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Crystal structure of *aqua-bis(5-bromo-6-methylpicolinato- $\kappa^2 N,O$)zinc(II) dihydrate*, $C_{14}H_{16}Br_2N_2O_7Zn$

Figure 1: The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level.

<https://doi.org/10.1515/ncrs-2019-0486>

Received July 11, 2019; accepted September 5, 2019; available online September 26, 2019

Abstract

$C_{14}H_{16}Br_2N_2O_7Zn$, orthorhombic, $Pna2_1$ (no. 33), $a = 15.4300(3)$ Å, $b = 10.6264(2)$ Å, $c = 11.4638(2)$ Å, $V = 1879.66(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0328$, $wR_{ref}(F^2) = 0.0709$, $T = 293$ K.

CCDC no.: 1890138

The molecular structure is shown in the Figure 1. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

$Zn(CH_3COOH)_2 \cdot 2 H_2O$ (0.5 mmol, 0.112 g) and 5-bromo-6-methylpicolinic acid (Hbmp, 0.5 mmol, 0.112 g) were dis-

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.29 \times 0.21 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	5.60 mm^{-1}
Diffractometer, scan mode:	CCD,
$\theta_{\max}$, completeness:	30.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	35861, 4358, 0.049
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3668
$N(\text{param})_{\text{refined}}$:	238
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

solved in 20 mL distilled H_2O . Then, the pH of the obtained mixture was neutralized with KOH ($0.5 \text{ mol} \cdot \text{L}^{-1}$) to pH = 6.0. After that, the mixed solution was cooled and filtered after stirring for 4 h at 80 °C. Two weeks later, light yellow block crystals were grown by slow evaporation at room temperature.

Yield: 16 mg (12%, based on Hbmp). Anal. Calcd for $C_{14}H_{16}Br_2N_2O_7Zn$ (%): C, 30.57; H, 2.76; N, 5.10. Found: C, 30.51; H, 2.71; N, 5.16.

Experimental details

Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with ShelXL [4]. The H atoms bonded to C atoms were fixed, with C–H distance of 0.93 Å; and/or positioned geometrically in the riding-model approximation, with C–H distance of 0.97 Å; $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. The structure was refined as inversion twin: (0.568(11)/0.432(11)).

Comment

In our previous research, we have described the complexes of *N*-heterocyclic carboxylate ligands such as imidazole-, pyrazine- and pyridine-carboxylates [5, 6].

Nowadays, the modification of picolinate such as by Me– [7], F– [8], –Cl and –NH₂ [9, 10], Br [11, 12] has been employed.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Br1	−0.02250(3)	0.53137(5)	0.46855(9)	0.0637(2)
Br2	0.75759(3)	0.58473(5)	0.50371(6)	0.0569(2)
Zn1	0.36788(3)	0.58739(4)	0.47604(5)	0.03311(14)
O1	0.3855(2)	0.6475(4)	0.6491(3)	0.0462(9)
O2	0.3228(2)	0.6862(4)	0.8306(4)	0.0626(12)
O3	0.3475(2)	0.6786(3)	0.3202(3)	0.0385(8)
O4	0.4100(2)	0.7768(3)	0.1641(3)	0.0436(9)
O5	0.3728(2)	0.4159(3)	0.4534(4)	0.0504(11)
H5A	0.416376	0.372325	0.440548	0.076*
H5B	0.344136	0.376245	0.500108	0.076*
N1	0.2352(2)	0.5859(3)	0.5437(4)	0.0305(9)
N2	0.4992(2)	0.6233(3)	0.4222(4)	0.0291(9)
C1	0.3205(3)	0.6567(4)	0.7191(4)	0.0382(12)
C2	0.2329(3)	0.6287(4)	0.6607(5)	0.0350(11)
C3	0.1562(4)	0.6476(5)	0.7240(5)	0.0496(14)
H3	0.156576	0.676770	0.800491	0.059*
C4	0.0792(3)	0.6200(5)	0.6654(6)	0.0508(15)
H4	0.026108	0.631930	0.702149	0.061*
C5	0.0826(3)	0.5729(4)	0.5475(5)	0.0399(13)
C6	0.1616(3)	0.5558(3)	0.4862(6)	0.0333(12)
C7	0.1694(4)	0.5036(5)	0.3562(6)	0.0500(14)
H7A	0.225708	0.523482	0.325621	0.075*
H7B	0.125732	0.542018	0.308376	0.075*
H7C	0.161531	0.414034	0.356380	0.075*
C8	0.4121(3)	0.7171(4)	0.2611(4)	0.0330(10)
C9	0.5010(3)	0.6861(4)	0.3151(4)	0.0278(10)
C10	0.5773(3)	0.7196(5)	0.2598(5)	0.0385(12)
H10	0.577045	0.761540	0.188539	0.046*
C11	0.6542(3)	0.6880(5)	0.3150(5)	0.0446(13)
H11	0.707060	0.707352	0.280354	0.053*
C12	0.6521(3)	0.6260(4)	0.4249(5)	0.0351(11)
C13	0.5739(2)	0.5939(3)	0.4822(7)	0.0311(9)
C14	0.5684(3)	0.5284(5)	0.6015(6)	0.0508(15)
H14A	0.576490	0.589343	0.662312	0.076*
H14B	0.612793	0.465277	0.606751	0.076*
H14C	0.512604	0.489528	0.609911	0.076*
O6	0.5096(2)	0.2792(3)	0.4250(4)	0.0543(11)
H6A	0.531534	0.276551	0.493000	0.081*
H6B	0.549864	0.287081	0.374860	0.081*
O7	0.2549(2)	0.2683(4)	0.5430(4)	0.0554(11)
H7D	0.210581	0.281849	0.585258	0.083*
H7E	0.242861	0.239989	0.477959	0.083*

The title compound contains a monomer in which the asymmetric unit contains one Zn^{II} ion, two 5-bromo-6-methylpicolinate (bmp[−]) ligands, one coordinated aqua as well as two water molecules. Bond lengths and angles are in the expected ranges [13].

The Zn^{II} ion is in a distorted square-pyramidal N₂O₃ geometry formed by two bmp[−] ligands and a coordinated aqua. The bmp[−] ions bind to the Zn^{II} center through bidentate chelate mode and form two five-membered chelate rings

in the base, and the water ligand is at the apex. The Zn^{II} ion deviated from the least squares plane of the basal plane N1/O1/N2/O3 about 0.5 Å towards O5.

The lattice water molecules are involved in inter-molecular hydrogen bonds with the coordinated aqua and uncoordinated carboxyl oxygen atoms of bmp[−].

Acknowledgements: This work was supported by the Key scientific research projects in Colleges and Universities of Henan province (No. 17A150040), the Foundation for Science & Technology Innovation Talents in Henan province (No.164100510012), Natural Science Foundation of China (Nos. 21671114, and U1804131) as well as the Tackle Key Problem of Science and Technology Project of Henan Province, China (no. 182102310897).

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