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# Tetraaquabis[2-(pyridin-4-yl-$\kappa N$)-pyrimidine-5-carboxylato]zinc

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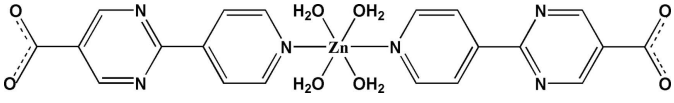
Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.033; $wR$ factor = 0.089; data-to-parameter ratio = 12.4.

In the title complex, $[Zn(C_{10}H_6N_3O_2)_2(H_2O)_4]$, the $Zn^{II}$ ion lies on an inversion center and is coordinated in a slightly distorted octahedral geometry by two N atoms from two 2-(pyridin-4-yl)pyrimidine-5-carboxylate ligands and four water molecules. In the symmetry-unique part of the molecule, the pyridine and pyrimidine rings form a dihedral angle of 7.0 (1)°. In the crystal, the coordinating water molecules act as donor groups and carboxylate O atoms act as acceptors in O—H···O hydrogen bonds, forming a three-dimensional network.

## Related literature

For a general background to supramolecular chemistry, see: Collet *et al.* (1996). For general syntheses and applications of MOFs, see: Sen *et al.* (2012); Saha *et al.* (2012). For a related structure, see: Piao & Xuan (2011).




## Experimental

### Crystal data

$[Zn(C_{10}H_6N_3O_2)_2(H_2O)_4]$
$M_r$ = 537.79
Triclinic, $P\overline{1}$
$a$ = 6.2764 (7) Å
$b$ = 6.9208 (7) Å
$c$ = 12.7810 (17) Å
$\alpha$ = 99.676 (7)°
$\beta$ = 92.638 (7)°
$\gamma$ = 112.639 (5)°
$V$ = 501.36 (10) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.29 mm$^{-1}$
$T$ = 150 K
0.26 × 0.20 × 0.04 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.730, $T_{max}$ = 0.950
8143 measured reflections
2184 independent reflections
2030 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.089
$S$ = 1.14
2184 reflections
176 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.05 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.61 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1$A$···O16$^{i}$ | 0.83 (2) | 1.98 (2) | 2.805 (3) | 175 (3) |
| O1—H1$B$···O17$^{ii}$ | 0.82 (3) | 1.81 (3) | 2.631 (3) | 175 (4) |
| O2—H2$A$···O16$^{iii}$ | 0.83 (4) | 2.04 (4) | 2.840 (3) | 162 (4) |
| O2—H2$B$···O17$^{iv}$ | 0.83 (3) | 1.94 (3) | 2.767 (3) | 173 (3) |

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

Data collection: *SMART* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

RS wishes to thank FCT(SFRH/BPD/71798/2010) for a postdoctoral grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5541).

## References

Bruker (2008). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Collet, A. (1996). *Comprehensive Supramolecular Chemistry*, edited by J. L. Atwood, J. E. D. Davies, D. D. M. Nicol, F. Vögtle & J. M. Lehn, Vol. 6, pp. 281–303. Oxford: Pergamon.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Piao, Y.-A. & Xuan, Z.-Y. (2011). *Acta Cryst.* E**67**, m1072.
Saha, D., Sen, R., Maity, T. & Koner, S. (2012). *Dalton Trans.* **41**, 7399–7408.
Sen, R., Saha, D. & Koner, S. (2012). *Chem. Eur. J.* **18**, 5979–5986.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2012). E**68**, m1429 [doi:10.1107/S160053681204411X]

## Tetraaquabis[2-(pyridin-4-yl-$\kappa N$)pyrimidine-5-carboxylato]zinc

**Rupam Sen, Dasarath Mal, Paula Brandao and Zhi Lin**

### S1. Comment

The aim of designing coordination frameworks is now been motivated through the field of supramolecular chemistry (Collet *et al.*, 1996) and crystal engineering (Sen *et al.*, 2012) from the viewpoints of the development of novel multi-functional MOFs. Fabricating MOFs with the desired properties are now the present day challenges of the chemist. N-Heterocyclic carboxylic acids share a major role in developing MOFs based material synthesis (Sen *et al.*, 2012, Saha *et al.* 2012). Herein, we wish to report a new compound having an N-heterocyclic carboxylate ligand (2-pyridin-4-yl-pyrimidine-5-carboxylato).

The molecular structure of the title compound is shown in Fig. 1. The $Zn^{II}$ ion lies on an inversion center and is coordinated in a slightly distorted octahedral geometry by two N atoms from two 2-pyridin-4-ylpyrimidine-5-carboxylato ligands and four water molecules. The equatorial plane is formed by the four water molecule and the two axial sites are occupied by the N-donor sites of the ligand. In the crystal, O—H···O hydrogen bonds form a three-dimensional network (Fig. 2). The related structure, tetraaquabis[4-(4H-1,2,4-triazol-4-yl)benzoato- $\kappa N^1$]manganese(II) decahydrate, has been published (Piao & Xuan, 2011).

### S2. Experimental

To prepare the complex we followed a routine hydrothermal process. $Zn(NO_3)_2$ hydrate and 2-pyridin-4-ylpyrimidine-5-carboxylic acid were mixed in a 1:1 ratio, and kept in a reaction bomb at 433 K for 2 days in autogenously created pressure. After cooling to room temperature colourless block-shaped crystals were obtained. Yield *ca*. 45% (based on metal). The crystals were collected by filtration, washed thoroughly with water and dried in ambient conditions.

### S3. Refinement

The hydrogen atoms of the C—H bonds were placed at calculated positions and refined as riding atoms, with C—H = 0.95 Å with $U_{iso}$(H) =1.2$U_{eq}$(C) of the atom to which they are attached. The positions of the hydrogen atoms of the water molecules were discernible in difference Fourier maps and they were included in the structure refinement with individual isotropic thermal parameters and refined with an O—H distance restraint of 0.83 (2) Å.

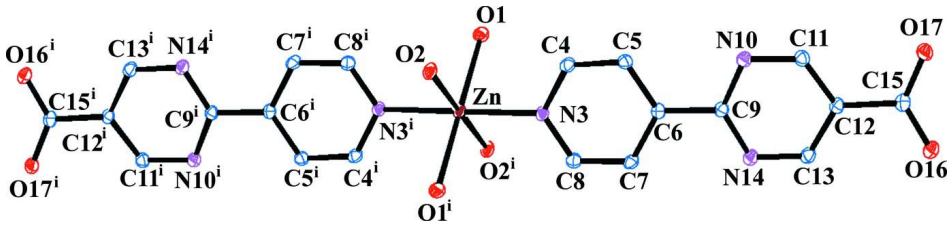



**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level [Symmetry code: (i) -x,-*y*, -*z*].

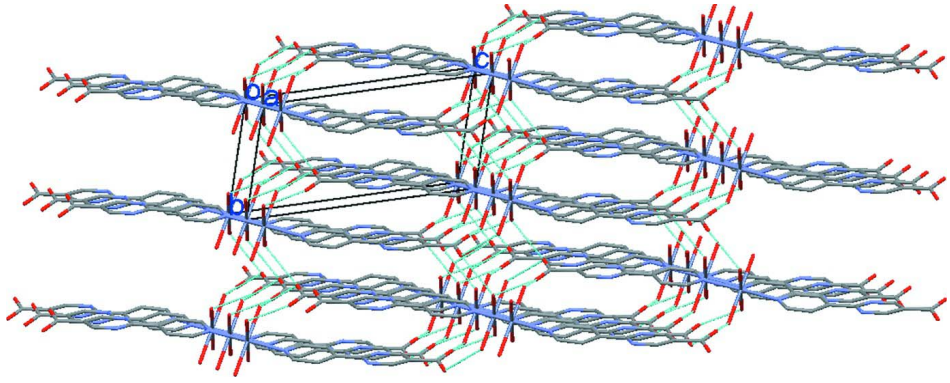



**Figure 2**

Part of the crystal structure showing the three-dimensional hydrogen-bonded network.

### Tetraaquabis[2-(pyridin-4-yl-*κN*)pyrimidine-5-carboxylato]zinc

*Crystal data*

$[Zn(C_{10}H_6N_3O_2)_2(H_2O)_4]$
$M_r$ = 537.79
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 6.2764 (7) Å
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$c$ = 12.7810 (17) Å
$\alpha$ = 99.676 (7)°
$\beta$ = 92.638 (7)°
$\gamma$ = 112.639 (5)°
$V$ = 501.36 (10) Å$^3$
$Z$ = 1
$F(000)$ = 276
$D_x$ = 1.781 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 246 reflections
$\theta$ = 2.6–27.6°
$\mu$ = 1.29 mm$^{-1}$
$T$ = 150 K
Block, colourless
0.26 × 0.20 × 0.04 mm

*Data collection*

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
fine–focus sealed tube scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.730, $T_{max}$ = 0.950
8143 measured reflections
2184 independent reflections
2030 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032
$\theta_{max}$ = 27.4°, $\theta_{min}$ = 3.3°
$h$ = −8→8
$k$ = −8→8
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.089$
$S = 1.14$
2184 reflections
176 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.1478P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.05$ e Å$^{-3}$
$\Delta\rho_{min} = -0.61$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.
**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn | 0.0000 | 0.0000 | 0.0000 | 0.01467 (13) |
| O1 | 0.1899 (3) | −0.1897 (2) | −0.03156 (12) | 0.0170 (3) |
| H1A | 0.129 (5) | −0.303 (3) | −0.0767 (17) | 0.028 (7)* |
| H1B | 0.238 (6) | −0.227 (6) | 0.0190 (19) | 0.051 (10)* |
| O2 | 0.2499 (3) | 0.2665 (3) | −0.05357 (13) | 0.0196 (3) |
| H2A | 0.184 (5) | 0.334 (5) | −0.080 (2) | 0.044 (9)* |
| H2B | 0.365 (4) | 0.265 (5) | −0.082 (2) | 0.046 (10)* |
| N3 | 0.1681 (3) | 0.1214 (3) | 0.16096 (14) | 0.0152 (4) |
| C4 | 0.0418 (4) | 0.1047 (3) | 0.24398 (17) | 0.0165 (4) |
| H4 | −0.1216 | 0.0610 | 0.2296 | 0.020* |
| C5 | 0.1386 (4) | 0.1481 (3) | 0.34911 (16) | 0.0159 (4) |
| H5 | 0.0430 | 0.1334 | 0.4053 | 0.019* |
| C6 | 0.3782 (4) | 0.2137 (3) | 0.37137 (16) | 0.0138 (4) |
| C7 | 0.5107 (4) | 0.2394 (3) | 0.28616 (17) | 0.0167 (4) |
| H7 | 0.6751 | 0.2890 | 0.2985 | 0.020* |
| C8 | 0.3995 (4) | 0.1916 (3) | 0.18334 (17) | 0.0173 (4) |
| H8 | 0.4914 | 0.2094 | 0.1259 | 0.021* |
| C9 | 0.4895 (4) | 0.2521 (3) | 0.48227 (16) | 0.0148 (4) |
| N10 | 0.3511 (3) | 0.2432 (3) | 0.56043 (14) | 0.0167 (4) |
| C11 | 0.4536 (4) | 0.2753 (3) | 0.65945 (17) | 0.0169 (4) |
| H11 | 0.3620 | 0.2685 | 0.7169 | 0.020* |
| C12 | 0.6871 (4) | 0.3180 (3) | 0.68231 (16) | 0.0146 (4) |
| C13 | 0.8139 (4) | 0.3264 (4) | 0.59538 (17) | 0.0179 (4) |
| H13 | 0.9751 | 0.3571 | 0.6078 | 0.022* |

| | | | | |
|---|---|---|---|---|
| N14 | 0.7165 (3) | 0.2928 (3) | 0.49487 (14) | 0.0179 (4) |
| C15 | 0.7950 (4) | 0.3495 (3) | 0.79525 (16) | 0.0166 (4) |
| O16 | 1.0133 (3) | 0.4300 (3) | 0.81382 (12) | 0.0203 (3) |
| O17 | 0.6557 (3) | 0.2901 (3) | 0.86250 (12) | 0.0214 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn | 0.01318 (19) | 0.0201 (2) | 0.01366 (19) | 0.00978 (14) | 0.00064 (12) | 0.00383 (13) |
| O1 | 0.0168 (7) | 0.0215 (8) | 0.0163 (8) | 0.0118 (7) | −0.0000 (6) | 0.0033 (6) |
| O2 | 0.0167 (8) | 0.0232 (9) | 0.0225 (8) | 0.0101 (7) | 0.0040 (6) | 0.0086 (6) |
| N3 | 0.0151 (8) | 0.0197 (9) | 0.0140 (8) | 0.0103 (7) | 0.0014 (7) | 0.0033 (7) |
| C4 | 0.0140 (10) | 0.0187 (11) | 0.0192 (10) | 0.0090 (8) | 0.0020 (8) | 0.0038 (8) |
| C5 | 0.0160 (10) | 0.0186 (11) | 0.0160 (10) | 0.0091 (9) | 0.0040 (8) | 0.0048 (8) |
| C6 | 0.0168 (10) | 0.0114 (10) | 0.0157 (10) | 0.0080 (8) | 0.0011 (8) | 0.0036 (7) |
| C7 | 0.0132 (10) | 0.0192 (11) | 0.0198 (11) | 0.0088 (9) | 0.0016 (8) | 0.0036 (8) |
| C8 | 0.0161 (10) | 0.0213 (11) | 0.0163 (10) | 0.0092 (9) | 0.0035 (8) | 0.0038 (8) |
| C9 | 0.0162 (10) | 0.0140 (10) | 0.0166 (10) | 0.0079 (8) | 0.0014 (8) | 0.0044 (8) |
| N10 | 0.0160 (9) | 0.0193 (9) | 0.0170 (9) | 0.0089 (7) | 0.0017 (7) | 0.0051 (7) |
| C11 | 0.0185 (10) | 0.0178 (11) | 0.0161 (10) | 0.0084 (9) | 0.0022 (8) | 0.0051 (8) |
| C12 | 0.0161 (10) | 0.0130 (10) | 0.0174 (10) | 0.0082 (8) | 0.0004 (8) | 0.0046 (8) |
| C13 | 0.0158 (10) | 0.0213 (11) | 0.0190 (11) | 0.0100 (9) | 0.0006 (8) | 0.0045 (8) |
| N14 | 0.0159 (9) | 0.0225 (10) | 0.0170 (9) | 0.0094 (8) | 0.0008 (7) | 0.0045 (7) |
| C15 | 0.0201 (10) | 0.0160 (11) | 0.0177 (10) | 0.0118 (9) | 0.0008 (8) | 0.0030 (8) |
| O16 | 0.0170 (7) | 0.0255 (8) | 0.0198 (8) | 0.0100 (7) | −0.0008 (6) | 0.0053 (6) |
| O17 | 0.0199 (8) | 0.0330 (9) | 0.0179 (8) | 0.0156 (7) | 0.0040 (6) | 0.0096 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn—O1 | 2.0923 (15) | C6—C7 | 1.394 (3) |
| Zn—O1$^{i}$ | 2.0923 (15) | C6—C9 | 1.486 (3) |
| Zn—N3$^{i}$ | 2.1419 (17) | C7—C8 | 1.384 (3) |
| Zn—N3 | 2.1420 (17) | C7—H7 | 0.9500 |
| Zn—O2$^{i}$ | 2.1512 (15) | C8—H8 | 0.9500 |
| Zn—O2 | 2.1512 (15) | C9—N14 | 1.338 (3) |
| O1—H1A | 0.830 (10) | C9—N10 | 1.348 (3) |
| O1—H1B | 0.822 (10) | N10—C11 | 1.336 (3) |
| O2—H2A | 0.833 (10) | C11—C12 | 1.385 (3) |
| O2—H2B | 0.827 (10) | C11—H11 | 0.9500 |
| N3—C8 | 1.341 (3) | C12—C13 | 1.392 (3) |
| N3—C4 | 1.347 (3) | C12—C15 | 1.510 (3) |
| C4—C5 | 1.383 (3) | C13—N14 | 1.340 (3) |
| C4—H4 | 0.9500 | C13—H13 | 0.9500 |
| C5—C6 | 1.393 (3) | C15—O16 | 1.257 (3) |
| C5—H5 | 0.9500 | C15—O17 | 1.258 (3) |
| | | | |
| O1—Zn—O1$^{i}$ | 180.0 | C4—C5—H5 | 120.5 |
| O1—Zn—N3$^{i}$ | 88.59 (6) | C6—C5—H5 | 120.5 |

| | | | |
|---|---|---|---|
| O1$^{i}$—Zn—N3$^{i}$ | 91.41 (6) | C5—C6—C7 | 118.01 (19) |
| O1—Zn—N3 | 91.41 (6) | C5—C6—C9 | 121.15 (18) |
| O1$^{i}$—Zn—N3 | 88.59 (6) | C7—C6—C9 | 120.83 (19) |
| N3$^{i}$—Zn—N3 | 180.0 | C8—C7—C6 | 119.2 (2) |
| O1—Zn—O2$^{i}$ | 86.31 (6) | C8—C7—H7 | 120.4 |
| O1$^{i}$—Zn—O2$^{i}$ | 93.69 (6) | C6—C7—H7 | 120.4 |
| N3$^{i}$—Zn—O2$^{i}$ | 91.45 (6) | N3—C8—C7 | 123.13 (19) |
| N3—Zn—O2$^{i}$ | 88.55 (6) | N3—C8—H8 | 118.4 |
| O1—Zn—O2 | 93.69 (6) | C7—C8—H8 | 118.4 |
| O1$^{i}$—Zn—O2 | 86.31 (6) | N14—C9—N10 | 126.45 (19) |
| N3$^{i}$—Zn—O2 | 88.55 (6) | N14—C9—C6 | 117.08 (18) |
| N3—Zn—O2 | 91.45 (6) | N10—C9—C6 | 116.48 (19) |
| O2$^{i}$—Zn—O2 | 180.0 | C11—N10—C9 | 115.59 (19) |
| Zn—O1—H1A | 118 (2) | N10—C11—C12 | 123.16 (19) |
| Zn—O1—H1B | 118 (2) | N10—C11—H11 | 118.4 |
| H1A—O1—H1B | 103 (3) | C12—C11—H11 | 118.4 |
| Zn—O2—H2A | 110 (2) | C11—C12—C13 | 116.22 (19) |
| Zn—O2—H2B | 125 (2) | C11—C12—C15 | 121.41 (18) |
| H2A—O2—H2B | 114 (3) | C13—C12—C15 | 122.36 (19) |
| C8—N3—C4 | 117.43 (18) | N14—C13—C12 | 122.3 (2) |
| C8—N3—Zn | 121.52 (14) | N14—C13—H13 | 118.8 |
| C4—N3—Zn | 120.54 (14) | C12—C13—H13 | 118.8 |
| N3—C4—C5 | 123.19 (19) | C9—N14—C13 | 116.28 (18) |
| N3—C4—H4 | 118.4 | O16—C15—O17 | 125.88 (19) |
| C5—C4—H4 | 118.4 | O16—C15—C12 | 117.94 (18) |
| C4—C5—C6 | 118.99 (19) | O17—C15—C12 | 116.18 (19) |

Symmetry code: (i) $-x, -y, -z$.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···O16$^{ii}$ | 0.83 (2) | 1.98 (2) | 2.805 (3) | 175 (3) |
| O1—H1*B*···O17$^{iii}$ | 0.82 (3) | 1.81 (3) | 2.631 (3) | 175 (4) |
| O2—H2*A*···O16$^{iv}$ | 0.83 (4) | 2.04 (4) | 2.840 (3) | 162 (4) |
| O2—H2*B*···O17$^{v}$ | 0.83 (3) | 1.94 (3) | 2.767 (3) | 173 (3) |

Symmetry codes: (ii) $x-1, y-1, z-1$; (iii) $-x+1, -y, -z+1$; (iv) $x-1, y, z-1$; (v) $x, y, z-1$.