Dinuclear zinc(II) complexes have been found to be present in the active site of various enzymes, such as metallo-β-lactamases\(^1\) and aminopeptidases.\(^2\) We have investigated the mechanism of metallo-β-lactamase using a series of zinc(II) complexes based on tripodal ligands.\(^3,4\)

We newly synthesized an N\(_2\)O\(_2\)-type tripodal ligand, 2-[(Bis(1-hydroxy-4-nitrobenzyl)aminoethyl)]pyridine \(^1\), and isolated its zinc(II) complex \(2\cdot\text{CH}_3\text{CN}\) (Fig. 1). In order to elucidate the coordination mode of complex \(2\), we carried out an X-ray diffraction study on zinc(II) complex \(2\cdot\text{CH}_3\text{CN}\).

The tripodal ligand \(1\) was prepared by reacting 2-aminoethylpyridine with 2 equimolar amounts of Koshland’s reagent in the presence of 2 equimolar amounts of triethylamine in THF at 50˚C. The zinc(II) complex \(2\cdot\text{CH}_3\text{CN}\) was prepared by reacting \(1\) with an equimolar amount of ZnCl\(_2\) in methanol in the presence of 2 equimolar amounts of piperidine at room temperature. The precipitated powder was collected and dried under a vacuum. Recrystallization from acetonitrile gave colorless single crystals of \(2\cdot\text{CH}_3\text{CN}\) suitable for an X-ray diffraction study. Data collections were performed at 293 K with graphite-monochromated Mo K\(_\alpha\) radiation on a Rigaku AFC7R diffractometer (\(\lambda = 0.71069 \text{ Å}\)). The structure was solved by the heavy-atom Patterson method, 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 calculation and were not refined. All calculations were performed using the teXsan crystallographic software package.\(^5\) 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 \(2\) with the atomic labeling scheme is shown in Fig. 1.

### Table 1 Crystal and experimental data

| Formula: ZnO\(_2\)N\(_3\)C\(_6\)H\(_8\) | Formula weight = 1057.66 |
| Crystal system: triclinic |
| Space group: \(P\bar{1}\) |
| \(a = 10.205(3)\)Å |
| \(b = 11.163(6)\) |
| \(c = 11.340(5)\) |
| \(\alpha = 108.23(4)^\circ\) |
| \(\beta = 104.57(3)^\circ\) |
| \(\gamma = 109.44(3)^\circ\) |
| \(V = 1170.3(9)\)Å\(^3\) |
| \(D_{calc} = 1.501 \text{ g/cm}^3\) |
| No. measured reflections = 5660 (unique: 5383 (\(R_{int} = 0.069\))) |
| No. reflections used in refinement of reflections = 3312 (\(I > 2\sigma(I)\)) |
| \(2\theta_{max} = 55^\circ\) with Mo K\(_\alpha\) |
| \(R_1 = 0.062\) |
| \(R_w = 0.108\) |
| Goodness of Fit = 1.33 |
| \((\Delta\sigma)_{max} = 0.040\) |
| \((\Delta\rho)_{max} = 0.86 \text{ eÅ}^{-3}\) |
| \((\Delta\rho)_{min} = -0.51 \text{ eÅ}^{-3}\) |

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*
shown in Fig. 2. The unit cell contains two halves, which are trans to each other through a crystallographical inversion center, and one acetonitrile molecule. Each zinc(II) center is coordinated by one pyridine nitrogen atom, the tertiary amine nitrogen atom and three p-nitrophenolate oxygen atoms; one of these is derived from the same ligand, with the others acting as bridging atoms linking the two halves of the dimer. The geometry around each zinc atom is described as trigonal bipyramid with a value of \( \tau = 0.71 \) (\( \tau = (\beta - \alpha)/60 \), where \( \beta = \angle O(4*)-Zn(1)-O(4) \) and \( \alpha = \angle O(1)-Zn(1)-N(2) \)).

The Zn(1)–O(1) bond distance of 1.923(3) Å is shorter than that of Zn(1)–O(4) [1.994(3) Å], which is slightly shorter than those observed in [Zn(II)-L2][Zn(NCS)4]·0.5H2O [2.015(3)–2.147(3) Å].

References