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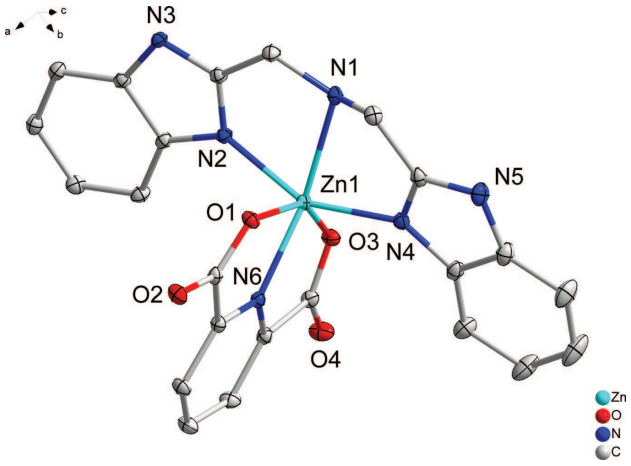
Crystal structure of (bis((1*H*-benzo[*d*]imidazol2-yl)methyl)amine-κ^3*N*,*N*′,*N*″)-(pyridine-2,6-dicarboxylato-κ^3*N*,*O*,*O*′)zinc(II) — methanol — water (1/2/1), $C_{25}H_{28}N_6O_7Zn$



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Abstract

$C_{25}H_{28}N_6O_7Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 7.8073(19)$ Å, $b = 11.350(3)$ Å, $c = 15.515(4)$ Å, $\alpha = 95.006(2)°$, $\beta = 101.828(3)°$, $\gamma = 102.050(4)°$, $V = 1303.8(5)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0429$, $wR_{ref}(F^2) = 0.1153$, $T = 153(2)$ K.

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The crystal structure is shown in the figure. (Solvent molecules and hydrogen atoms at the organic ligands are omitted for clarity.) Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Bis(benzimidazol-2-yl-methyl)amine (bbma) was synthesized according to a literature procedure [3]. $Zn(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.20 mmol) in 10 mL of methanol was dropped carefully to a stirred methanol solution (10 mL) containing bbma (0.056 g, 0.20 mmol) to give a clear colorless solution.

Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	0.34 × 0.09 × 0.03 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.00 mm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ and ω-scans
θ_{max}, completeness:	31.5°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19781, 8528, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7238
$N(param)_{refined}$:	378
Programs:	CrystalClear [1], SHELX [2]

Afterwards, a methanol solution (10 mL) of pyridine-2,6-dicarboxylic acid (0.017 g, 0.1 mmol) and triethylamine (0.020 g, 0.20 mmol) were added to the solution. After stirring for 2.5 h, the filtrate of the resulting solution was allowed to stand at room temperature for slow evaporation. Colorless and needle crystals formed after 3 days.

Experimental details

The methyl groups were idealized and refined using rigid groups allowed to rotate about the N—C bond (with the SHELX program). The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5 U_{eq}(C) and the U_{iso} values of all other hydrogen atoms were set to 1.2 U_{eq}(C). The one oxygen of methanol (O7) is disordered with occupancies of 0.6 and 0.4.

Discussion

Histidine imidazole plays an important role in the synthesis of numerous metalloproteins. Therefore, complexes with imidazole or benzimidazole ligands attract a great deal of attention. Bis(benzimidazol-2-yl-methyl)amine (bbma) is a ligand containing two benzimidazole groups. Because of the similarity with histidine imidazole, we select bbma as the first ligands and report a new complex, $[Zn(bbma)(dipic)] \cdot 2CH_3OH \cdot H_2O$.

Some zinc(II) complexes of bbma have been reported, such as $[ZnCl(H_2O)(C_{16}H_{15}N_5)]ClO_4 \cdot H_2O$ [4], $[Zn(bbma)(pic)]NO_3 \cdot 2CH_3OH$ [5], $[Zn_2(bbma)_2(\mu_2\text{-}\eta^4\text{-ox})](ClO_4)_2$ [6]. The central Zn(II) of them are five-coordinate in distorted trigonal bipyramidal geometry. Different from the above, in this study, we report the crystal structure of a complex in which Zn(II) is six-coordinate. Pyridine-2,6-dicarboxylate (dipic) can act as a

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Zn1	0.30849(3)	0.26364(2)	0.70831(2)	0.01560(7)
O1	0.52503(17)	0.18112(11)	0.78450(8)	0.0190(2)
O2	0.82162(17)	0.19468(12)	0.81047(9)	0.0219(3)
O3	0.22693(17)	0.40051(11)	0.62831(9)	0.0196(2)
O4	0.34267(19)	0.56990(13)	0.57489(10)	0.0279(3)
O5	0.0558(2)	−0.31970(13)	0.52843(11)	0.0271(3)
O6	0.0864(3)	0.18042(18)	1.08766(12)	0.0503(5)
H6O	0.1559	0.1328	1.0911	0.060*
O7[a]	0.7417(5)	−0.0141(3)	0.8792(2)	0.0412(7)
H7O	0.7803	0.0169	0.8376	0.049*
O7′[b]	0.8003(9)	0.0488(6)	0.9423(6)	0.080(2)
N1	0.1165(2)	0.10698(14)	0.75129(10)	0.0180(3)
N2	0.2511(2)	0.12567(13)	0.60457(10)	0.0168(3)
N3	0.1716(2)	−0.07199(13)	0.55222(10)	0.0176(3)
H3N	0.1270	−0.1505	0.5492	0.021*
N4	0.2656(2)	0.33909(14)	0.82568(10)	0.0184(3)
N5	0.2008(2)	0.31179(16)	0.95660(10)	0.0251(3)
H5N	0.1687	0.2742	1.0001	0.030*
N6	0.54825(19)	0.36949(12)	0.69652(9)	0.0150(3)
C1	0.1277(3)	−0.00907(16)	0.70501(12)	0.0214(3)
H1A	0.0097	−0.0680	0.6927	0.026*
H1B	0.2180	−0.0438	0.7425	0.026*
C2	0.1810(2)	0.01511(15)	0.61936(11)	0.0172(3)
C3	0.2459(2)	−0.01380(15)	0.48887(11)	0.0170(3)
C4	0.2779(3)	−0.05803(16)	0.40862(12)	0.0207(3)
H4	0.2447	−0.1424	0.3867	0.025*
C5	0.3610(3)	0.02748(17)	0.36202(12)	0.0222(3)
H5	0.3843	0.0011	0.3066	0.027*
C6	0.4114(3)	0.15210(17)	0.39513(12)	0.0222(3)
H6	0.4676	0.2078	0.3614	0.027*
C7	0.3812(3)	0.19585(16)	0.47546(12)	0.0202(3)
H7	0.4173	0.2800	0.4979	0.024*
C8	0.2954(2)	0.11088(15)	0.52216(11)	0.0165(3)
C9	0.1750(2)	0.12487(16)	0.84917(12)	0.0202(3)
H9A	0.2841	0.0935	0.8681	0.024*
H9B	0.0788	0.0816	0.8756	0.024*
C10	0.2143(2)	0.25907(17)	0.87791(11)	0.0196(3)
C11	0.2467(3)	0.43668(19)	0.95630(13)	0.0262(4)
C12	0.2537(4)	0.5346(2)	1.01862(15)	0.0397(5)
H12	0.2256	0.5231	1.0745	0.048*
C13	0.3033(4)	0.6490(2)	0.99528(16)	0.0473(7)
H13	0.3095	0.7179	1.0362	0.057*
C14	0.3451(4)	0.6666(2)	0.91271(16)	0.0406(6)
H14	0.3787	0.7470	0.8991	0.049*
C15	0.3382(3)	0.56926(19)	0.85087(14)	0.0299(4)
H15	0.3666	0.5811	0.7951	0.036*
C16	0.2880(3)	0.45295(17)	0.87378(12)	0.0217(3)
C17	0.6822(2)	0.22941(15)	0.77952(10)	0.0158(3)
C18	0.7032(2)	0.33953(15)	0.72990(11)	0.0160(3)
C19	0.8649(2)	0.40324(16)	0.71581(12)	0.0202(3)
H19	0.9744	0.3811	0.7388	0.024*
C20	0.8626(3)	0.50072(17)	0.66702(13)	0.0235(4)
H20	0.9715	0.5457	0.6563	0.028*
C21	0.7020(2)	0.53187(17)	0.63428(12)	0.0217(3)
H21	0.6989	0.5989	0.6018	0.026*
C22	0.5447(2)	0.46243(15)	0.65014(11)	0.0171(3)
C23	0.3554(2)	0.48081(15)	0.61426(11)	0.0183(3)
C24	0.1300(6)	0.2614(4)	1.1685(2)	0.0883(14)
H24A	0.2136	0.3364	1.1630	0.106*
H24B	0.1866	0.2229	1.2173	0.106*
H24C	0.0200	0.2807	1.1808	0.106*
C25	0.6598(7)	0.0100(4)	0.9498(3)	0.0863(13)
H25A	0.6448	0.0453	1.0069	0.104*
H25B	0.6402	−0.0785	0.9476	0.104*
H25C	0.5723	0.0293	0.9014	0.104*
H1N	0.001(3)	0.119(2)	0.7338(15)	0.023(6)*
H5A	0.131(5)	−0.353(3)	0.533(2)	0.061(11)*
H5B	−0.020(4)	−0.352(3)	0.481(2)	0.053(9)*

Occupancies: [a] = 0.6, [b] = 0.4.

bidentate, tridentate and bridging ligand [7]. In combination with Zn(II) dipic often act as a tridentate ligand.

The structure consists of one [Zn(bbma)(dipic)], two methanol molecules and one water molecule. The central Zn(II) is six-coordinate in a distorted octahedral N4O2 ligand set formed by three nitrogen atoms of bbma, one pyridine N(6) and two carboxylate O atoms of dipic. The three nitrogen atoms (N1, N2, N4) of bbma and a nitrogen atom (N6) of dipic constitute the equatorial plane. Two distances $Zn—N_{benzimidazole}$ are nearly the same: d(Zn1—N2) = 2.053(15) Å and d(Zn1—N4) = 2.064(15) Å. The $Zn—N_{alkylamine}$ distance [2.314(16) Å] is longer than the bond lengths of $Zn—N_{benzimidazole}$. Equatorial bond angles are 74.65(5)°–125.82(5)°. Axial positions are occupied by O1 and O3 with a bond angle O(1)—Zn(1)—O(3) of 150.99(5)°, showing seriously distorted octahedral environment. In addition, hydrogen bonds are existing in the title complex. Finally, a 3-D network is formed by hydrogen bonds and π–π interactions.

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References

1. Rigaku/MSC. CrystalClear. Rigaku/MSC Inc., The Woodlands, TX, USA (2006).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–C122.
3. Sivagnanam, U.; Pandiyan, T.; Palaniandavar, M.: Synthesis of certain multidentate benzimidazole-derived ligands. Indian J. Chem. **32B** (1993) 572.
4. Li, G. N.; Nie, F. M.: Crystal structure of chloro-aqua(bis(benzimidazol-2-yl-methyl)-amine)-zinc(II) perchlorate monohydrate, $[ZnCl(H_2O)(C_{16}H_{15}N_5)]ClO_4.H_2O$,$C_{16}H_{19}Cl_2N_5O_6Zn$. Z. Kristallogr. NCS. **227** (2012) 369–370.
5. Feng, R.; Huang, F. F.; Yuan, J. L.; Lu, Z.; Fang, T.; Nie, F. M.: Structures and fluorescent properties of picolinato zinc(II) and cadmium(II) complexes based on tridentate and tetradentate benzimidazole ligands. J. Coord. Chem. **69** (2016) 1–32.
6. Li, L. Q.; Li, M.; Zhang, H.; Li, S.; Nie, F. M.: Synthesis, structures, and fluorescent properties of two oxalato-bridged

dinuclear zinc(II) complexes with tridentate and tetradentate polybenzimidazole ligands. J. Coord. Chem. **67** (2014) 847–C856.
7. Ghasemi, K.; Ghasemi, F.; Rezvani, A. R.; Shokrollahi, A.; Refahi, M.; Garcia-Granda, S.; Mendoza-Merono, R.: Mn(II) and Zn(II) ions catalytic oxidation of *o*-phenylenediamine and characterization, X-ray crystal structure and solution study of the final products $DAPH^+Cl^- \cdot 3H_2O$ and $[DAPH][Zn(dipicH)(dipic)] \cdot 4H_2O$. Polyhedron **110** (2016) 55–C62.