μ -Phenolato- μ -azido-bridged Dinuclear Zinc(II) Complex with a Schiff-base Having Imidazolyl Groups

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A μ -phenolato- μ -azido-bridged dinuclear zinc(II) complex with 2,6-bis(*N*-(4-imidazolylethyl)iminomethyl)-4-methylphenol (Hbimmp), $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$, was synthesized. The crystal structure was determined by a single-crystal X-ray diffraction method at 293 K. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.2278(10)$, $b = 26.069(3)$, $c = 10.0068(11)$ Å, $\beta = 93.261(2)^\circ$, $V = 2403.4(4)$ Å³, $D_x = 1.657$ g/cm³, $Z = 4$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0342 and 0.0892, respectively, for all 5717 independent reflections. The two zinc(II) atoms are bridged by a phenolato-oxygen of bimmp[−] and a μ -azido-nitrogen atom, where each zinc(II) atom is further coordinated by imino- and imidazolyl-nitrogen atoms of bimmp[−] and azido-nitrogen and chlorido atoms with half occupation to form a square-pyramidal or trigonal-bipyramidal geometry.

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A Schiff-base ligand, 2,6-bis(*N*-(4-imidazolylethyl)iminomethyl)-4-methylphenol (Hbimmp), is an interesting dinucleating ligand, because it has imidazolyl groups. Zinc complexes with this ligand can be expected to have some relevance to active centers in biological systems, such as carboxypeptidases, leucine aminopeptidases, and alkaline phosphatases, where imidazole groups are bound to zinc ions.¹ So far, dinuclear copper,^{2–4} tetranuclear manganese,⁵ and pentanuclear iron⁶ complexes with the bimmp[−] ligand were reported. In this study, we isolated a dinuclear zinc(II) complex with bimmp[−], and determined the crystal structure of this complex, which shows a dinuclear core with μ -phenolato- μ -azido bridges, as shown in Fig. 1. This paper describes the synthesis and crystal structure of $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$.

The complex was prepared by a template reaction of 2,6-diformyl-4-methylphenol (Hdfmp)⁷ and histamine in the presence of zinc(II) salt and sodium azide in methanol. Hdfmp (8.4 mg, 0.05 mmol) and histamine dihydrochloride (18.2 mg,

0.1 mmol) were dissolved in 12 cm³ of methanol. Then, triethylamine (15.8 mg, 0.15 mmol), zinc(II) nitrate hexahydrate (29.9 mg, 0.1 mmol), and sodium azide (14.4 mg, 0.22 mmol) were successively added. The reaction mixture was stirred for a while, and then filtered. The resulting yellow filtrate was left

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{19}\text{H}_{21}\text{ClN}_{12}\text{OZn}_2$
Formula weight = 599.67
$T = 293$ K
Crystal system: monoclinic
Space group: $P2_1/c$
$a = 9.2278(10)$ Å
$b = 26.069(3)$ Å
$c = 10.0068(11)$ Å
$V = 2403.4(4)$ Å ³
$Z = 4$
$D_x = 1.657$ g/cm ³
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)
$\mu(\text{Mo } K\alpha) = 2.147$ mm ^{−1}
$F(000) = 1216$
Crystal size = $0.50 \times 0.39 \times 0.23$ mm ³
No. of reflections collected = 15138
No. of independent reflections = 5717
θ range for data collection: 2.183 to 28.495°
Data/Restraints/Parameters = 5717/0/353
Goodness-of-fit on $F^2 = 1.037$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0342$, $wR2 = 0.0553$
R indices (all data): $R1 = 0.0827$, $wR2 = 0.0892$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$(\Delta\rho)_{\text{max}} = 0.375$ e Å ^{−3}
$(\Delta\rho)_{\text{min}} = -0.263$ e Å ^{−3}
Measurement: Bruker Smart APEX CCD diffractometer
Program system: SHELXTL
Structure determination: intrinsic phasing (SHELXT-2014/4)
Refinement: full matrix least-squares (SHELXL-2014/7)
CCDC deposition number: 1845621

Fig. 1 Chemical structure of $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$.

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Fig. 2 ORTEP drawing of $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$, showing the thermal ellipsoids at the 50% probability level. One of the disordered atoms, N_3 and Cl , are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°)

Zn1–Zn2	3.3313(5)	Zn2–O1	2.0316(17)
Zn1–O1	2.1018(17)	Zn2–N4	2.099(2)
Zn1–N1	2.090(2)	Zn2–N5	2.058(2)
Zn1–N3	2.071(2)	Zn2–N7	2.217(2)
Zn1–N7	2.097(2)	Zn2–N13	1.999(15)
Zn1–N10	1.986(10)	Zn2–Cl2	2.300(3)
Zn1–Cl1	2.355(3)		
Zn1–O1–Zn2	107.39(7)	Zn1–N7–Zn2	101.06(9)

Table 3 Hydrogen-bonding geometry (Å, °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N2–H2B···Cl2 ⁱ	0.86	2.31	3.166(4)	172.3
N2–H2B···N13 ⁱ	0.86	2.05	2.903(14)	169.3
N6–H6B···Cl1 ⁱⁱ	0.86	2.40	3.163(6)	148.2
N6–H6B···N10 ⁱⁱ	0.86	2.27	3.086(11)	159.3

Symmetry codes: (i) $x, y, z-1$; (ii) $x-1, y, z$.

for several days to give yellow crystals. The crystals were collected. Yield, 6 mg (20%). *Anal.* Found: C, 37.79; H, 3.50; N, 27.94%. Calcd for $\text{C}_{19}\text{H}_{21}\text{ClN}_{12}\text{OZn}_2$: C, 38.06; H, 3.53; N, 28.03%. IR (KBr, cm^{-1}): $\nu(\text{N}_3)$ 2077, $\nu(\text{C}=\text{N})$ 1626.

A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by an intrinsic phasing method and refined by full-matrix least-squares methods. The fifth ligand of each zinc atom was found to be occupied by chloride ion and azido ions with half occupancy. The hydrogen atoms were inserted at their calculated positions, and fixed there. All of the calculations were carried out on a Windows 7 Core i7 computer utilizing the SHELXT-2014/4 and SHELXL-2014/7.⁸ Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (Deposit numbers CCDC-1845621). Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

Fig. 3 Packing diagram of $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$.

The asymmetric unit consists of one dinuclear molecule $[\text{Zn}_2(\text{bimmp})(\mu\text{-N}_3)(\text{N}_3)(\text{Cl})]$. The dinuclear molecule was drawn by the ORTEP program (Fig. 2). The Zn1–Zn2 distance is 3.3313(5)Å. In the dinuclear molecule, each zinc(II) atom is coordinated by μ -phenolato-oxygen, imino-nitrogen, and imidazolyl-nitrogen atoms of bimmp[−] ligand with Zn–O and Zn–N distances of 2.0316(17)–2.1018(17)Å and 2.058(2)–2.099(2)Å, respectively, in a *meridional* fashion (Table 2). The fourth position of the coordination geometry is occupied by μ -azido-nitrogen in an end-on fashion with different bond distances of Zn1–N7 (2.097(2)Å) and Zn2–N7 (2.217(2)Å). Besides these coordinations, other azido-nitrogen and chlorido atoms are coordinated to the Zn1 and Zn2 atoms with an occupancy factor of 0.5 to form a five-coordination. The τ values⁹ of Zn1 and Zn2 are 0.597 and 0.008, respectively, showing distorted trigonal-bipyramidal and square-pyramidal geometries, respectively. The Zn–O and Zn–N bond distances are within the range for five-coordinate zinc(II) complexes with related Schiff-base ligands.^{10,11} The chlorido ligands came from the reaction material, histamine dihydrochloride. In the crystal, the dinuclear molecule is loosely bound by hydrogen bonds between the imidazolyl nitrogen and the chlorido and azido ligands of the neighboring dinuclear molecules (Table 3, Fig. 3).

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