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# Bis[3-(2-carboxyethenyl)pyridinium-1-acetato]dichloridozinc(II)

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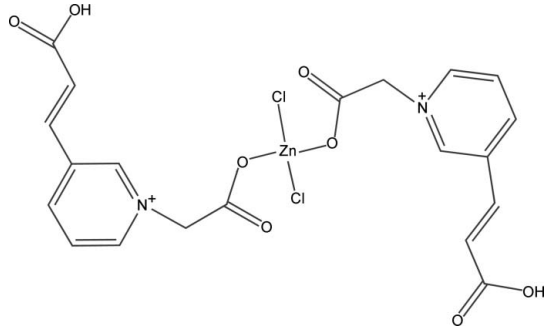
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.028; $wR$ factor = 0.077; data-to-parameter ratio = 15.9.

In the title complex, $[ZnCl_2(C_{10}H_9NO_4)_2]$, the $Zn^{II}$ ion lies on a twofold rotation axis and is four-coordinated by two carboxylate O atoms from two 3-(2-carboxyethenyl)-pyridinium-1-acetate ligands in a monodentate mode and two Cl atoms in a distorted tetrahedral geometry. In the crystal structure, intermolecular O—H···O hydrogen bonds link the molecules into a double-chain structure extending parallel to [101].

## Related literature

For general background to hydrogen bonds, see: Beatty (2003); Liu *et al.* (2008); Steiner (2002). For related structures, see: Mao *et al.* (1999); Sun *et al.* (2009); Wu *et al.* (2006); Zhang *et al.* (2002).




## Experimental

### Crystal data

$[ZnCl_2(C_{10}H_9NO_4)_2]$
$M_r$ = 550.63
Monoclinic, $C2/c$
$a$ = 16.6247 (6) Å
$b$ = 7.1973 (3) Å
$c$ = 18.8873 (7) Å
$\beta$ = 108.685 (1)°
$V$ = 2140.81 (14) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.45 mm$^{-1}$
$T$ = 296 K
0.12 × 0.12 × 0.08 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.845, $T_{max}$ = 0.893
27422 measured reflections
2450 independent reflections
2309 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.077
$S$ = 1.06
2450 reflections
154 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Zn1—O1 | 1.9983 (13) | Zn1—Cl1 | 2.2566 (4) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H4$B$···O2$^{i}$ | 0.97 (4) | 1.60 (4) | 2.560 (2) | 169 (3) |

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2249).

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# supporting information

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## Bis[3-(2-carboxyethenyl)pyridinium-1-acetato]dichloridozinc(II)

**Xue-Hui Jing, Wei-Wei Sun and En-Qing Gao**

### S1. Comment

As we know, hydrogen bond is the most important of all directional intermolecular interactions. It is operative in determining molecular conformation, molecular aggregation, and the function of a vast number of chemical systems ranging from inorganic to biological (Beatty, 2003; Liu *et al.*, 2008; Steiner, 2002). In this paper, we report the coordination and hydrogen-bond structure of the title complex derived from a zwitterionic dicarboxylic ligand, 1-carboxymethylpyridinium-3-acrylic acid. Zwitterionic dicarboxylic acids as ligands have received less attention in coordination chemistry than the common dicarboxylic acids, although an increasing number of coordination compounds with such ligands have been reported in recent years (Mao *et al.*, 1999; Wu *et al.*, 2006; Zhang *et al.*, 2002).

The molecular structure is shown in Fig. 1. The $Zn^{II}$ ion, lying on a twofold rotation axis, is coordinated by two Cl atoms and the two zwitterionic ligands through carboxylate O atoms, with a distorted tetrahedral coordination geometry. The Zn—Cl and Zn—O distances lie in the usual range for a tetrahedral $Zn^{II}$ center (Table 1). The zwitterionic ligand is neutral with an anionic *N*-acetate group in a monodentate coordination mode and a cationic pyridinium ring. The acrylic group remains protonated and uncoordinated. This is in contrast with the only previous coordination compound with this ligand, $[Ni_3(C_{10}H_8NO_4)_2(N_3)_4(H_2O)_2].5H_2O$ (Sun *et al.*, 2009), in which both carboxylate groups are deprotonated and coordinated in a bidentate bridging mode, giving an extended coordination network. As shown in Fig. 2, the mononuclear complex molecules in the title compound are associated into a one-dimensional chain along the [101] direction through intermolecular O—H···O hydrogen bonds (Table 2). The hydrogen bond involves the acrylic hydroxyl group (O4—H4B) from one molecule and the uncoordinated acetate O atom (O2) from another molecule.

### S2. Experimental

The zwitterionic ligand was synthesized from ethyl pyridine-3-acrylate and ethyl bromoacetate according to the procedure for similar compounds (Mao *et al.*, 1999). A mixture of the ligand (0.021 g, 0.10 mmol), $ZnCl_2$ (0.014 g, 0.10 mmol), $NaN_3$ (0.026 g, 0.40 mmol), ethanol (1.0 ml) and $H_2O$ (2.0 ml) was sealed in a Teflon-lined autoclave and heated at 343 K for 3 d, then cooled to room temperature at a rate of 5 K $h^{-1}$, giving a pale yellow solution. Slow evaporation of the solution at room temperature for several days afforded colorless block crystals of the title compound (yield 46%). Analysis, calculated for $C_{20}H_{18}Cl_2N_2O_8Zn$: C 27.22, H 3.43, N 22.22%; found: C 27.11, H 3.82, N 22.50%. FT—IR (KBr, $cm^{-1}$): 3530*m*, 3348br, 2084vs, 2059vs, 1630vs, 1582 s, 1505*m*, 1461w, 1388vs, 1307*m*, 985*m*.

### S3. Refinement

H atoms attached to C atoms were placed at calculated positions and refined as riding atoms, with C—H = 0.93 (CH) and 0.97 ($CH_2$) Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The carboxylic H atom (H4B) was located from a difference Fourier map and refined isotropically.

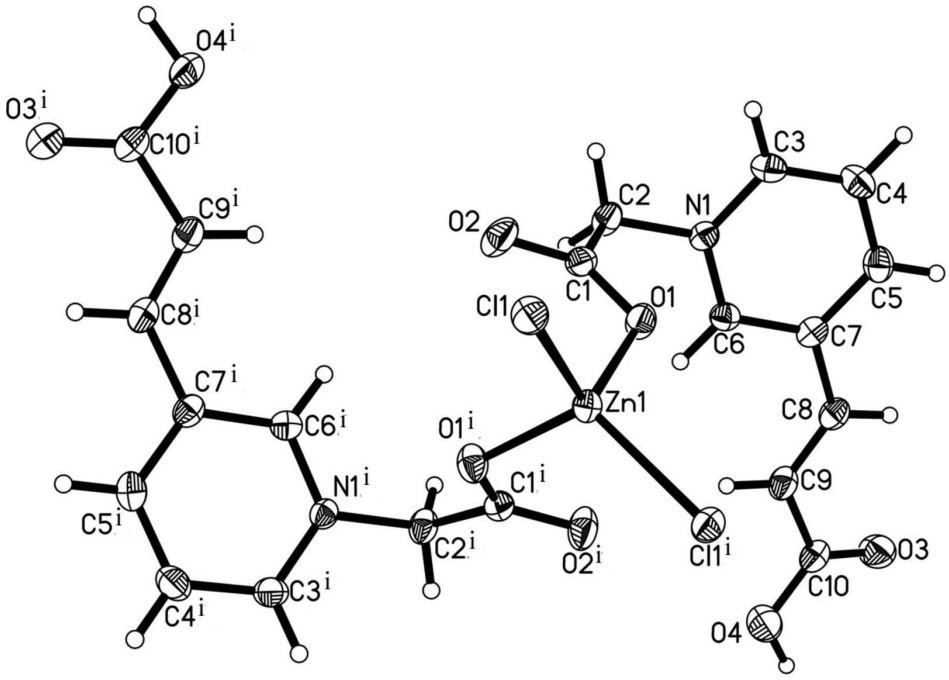


**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) -*x*, *y*, -*z* + 1/2.]

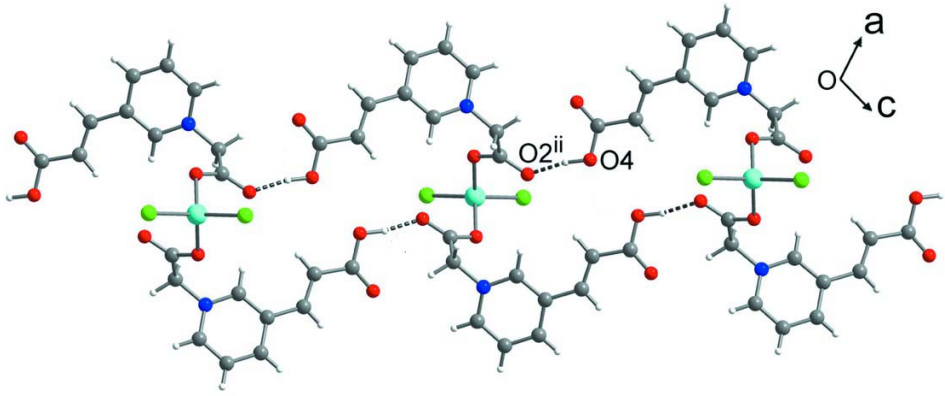


**Figure 2**

One-dimensional chain structure connected through intermolecular O—H···O hydrogen bonds (dashed lines). [Symmetry code: (ii) *x* - 1/2, -*y* + 3/2, *z* - 1/2.]

**Bis[3-(2-carboxyethenyl)pyridinium-1-acetato]dichloridozinc(II)**

*Crystal data*

$[ZnCl_2(C_{10}H_9NO_4)_2]$
$M_r$ = 550.63
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 16.6247 (6) Å
*b* = 7.1973 (3) Å
*c* = 18.8873 (7) Å
*β* = 108.685 (1)°
*V* = 2140.81 (14) Å$^3$
*Z* = 4
*F*(000) = 1120
$D_x$ = 1.708 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9202 reflections

$\theta$ = 2.3–26.0°
$\mu$ = 1.45 mm$^{-1}$
$T$ = 296 K

Block, colorless
0.12 × 0.12 × 0.08 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.845, $T_{max}$ = 0.893

27422 measured reflections
2450 independent reflections
2309 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 2.3°
$h$ = −21→20
$k$ = −9→8
$l$ = −24→23

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.077
$S$ = 1.06
2450 reflections
154 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 2.553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.0000 | 0.21438 (4) | 0.2500 | 0.02879 (10) |
| C1 | 0.10900 (11) | 0.5110 (3) | 0.25776 (10) | 0.0324 (4) |
| C2 | 0.14353 (12) | 0.6811 (3) | 0.22916 (10) | 0.0360 (4) |
| H2A | 0.1139 | 0.7904 | 0.2379 | 0.043* |
| H2B | 0.2032 | 0.6953 | 0.2576 | 0.043* |
| C3 | 0.20158 (11) | 0.6192 (3) | 0.12864 (11) | 0.0370 (4) |
| H3A | 0.2525 | 0.5883 | 0.1649 | 0.044* |
| C4 | 0.19519 (13) | 0.6114 (3) | 0.05458 (12) | 0.0432 (4) |
| H4A | 0.2413 | 0.5734 | 0.0405 | 0.052* |
| C5 | 0.12009 (13) | 0.6600 (3) | 0.00115 (11) | 0.0395 (4) |
| H5A | 0.1155 | 0.6563 | −0.0492 | 0.047* |
| C6 | 0.06027 (11) | 0.7173 (2) | 0.09822 (10) | 0.0318 (4) |
| H6A | 0.0146 | 0.7511 | 0.1137 | 0.038* |
| C7 | 0.05107 (12) | 0.7146 (2) | 0.02242 (10) | 0.0323 (4) |
| C8 | −0.02829 (13) | 0.7712 (3) | −0.03508 (10) | 0.0371 (4) |
| H8A | −0.0273 | 0.7784 | −0.0840 | 0.044* |
| C9 | −0.10021 (13) | 0.8126 (3) | −0.02414 (11) | 0.0401 (4) |
| H9A | −0.1045 | 0.8061 | 0.0237 | 0.048* |
| C10 | −0.17521 (12) | 0.8700 (3) | −0.08844 (10) | 0.0380 (4) |
| N1 | 0.13464 (9) | 0.6713 (2) | 0.14914 (8) | 0.0290 (3) |
| O1 | 0.06462 (9) | 0.39902 (19) | 0.21043 (7) | 0.0371 (3) |

| | | | | |
|---|---|---|---|---|
| O2 | 0.12548 (10) | 0.5002 (2) | 0.32652 (7) | 0.0509 (4) |
| O3 | −0.17174 (10) | 0.9091 (3) | −0.14938 (9) | 0.0574 (4) |
| O4 | −0.24415 (10) | 0.8769 (3) | −0.07066 (9) | 0.0592 (5) |
| H4B | −0.290 (2) | 0.919 (5) | −0.1137 (19) | 0.091 (11)* |
| Cl1 | 0.07978 (3) | 0.02552 (6) | 0.34083 (2) | 0.03619 (12) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.03138 (16) | 0.03059 (16) | 0.02483 (15) | 0.000 | 0.00960 (11) | 0.000 |
| C1 | 0.0285 (8) | 0.0387 (9) | 0.0288 (8) | −0.0027 (7) | 0.0075 (6) | 0.0018 (7) |
| C2 | 0.0417 (9) | 0.0378 (9) | 0.0263 (8) | −0.0084 (8) | 0.0076 (7) | −0.0012 (7) |
| C3 | 0.0288 (8) | 0.0389 (9) | 0.0422 (9) | 0.0025 (7) | 0.0099 (7) | 0.0063 (8) |
| C4 | 0.0391 (10) | 0.0484 (11) | 0.0485 (11) | 0.0031 (8) | 0.0231 (8) | 0.0044 (9) |
| C5 | 0.0492 (11) | 0.0384 (9) | 0.0343 (9) | −0.0016 (8) | 0.0183 (8) | 0.0024 (8) |
| C6 | 0.0289 (8) | 0.0313 (8) | 0.0345 (9) | 0.0009 (6) | 0.0090 (7) | 0.0001 (7) |
| C7 | 0.0356 (9) | 0.0271 (8) | 0.0308 (8) | −0.0020 (6) | 0.0059 (7) | 0.0030 (6) |
| C8 | 0.0411 (10) | 0.0382 (9) | 0.0283 (8) | −0.0014 (8) | 0.0060 (7) | 0.0027 (7) |
| C9 | 0.0447 (10) | 0.0434 (10) | 0.0292 (9) | 0.0027 (8) | 0.0077 (8) | −0.0009 (8) |
| C10 | 0.0422 (10) | 0.0332 (9) | 0.0329 (9) | 0.0023 (7) | 0.0040 (7) | −0.0018 (7) |
| N1 | 0.0304 (7) | 0.0282 (6) | 0.0268 (7) | −0.0021 (5) | 0.0069 (5) | 0.0026 (5) |
| O1 | 0.0436 (7) | 0.0394 (7) | 0.0300 (6) | −0.0126 (6) | 0.0142 (5) | −0.0051 (5) |
| O2 | 0.0545 (9) | 0.0663 (10) | 0.0266 (6) | −0.0263 (8) | 0.0056 (6) | 0.0030 (6) |
| O3 | 0.0447 (8) | 0.0801 (12) | 0.0441 (8) | 0.0034 (8) | 0.0094 (7) | 0.0092 (8) |
| O4 | 0.0445 (8) | 0.0929 (14) | 0.0360 (8) | 0.0210 (9) | 0.0070 (6) | 0.0123 (8) |
| Cl1 | 0.0369 (2) | 0.0387 (2) | 0.0321 (2) | 0.00658 (17) | 0.00991 (17) | 0.00704 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O1 | 1.9983 (13) | C5—C7 | 1.388 (3) |
| Zn1—Cl1 | 2.2566 (4) | C5—H5A | 0.9300 |
| C1—O2 | 1.241 (2) | C6—N1 | 1.342 (2) |
| C1—O1 | 1.253 (2) | C6—C7 | 1.390 (3) |
| C1—C2 | 1.522 (3) | C6—H6A | 0.9300 |
| C2—N1 | 1.472 (2) | C7—C8 | 1.473 (2) |
| C2—H2A | 0.9700 | C8—C9 | 1.311 (3) |
| C2—H2B | 0.9700 | C8—H8A | 0.9300 |
| C3—N1 | 1.343 (2) | C9—C10 | 1.493 (3) |
| C3—C4 | 1.370 (3) | C9—H9A | 0.9300 |
| C3—H3A | 0.9300 | C10—O3 | 1.204 (3) |
| C4—C5 | 1.376 (3) | C10—O4 | 1.294 (3) |
| C4—H4A | 0.9300 | O4—H4B | 0.97 (4) |
| | | | |
| O1$^{i}$—Zn1—O1 | 96.63 (8) | C4—C5—H5A | 120.0 |
| O1$^{i}$—Zn1—Cl1$^{i}$ | 115.43 (4) | C7—C5—H5A | 120.0 |
| O1—Zn1—Cl1$^{i}$ | 111.82 (4) | N1—C6—C7 | 120.43 (17) |
| O1$^{i}$—Zn1—Cl1 | 111.82 (4) | N1—C6—H6A | 119.8 |
| O1—Zn1—Cl1 | 115.43 (4) | C7—C6—H6A | 119.8 |

| | | | |
|---|---|---|---|
| Cl1$^{i}$—Zn1—Cl1 | 105.92 (3) | C5—C7—C6 | 118.26 (17) |
| O2—C1—O1 | 126.04 (17) | C5—C7—C8 | 119.55 (17) |
| O2—C1—C2 | 116.10 (16) | C6—C7—C8 | 122.18 (17) |
| O1—C1—C2 | 117.82 (15) | C9—C8—C7 | 126.40 (18) |
| N1—C2—C1 | 113.62 (15) | C9—C8—H8A | 116.8 |
| N1—C2—H2A | 108.8 | C7—C8—H8A | 116.8 |
| C1—C2—H2A | 108.8 | C8—C9—C10 | 120.04 (18) |
| N1—C2—H2B | 108.8 | C8—C9—H9A | 120.0 |
| C1—C2—H2B | 108.8 | C10—C9—H9A | 120.0 |
| H2A—C2—H2B | 107.7 | O3—C10—O4 | 123.81 (18) |
| N1—C3—C4 | 120.36 (17) | O3—C10—C9 | 123.98 (19) |
| N1—C3—H3A | 119.8 | O4—C10—C9 | 112.19 (17) |
| C4—C3—H3A | 119.8 | C6—N1—C3 | 121.35 (16) |
| C3—C4—C5 | 119.60 (18) | C6—N1—C2 | 119.36 (15) |
| C3—C4—H4A | 120.2 | C3—N1—C2 | 119.28 (15) |
| C5—C4—H4A | 120.2 | C1—O1—Zn1 | 115.16 (11) |
| C4—C5—C7 | 119.98 (18) | C10—O4—H4B | 109 (2) |
| | | | |
| O2—C1—C2—N1 | 170.27 (17) | C8—C9—C10—O4 | 169.7 (2) |
| O1—C1—C2—N1 | −12.1 (2) | C7—C6—N1—C3 | −1.0 (3) |
| N1—C3—C4—C5 | 1.0 (3) | C7—C6—N1—C2 | 178.06 (16) |
| C3—C4—C5—C7 | −0.7 (3) | C4—C3—N1—C6 | −0.2 (3) |
| C4—C5—C7—C6 | −0.4 (3) | C4—C3—N1—C2 | −179.18 (18) |
| C4—C5—C7—C8 | 178.33 (19) | C1—C2—N1—C6 | 82.1 (2) |
| N1—C6—C7—C5 | 1.2 (3) | C1—C2—N1—C3 | −98.9 (2) |
| N1—C6—C7—C8 | −177.45 (16) | O2—C1—O1—Zn1 | 11.0 (3) |
| C5—C7—C8—C9 | 174.5 (2) | C2—C1—O1—Zn1 | −166.35 (13) |
| C6—C7—C8—C9 | −6.8 (3) | O1$^{i}$—Zn1—O1—C1 | 57.77 (12) |
| C7—C8—C9—C10 | 179.31 (18) | Cl1$^{i}$—Zn1—O1—C1 | 178.59 (12) |
| C8—C9—C10—O3 | −11.8 (3) | Cl1—Zn1—O1—C1 | −60.24 (14) |

Symmetry code: (i) $-x, y, -z+1/2$.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O4—H4*B*···O2$^{ii}$ | 0.97 (4) | 1.60 (4) | 2.560 (2) | 169 (3) |

Symmetry code: (ii) $x-1/2, -y+3/2, z-1/2$.