH}_2\text{CH}_2\text{OH}$, $J = 4.8, 4.8$ Hz), 2.12 (s, $\text{CH}_3\text{-Pz}$), 2.08 (s, $\text{CH}_3\text{-Pz}$).

$[\text{Zn}(\text{bpeae})(\text{ZnCl}_3)]\cdot\text{CH}_2\text{Cl}_2$. To a suspension of NaH (0.163 g, 6.50 mmol) in dry THF was added a solution of bpeaeH (1.97 g, 6.45 mmol) in THF. The mixture was refluxed for 1 day and the resulting suspension gradually converted into a yellow clear solution. To the resulting solution was added a solution of ZnCl_2 (1.76 g, 12.90 mmol) in methanol (25 mL) and was precipitated a white solid after several minutes. The mixture was stirred for 1 day at ambient temperature, the solution was filtered and the solvent was removed in *vacuo* to give a white solid. The product was washed with ether and dried in *vacuo*. The recrystallization of a white solid in dichloromethane gave colorless crystals within a week. Yield: 1.8 g (51%). Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{Cl}_3\text{N}_5\text{OZn}_2\cdot\text{CH}_2\text{Cl}_2$: C, 32.59; H, 4.50; N, 11.18. Found: C, 32.53; H, 4.59; N, 11.11. ¹H NMR ($\text{DMSO-}d_6$): δ 5.72 (s, 4-*H*-Pz), 3.80 (t, $\text{NCH}_2\text{CH}_2\text{-Pz}$, $J = 6.6, 6.9$ Hz), 3.35 (t, $\text{NCH}_2\text{CH}_2\text{O}$, $J = 6.0, 5.7$ Hz), 2.75 (t, $\text{NCH}_2\text{CH}_2\text{-Pz}$, $J = 6.9, 6.6$ Hz), 2.55 (t, $\text{NCH}_2\text{CH}_2\text{O}$, $J = 6.0$,

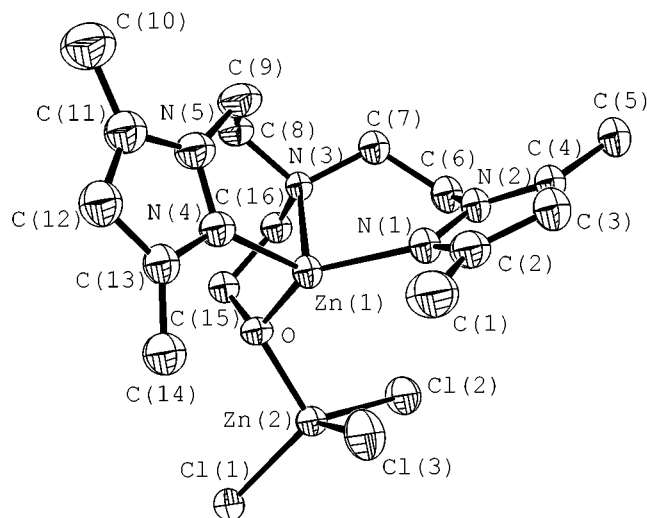
Table 1. Details of the X-ray crystal analyses of $[\text{Zn}(\text{bpeae})(\text{ZnCl}_3)]\cdot\text{CH}_2\text{Cl}_2$

Empirical formula	$\text{C}_{16}\text{H}_{26}\text{Cl}_3\text{N}_5\text{OZn}_2\cdot\text{CH}_2\text{Cl}_2$
Formula weight	626.43
Crystal system	Monocline
Space group	$P2_1/c$
<i>a</i> (Å)	9.2536(7)
<i>b</i> (Å)	17.499(1)
<i>c</i> (Å)	16.119(2)
β (°)	108.821(7)
<i>V</i> (Å ³)	2455.0(4)
<i>Z</i>	4
<i>d</i> _{calc.} (mg/m ³)	1.695
μ (mm ⁻¹)	2.518
<i>F</i> (000)	1272
Reflections collected unique	5226 4725 [<i>R</i> (int) = 0.0104]
Data/restraints/parameters	4725 0/272
Goodness-of-fit on F^2	1.002
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> = 0.0372, <i>wR</i> = 0.1127
Largest diff. Peak and hole	0.961 and -0.725 e Å ⁻³

^a $R = \sum |F_o - F_c| / \sum F_o$, $wR = [\sum \{w(F_o^2 - F_c^2)\}^2 / \sum \{w(F_o^2)\}^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [F_o^2 + 2F_c^2]/3$.

Table 2. Selected bond lengths [Å] and angles [°] for [Zn(bpeae)(ZnCl₃)]·CH₂Cl₂

Bond lengths (Å)			
Zn(1)-N(1)	1.985(3)	Zn(1)-N(3)	2.170(3)
Zn(1)-N(4)	1.896(3)	Zn(1)-O	2.017(3)
Zn(2)-O	1.930(3)	Zn(2)-Cl(1)	2.228(1)
Zn(2)-Cl(2)	2.098(1)	Zn(2)-Cl(3)	2.404(1)
N(1)-N(2)	1.294(4)	N(4)-N(5)	1.366(5)
Bond Angles (°)			
N(1)-Zn(1)-N(3)	100.6(1)	N(1)-Zn(1)-N(4)	104.0(2)
N(3)-Zn(1)-N(4)	95.9(1)	N(1)-Zn(1)-O	142.3(1)
N(3)-Zn(1)-O	82.7(1)	N(4)-Zn(1)-O	113.1(1)
Cl(1)-Zn(2)-O	114.89(8)	Cl(2)-Zn(2)-O	106.17(9)
Cl(3)-Zn(2)-O	91.0(1)	Cl(1)-Zn(2)-Cl(2)	112.20(5)
Cl(1)-Zn(2)-Cl(3)	117.96(5)	Cl(2)-Zn(2)-Cl(3)	112.45(5)
C(7)-N(3)-Zn(1)	111.5(2)	C(8)-N(3)-Zn(1)	113.5(2)
C(15)-O-Zn(1)	113.6(2)	C(15)-O-Zn(2)	123.1(3)
N(2)-N(1)-Zn(1)	115.9(2)	N(5)-N(4)-Zn(1)	122.3(3)
Zn(1)-O-Zn(2)	114.3(1)		

**Figure 1.** Crystal structure with the labeling scheme for [Zn(bpeae)(ZnCl₃)].

6.0 Hz). 2.14 (s, CH₃-Pz), 2.04 (s, CH₃-Pz).

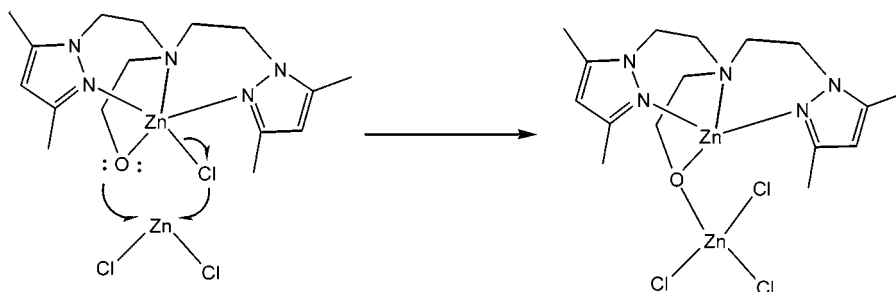
X-ray Structure Determination. A colorless single crystal of the title complex suitable for X-ray structural analysis crystallized in dichloromethane solutions was mounted on an Enraf-Nonius CAD-4 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Unit-cell dimensions with estimated standard deviations were determined by least-squares using 25 well-centered reflections. A total of 4725 unique reflections were collected in the θ range of 1.78–27.87° ($0 \leq h \leq 11$, $-21 \leq k \leq 0$, $-19 \leq l \leq 19$). The intensities of reflections were corrected for Lorentz and polarization effects. Crystal data, data collection, and refinement for the complex are listed in Table 1. Data reduction was carried out with a Molen program package and empirical absorption corrections were applied based on Ψ scans. The structure in $P2_1/c$ was determined by direct methods and refined by full-matrix least-squares using SHELXS-97 and SHELXL-97 program packages⁸ with reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained by using riding modes. The final cycle of the refinement yielded to $R = 0.037$, $wR = 0.113$. Selected bond distances and bond angles are given in Table 2.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-191169). The data can be obtained free of charge via www.cdc.cam.ac.uk/conts/retrieving.html (or the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting.

Results and Discussion

The tetradentate ligand bpeae was readily afforded from the reaction of bpea with 2-bromoethanol and triethylamine in refluxing acetone at 1 : 2.5 : 2.5 ratio for 2 weeks. Nucleophilic attack of the nitrogen atom of bpea at the

carbon atom of bromoethanol took place through the liberation of HBr, which was precipitated by triethylamine. Zn(II)(bpeae)(ZnCl₃) was afforded from the reaction of ZnCl₂ with the Na salt of bpeae as white crystals after usual workups. The compound is soluble in methanol and most chlorinated solvents and not soluble in etherated solvents. ¹H NMR spectrum shows all of the peaks as shown in the spectrum of the free ligand. The X-ray diffraction analysis was carried out to explore the structure of the compound as shown at Figure 1. The compound is a dinuclear zinc complex containing one bpeae ligand and three chloro ligands. The central atom Zn(1) at Figure 1 is in a distorted tetrahedral coordination geometry surrounded by two nitrogen atoms of two pyrazoles, one nitrogen atom of amine and one oxygen atom of ethanolate of bpeae, while the central atom Zn(2) is in a distorted tetrahedral coordination geometry consisting of one bridging oxygen atom of ethanolamine of bpeae and three chloro atoms. We can postulate the mechanism for the formation of compound that an oxygen atom of ethanolamine of bpeae at the first proposed product [Zn(bpeae)Cl] coordinates to the second ZnCl₂ accompanying chloro atom transfer to give [Zn(bpeae)ZnCl₃] (see Scheme 1). The bond distances of Zn-N(4) and Zn-N(1) are 1.896(3), 1.985(3) Å, which are somewhat shorter than those observed in related compounds of the type Zn(L-L)₂, i.e., 2.002(5)–2.007(5) Å with L-L being H₂B(3,5-Me₂Pz)₂, 2.014(3)–2.039(3) Å with L-L H₂B[3,5-(CF₃)₂Pz]₂,⁹ 2.029(3) and 2.157(3) Å in ZnCl₂(Clemizole),¹⁰ 2.006(3) and 2.008(3) Å in ZnCl₂(1,2-dimethylimidazole)₂,¹¹ and 2.050(3) and 2.074(3) Å in ZnCl₂(quinoline).¹² However, Zn-N(3), 2.170(3) Å, is similar to those in the above related compounds. The bond distances Zn(2)-Cl [average 2.243(1) Å] are also in accord with those of the related complexes, which are in the range of 2.196(2)–2.251(1) Å.^{11–13} The distance between Zn(1) and Cl(3) is 2.997(2) Å showing a little interaction. The bond distances of Zn(1)-O and Zn(2)-O are 2.017(3) and 1.930(3) Å in



Scheme 1

which the oxygen atom was bridged between Zn(1) and Zn(2). These distances are somewhat shorter than those [2.062(2) and 2.058(2) Å] in $[\text{Zn}\{\text{O}=\text{C}(\text{Me})\text{CH}_2\text{C}(\text{Me})_2\text{OH}\}_2][\text{ZnCl}_4]$.¹⁴ The bond angle of Zn(1)-O-Zn(2) is 114.3°. The bond angles [142.3(1)°] of N(1)-Zn(1)-O results in the distortion from an ideal tetrahedral geometry as a consequence of the opening due to the steric repulsion of methyl groups of pyrazole. In conclusion, a new dinuclear Zn complex with the bridging oxygen atom of alkoxide was synthesized accompanying one Cl atom transfer.

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