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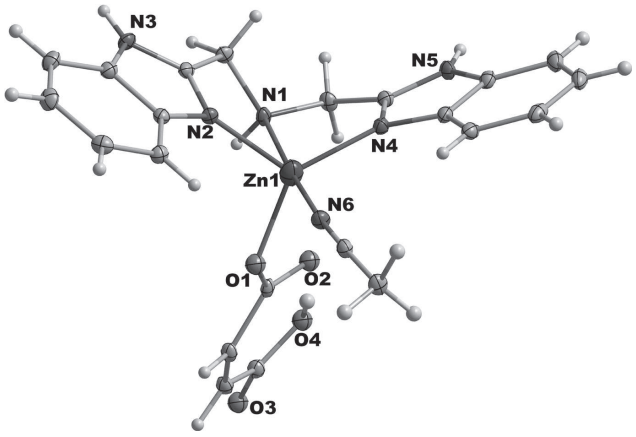
Crystal structure of acetonitrile{bis(2-benzimidazolylmethyl)amine-κ^3*N*,*N*′,*N*′′}-{maleato-κ*O*}zinc(II) perchlorate - acetonitrile (1/1), $C_{24}H_{24}ClN_7O_8Zn$



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Abstract

$C_{24}H_{24}ClN_7O_8Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 10.0834(7)$ Å, $b = 10.8269(7)$ Å, $c = 13.1958(8)$ Å, $\alpha = 77.658(5)°$, $\beta = 77.135(5)°$, $\gamma = 87.797(5)°$, $V = 1371.93(15)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0410$, $wR_{ref}(F^2) = 0.1015$, $T = 105.6$ K.

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The crystal structure is shown in the figure. 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(2-benzimidazolylmethyl)amine (bbma) was prepared according to the literature method [4]. A acetonitrile (10 mL) solution of bbma (0.069 g, 0.25 mmol) was dropped into a acetonitrile (15 mL) solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.093 g, 0.25 mmol), giving a colorless transparent solution. Then a mixture of maleic acid (H_2male; 0.029 g, 0.25 mmol), 5 mL of acetonitrile and 1 mL trimethylamine (0.25 mol/L) was added

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.45 × 0.40 × 0.12 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.05 mm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, Gemini, ω-scans
θ_{max}, completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10264, 5393, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4741
$N(param)_{refined}$:	373
Programs:	CrysAlis^{PRO} [1], SHELX [2], OLEX2 [3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.14859(3)	0.38017(3)	0.67765(2)	0.01779(10)
Cl1	0.25612(7)	−0.05864(6)	0.60573(5)	0.02569(17)
O1	−0.00177(19)	0.28542(17)	0.64985(14)	0.0216(4)
O2	−0.0394(2)	0.15319(18)	0.80777(14)	0.0237(4)
O3	−0.2717(2)	−0.18546(19)	0.83983(15)	0.0294(5)
O4	−0.1556(2)	−0.04996(19)	0.89043(15)	0.0265(5)
H4	−0.1201	0.0201	0.8656	0.040*
O5	0.2475(2)	−0.1631(2)	0.55559(17)	0.0329(5)
O6	0.3624(3)	−0.0832(2)	0.6637(2)	0.0474(7)
O7	0.2858(3)	0.0554(2)	0.5274(2)	0.0572(8)
O8	0.1315(3)	−0.0478(3)	0.6778(2)	0.0690(9)
N1	0.2620(2)	0.2011(2)	0.73867(17)	0.0190(5)
H1	0.2254	0.1325	0.7250	0.023*
N2	0.3098(2)	0.3851(2)	0.55450(17)	0.0179(5)
N3	0.4992(2)	0.2966(2)	0.48200(17)	0.0211(5)
H3	0.5690	0.2482	0.4766	0.025*
N4	0.1759(2)	0.4125(2)	0.81640(17)	0.0194(5)
N5	0.2301(2)	0.3425(2)	0.97308(17)	0.0208(5)
H5	0.2567	0.2920	1.0244	0.025*
N6	0.0512(2)	0.5527(2)	0.62466(18)	0.0230(5)
N7	0.5607(3)	0.1614(3)	0.9162(2)	0.0380(7)
C1	0.4043(3)	0.2192(3)	0.6786(2)	0.0213(6)
H1A	0.4450	0.1380	0.6714	0.026*
H1B	0.4565	0.2599	0.7159	0.026*
C2	0.4056(3)	0.3000(2)	0.5709(2)	0.0186(5)
C3	0.3455(3)	0.4415(2)	0.4464(2)	0.0183(5)
C4	0.4633(3)	0.3854(3)	0.4002(2)	0.0209(6)
C5	0.5213(3)	0.4168(3)	0.2916(2)	0.0261(6)
H5A	0.5989	0.3770	0.2614	0.031*
C6	0.4568(3)	0.5106(3)	0.2312(2)	0.0279(6)
H6	0.4924	0.5349	0.1585	0.033*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C7	0.3397(3)	0.5697(3)	0.2769(2)	0.0254(6)
H7	0.3000	0.6329	0.2338	0.030*
C8	0.2811(3)	0.5365(3)	0.3848(2)	0.0213(6)
H8	0.2028	0.5755	0.4148	0.026*
C9	0.2446(3)	0.1875(3)	0.8543(2)	0.0218(6)
H9A	0.3261	0.1523	0.8763	0.026*
H9B	0.1690	0.1306	0.8915	0.026*
C10	0.2178(3)	0.3145(3)	0.8808(2)	0.0191(6)
C11	0.1590(3)	0.5116(3)	0.8708(2)	0.0206(6)
C12	0.1923(3)	0.4672(3)	0.9703(2)	0.0214(6)
C13	0.1843(3)	0.5423(3)	1.0445(2)	0.0277(7)
H13	0.2064	0.5117	1.1100	0.033*
C14	0.1415(3)	0.6657(3)	1.0156(2)	0.0289(7)
H14	0.1339	0.7190	1.0632	0.035*
C15	0.1094(3)	0.7119(3)	0.9164(2)	0.0275(6)
H15	0.0814	0.7952	0.8998	0.033*
C16	0.1183(3)	0.6367(3)	0.8424(2)	0.0227(6)
H16	0.0978	0.6682	0.7764	0.027*
C17	−0.0593(3)	0.1894(2)	0.7151(2)	0.0193(6)
C18	−0.1561(3)	0.1196(3)	0.6756(2)	0.0209(6)
H18	−0.1745	0.1595	0.6105	0.025*
C19	−0.2200(3)	0.0094(3)	0.7197(2)	0.0219(6)
H19	−0.2762	−0.0154	0.6804	0.026*
C20	−0.2162(3)	−0.0817(3)	0.8221(2)	0.0227(6)
C21	−0.0136(3)	0.6404(3)	0.6115(2)	0.0211(6)
C22	−0.0969(3)	0.7532(3)	0.5986(2)	0.0264(6)
H22A	−0.1250	0.7649	0.5323	0.040*
H22B	−0.0450	0.8255	0.5990	0.040*
H22C	−0.1758	0.7434	0.6561	0.040*
C23	0.5702(3)	0.1452(3)	1.0026(3)	0.0293(7)
C24	0.5827(3)	0.1229(3)	1.1130(2)	0.0355(7)
H24A	0.6769	0.1127	1.1160	0.053*
H24B	0.5329	0.0477	1.1526	0.053*
H24C	0.5467	0.1937	1.1431	0.053*

dropwise. After being stirred at room temperature for 2 h, the solution was filtered and the filtrate was evaporated at room temperature. Colorless crystals suitable for X-ray structure determination formed.

Experimental details

Methyl groups were idealized and refined using rigid groups allowed to rotate about the N—C bond. 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).

Discussion

Multidentate ligands containing two or more benzimidazole donor units has been studied as models for the active sites of metalloproteins [5]. Bis(2-benzimidazolylmethyl)amine (bbma) is a linear tridentate ligand with two aromatic benzimidazole side arms [6–8].

The title complex consists of a $[Zn(bbma)(Hmale)(CH_3CN)]^+$, a perchlorate and a acetonitrile solvent molecule. In the complex, the Zn(II) is five-coordinated with N_4O donor sets derived from a Hmale-O atom, a acetonitrile-N atom and three bbma-N atoms. The equatorial plane is defined by two nitrogen atoms (N2, N4) of benzimidazole groups of bbma and one carboxylate O1. The distance between Zn(II) and all atoms of equatorial plan are Zn1—N2 = 2.020(2) Å, Zn1—N4 = 2.014(2) Å, Zn1—O1 = 2.0034(19) Å, and bond angles are N2—Zn1—N4 = 119.84(9)°, N2—Zn1—O1 = 107.59(8)°, N4—Zn1—O1 = 129.18(9)°. The axial positions are occupied by the N1 of bbma and N6 of acetonitrile molecule with a bond angle N1—Zn1—N6 of 176.51°, and the Zn1—N1 distance [2.299(2) Å] is longer than the bond lengths of Zn1—N6 [2.133(2) Å]. Thus, its coordination geometry is a distorted trigonal bipyramidal (tbp) and this is reflected in the index of trigonality, $\tau = 0.789$ ($\tau = 0$ for a perfect square pyramidal and 1 for a perfect trigonal bipyramidal geometry according to the Addison/Reedijk geometric criterion). In addition, the two benzimidazole groups of bbma can be twisted, resulting in the observation of dihedral angle of 134.21°.

In the title complex intramolecular hydrogen bonds can be observed, which derived from the O2, O4 atoms of of monodentate hydrogen maleate ($HO_2CCH = CHCO_2^-$) and the N1 atom of bbma (N1–H1···O2, O4–H4···O2). In addition, a double molecular unit is formed through intermolecular hydrogen bonds with type of N5–H5···O3, and the double molecular units are further connected *via* $\pi = \pi$ interactions from benzimidazole groups of neighbouring bbma ligands to form a 2-D network.

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References

1. Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.35.11, Agilent Technologies UK Ltd., Oxford, UK (2011).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. **42** (2009) 339–341.
4. Sivagnanam, U.; Pandiyan, T.; Palaniandavar, M.: Synthesis of certain multidentate benzimidazole-derived ligands. Indian J. Chem. **32B** (1993) 572–576.
5. Yin, X. C.; Lin, C. C.; Zhou, Z. F.; Chen, W. D.; Zhu, S. R.; Lin, H. K.; Su, X. C.; Chen, Y. T.: Studies of artificial hydrolytic metalloenzymes: the catalyzed carboxyester hydrolysis by copper(II), zinc(II) and cobalt(II) complexes of the tripod ligand tris(2-benzimidazylmethyl)amine. Transition Met. Chem. **24** (1999) 537–540.

6. Xu, J. Y.; Xie, C. Z.; Xue, F.; Hao, L. F.; Ma, Z. Y.; Liao, D. Z.; Yan, S. P.: Directed assembly and characterization of 1D polymers based on $[M^{II}(BMA)]^{2+}$ node (M = Cu, Mn, Ni and Zn; BMA = N,N-bis(benzimidazol-2-ylmethyl)amine) with linear bridging dicyanamide and terephthalate ligands. Dalton Trans. **39** (2010) 7159–7166.
7. 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) 3776–3791.
8. 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) 847–856.