# *catena*-Poly[[[triaquacopper(II)]-μ-pyridine-2,3-dicarboxylato-$\kappa^3N,O^2:O^3$] monohydrate]

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In the title compound, $\{[Cu(C_7H_3NO_4)(H_2O)_3]\cdot H_2O\}_n$, the Cu$^{II}$ ion is bonded to three water molecules, one $N,O$-bidentate pyridine-2,3-dicarboxylate dianion and one O-bonded symmetry-generated dianion, resulting in a distorted CuNO$_5$ octahedral geometry. The bridging ligand results in an infinite chain. A network of O—H···O hydrogen bonds helps to establish the crystal structure.

## Related literature

For background, see: Serre *et al.* (2005).
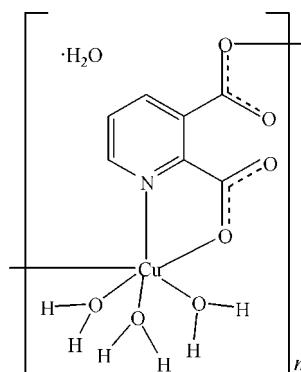


## Experimental

### Crystal data
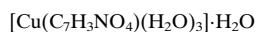
[Cu(C$_7$H$_3$NO$_4$)(H$_2$O)$_3$]·H$_2$O
$M_r$ = 300.71
Monoclinic, $Cc$
$a$ = 8.513 (3) Å
$b$ = 17.983 (3) Å
$c$ = 7.493 (3) Å
$\beta$ = 114.486 (10)°
$V$ = 1043.9 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.13 mm$^{-1}$
$T$ = 296 (2) K
0.40 × 0.28 × 0.22 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min}$ = 0.484, $T_{max}$ = 0.652
2686 measured reflections
1322 independent reflections
1310 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.028

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.089
$S$ = 1.00
1322 reflections
180 parameters
14 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.60 e Å$^{-3}$
Absolute structure: Flack (1983), 290 Friedel pairs
Flack parameter: 0.05 (3)

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

| Cu1—O7 | 2.061 (3) | Cu1—O1 | 2.119 (4) |
|---|---|---|---|
| Cu1—O6 | 2.068 (3) | Cu1—O5 | 2.178 (5) |
| Cu1—O3 | 2.071 (3) | Cu1—N1 | 2.187 (4) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O5—H3W···O4$^i$ | 0.82 (9) | 1.93 (8) | 2.735 (6) | 167 (8) |
| O5—H4W···O6$^{ii}$ | 0.82 (2) | 2.35 (8) | 2.966 (5) | 132 (10) |
| O6—H5W···O5$^{iii}$ | 0.82 (7) | 2.29 (7) | 2.966 (5) | 140 (9) |
| O7—H7W···O2$^{iv}$ | 0.83 (8) | 1.90 (9) | 2.720 (5) | 169 (8) |
| O7—H8W···O2$^{ii}$ | 0.83 (8) | 2.03 (4) | 2.825 (5) | 162 (11) |

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $x, y, z+1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

## References

Bruker (2004). *APEX2, SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Serre, C., Marrot, J. & Ferey, G. (2005). *Inorg. Chem.* **44**, 654–658.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

# *catena*-Poly[[[triaquacopper(II)]-*µ*-pyridine-2,3-dicarboxylato-*κ³N,O²:O³*] monohydrate]

**Lujiang Hao, Chunhua Mu and Binbin Kong**

### S1. Comment

In recent years, carboxylic acids have been widely used as polydentate ligands, which can coordinate to transition or rare earth ions yielding complexes with interesting properties in biological systems (e.g. Serre *et al.*, 2005). Herein, we report the synthesis and structure of the title compound, (I).

As shown in Fig. 1, the $Cu^{II}$ ion in (I) is hexacoordinated with five oxygen atoms and one nitrogen atom, exhibiting a slightly distorted octahedral geometry (Table 1). The pyridine-2,3-dicarboxyalto ligand affords the pyridine N and one carboxylato oxygen atom in chelating coordination mode and a symmetry-generated ligand bonds from its carboxylate O-atom. The bridging ligand links neighboring copper(II) ions into a chain (Fig. 2). Extensive hydrogen bonding (Table 2) *via* hydrogen bonds between carboxylate oxygen atoms of pyridine-2,3-dicarboxyalte and the uncoordinated water molecules or coordinated aqua ligands, giving rise to a three-dimensional network.

### S2. Experimental

A mixture of copper(II) chloride (0.5 mmol), pyridine-2,3-dicarboxylic acid (1 mmol), sodium hydroxide (1 mmol), $H_2O$ (8 ml), and ethanol (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was kept at 423 K for three days. Blue blocks of (I) were obtained after cooling to room temperature with a yield of 16%. Anal calc. for $C_7H_{11}CuNO_8$: C 27.93, H 2.99, N 4.66%; found: C 27.89, H 2.92, N 4.63%.

### S3. Refinement

The O-bound H atoms were located in a difference map and their positions were freely refined with a fixed $U_{iso}$ value. This has led to some extremely short intermolecular H···H contacts and the location of the water H atoms should be regarded as less certain. All the C-bound H atoms were placed in calculated positions with C—H = 0.93Å and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.
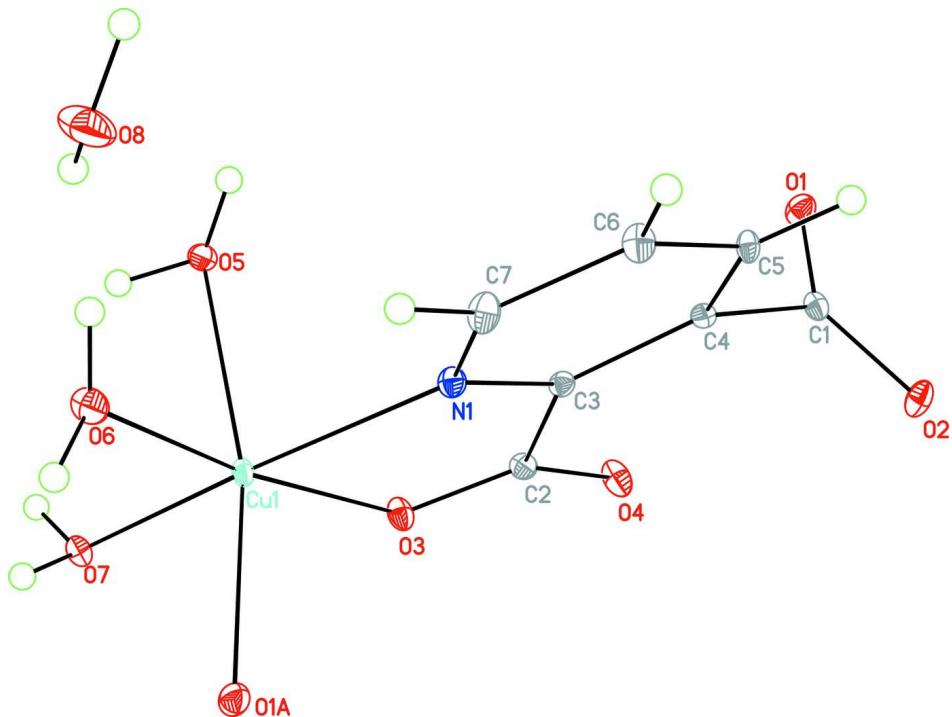
**Figure 1**

The molecular structure of (I), drawn with 30% probability displacement ellipsoids for the non-hydrogen atoms. Atoms labeled with i are at the symmetry position (*x* - 1/2,-*y* + 1/2,*z* - 1/2).
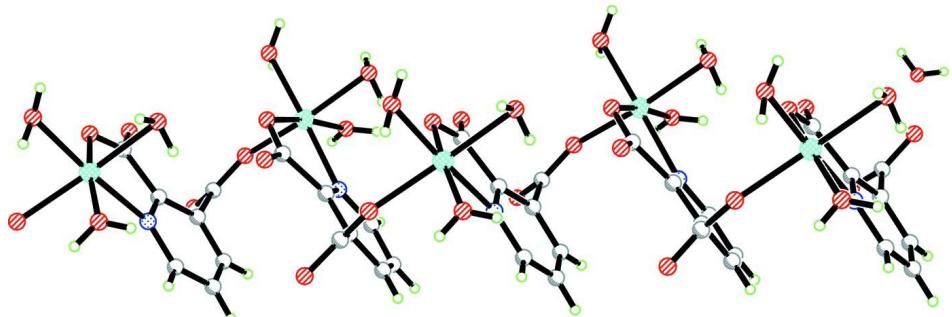


**Figure 2**

Part of a polymeric chain in (I).

*catena*-Poly[[[triaquacopper(II)]-*µ*-pyridine-2,3-dicarboxylato- *κ*³N,O²:O³] monohydrate]

*Crystal data*

| | |
|---|---|
| [Cu(C₇H₃NO₄)(H₂O)₃]·H₂O | $F(000) = 612$ |
| $M_r = 300.71$ | $D_x = 1.913$ Mg m⁻³ |
| Monoclinic, *Cc* | Mo *Kα* radiation, $\lambda = 0.71073$ Å |
| Hall symbol: C -2yc | Cell parameters from 2692 reflections |
| $a = 8.513$ (3) Å | $\theta = 2.9–28.1°$ |
| $b = 17.983$ (3) Å | $\mu = 2.13$ mm⁻¹ |
| $c = 7.493$ (3) Å | $T = 296$ K |
| $\beta = 114.486$ (10)° | Block, blue |
| $V = 1043.9$ (6) Å³ | $0.40 \times 0.28 \times 0.22$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 2686 measured reflections |
| Radiation source: fine-focus sealed tube | 1322 independent reflections |
| Graphite monochromator | 1310 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.028$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | $\theta_{max} = 26.0°$, $\theta_{min} = 2.9°$ |
| | $h = -10 \rightarrow 10$ |
| | $k = -22 \rightarrow 22$ |
| $T_{min} = 0.484$, $T_{max} = 0.652$ | $l = -4 \rightarrow 9$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H atoms treated by a mixture of independent and constrained refinement |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | $w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.0702P]$ |
| $wR(F^2) = 0.089$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1322 reflections | $\Delta\rho_{max} = 0.61$ e Å$^{-3}$ |
| 180 parameters | $\Delta\rho_{min} = -0.60$ e Å$^{-3}$ |
| 14 restraints | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | |
| | Extinction coefficient: 0.018 (2) |
| Secondary atom site location: difference Fourier map | Absolute structure: Flack (1983), 290 Friedel pairs |
| Hydrogen site location: difmap and geom | Absolute structure parameter: 0.05 (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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.00453 (5) | 0.118674 (19) | 0.25189 (5) | 0.0226 (2) |
| C1 | −0.1893 (6) | 0.1125 (2) | −0.2173 (8) | 0.0257 (10) |
| C2 | 0.0162 (7) | 0.2776 (2) | 0.2417 (8) | 0.0261 (9) |
| C3 | 0.1909 (5) | 0.2542 (2) | 0.2398 (6) | 0.0220 (8) |
| C4 | 0.3188 (5) | 0.3044 (2) | 0.2468 (6) | 0.0224 (8) |
| C5 | 0.4612 (5) | 0.2816 (2) | 0.2256 (6) | 0.0222 (9) |
| H5 | 0.5443 | 0.3154 | 0.2266 | 0.027* |
| C6 | 0.4781 (6) | 0.2094 (3) | 0.2034 (7) | 0.0325 (10) |
| H6 | 0.5747 | 0.1922 | 0.1878 | 0.039* |
| C7 | 0.3554 (7) | 0.1592 (3) | 0.2028 (8) | 0.0350 (10) |
| H7 | 0.3719 | 0.1088 | 0.1890 | 0.042* |
| N1 | 0.2118 (5) | 0.18178 (19) | 0.2218 (6) | 0.0262 (7) |
| O1 | −0.1400 (5) | 0.0911 (2) | −0.0470 (5) | 0.0356 (8) |
| O2 | −0.2392 (5) | 0.07157 (19) | −0.3667 (5) | 0.0363 (7) |

| | | | |
|---|---|---|---|
| O3 | −0.0834 (4) | 0.22671 (17) | 0.2399 (6) | 0.0323 (7) |
| O4 | −0.0130 (6) | 0.34452 (16) | 0.2387 (9) | 0.0401 (8) |
| O5 | 0.1420 (5) | 0.12328 (17) | 0.5699 (7) | 0.0311 (9) |
| O6 | 0.1266 (5) | 0.01799 (18) | 0.2664 (7) | 0.0427 (9) |
| O7 | −0.2021 (4) | 0.07356 (18) | 0.2898 (5) | 0.0309 (7) |
| O8 | 0.4601 (7) | −0.0181 (3) | 0.4257 (10) | 0.0777 (18) |
| H1W | 0.553 (6) | −0.004 (6) | 0.515 (11) | 0.093* |
| H2W | 0.377 (7) | −0.006 (6) | 0.451 (14) | 0.093* |
| H4W | 0.105 (10) | 0.080 (2) | 0.551 (16) | 0.093* |
| H5W | 0.092 (12) | −0.008 (5) | 0.167 (10) | 0.093* |
| H6W | 0.229 (5) | 0.011 (5) | 0.340 (12) | 0.093* |
| H7W | −0.214 (15) | 0.067 (5) | 0.393 (9) | 0.093* |
| H8W | −0.195 (16) | 0.034 (3) | 0.238 (13) | 0.093* |
| H3W | 0.248 (3) | 0.126 (4) | 0.620 (19) | 0.093* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0221 (3) | 0.0153 (3) | 0.0307 (3) | −0.0014 (2) | 0.0111 (2) | 0.0008 (2) |
| C1 | 0.024 (2) | 0.021 (2) | 0.033 (3) | 0.0026 (14) | 0.013 (2) | 0.0011 (15) |
| C2 | 0.0229 (19) | 0.0210 (17) | 0.0315 (18) | 0.0045 (18) | 0.0084 (15) | −0.0004 (19) |
| C3 | 0.0223 (19) | 0.0198 (18) | 0.0229 (18) | 0.0031 (15) | 0.0083 (15) | 0.0014 (14) |
| C4 | 0.0208 (18) | 0.0218 (19) | 0.0220 (17) | 0.0000 (14) | 0.0064 (15) | 0.0016 (15) |
| C5 | 0.026 (2) | 0.0141 (17) | 0.032 (2) | 0.0009 (13) | 0.017 (2) | 0.0013 (15) |
| C6 | 0.034 (3) | 0.027 (2) | 0.042 (3) | 0.0042 (18) | 0.022 (2) | 0.0008 (16) |
| C7 | 0.045 (3) | 0.0219 (18) | 0.044 (2) | 0.0067 (19) | 0.025 (2) | 0.0011 (18) |
| N1 | 0.0284 (18) | 0.0215 (16) | 0.0293 (17) | 0.0018 (14) | 0.0125 (15) | −0.0001 (14) |
| O1 | 0.0475 (19) | 0.0275 (18) | 0.0292 (16) | −0.0008 (15) | 0.0133 (15) | 0.0000 (14) |
| O2 | 0.055 (2) | 0.0236 (14) | 0.0343 (16) | −0.0049 (14) | 0.0230 (16) | −0.0069 (13) |
| O3 | 0.0226 (17) | 0.0253 (16) | 0.0519 (19) | 0.0004 (12) | 0.0185 (14) | 0.0011 (14) |
| O4 | 0.0274 (17) | 0.0214 (15) | 0.073 (2) | 0.0041 (14) | 0.0220 (17) | −0.0029 (19) |
| O5 | 0.0266 (16) | 0.0281 (19) | 0.033 (2) | −0.0011 (11) | 0.0062 (16) | −0.0014 (12) |
| O6 | 0.0362 (17) | 0.0247 (16) | 0.056 (2) | 0.0078 (15) | 0.0077 (15) | −0.0088 (16) |
| O7 | 0.0313 (16) | 0.0262 (15) | 0.0355 (16) | −0.0074 (13) | 0.0142 (14) | −0.0040 (14) |
| O8 | 0.035 (2) | 0.054 (3) | 0.108 (4) | 0.0047 (18) | −0.006 (3) | −0.023 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—O7 | 2.061 (3) | C4—C1ⁱⁱ | 1.525 (5) |
| Cu1—O6 | 2.068 (3) | C5—C6 | 1.325 (6) |
| Cu1—O3 | 2.071 (3) | C5—H5 | 0.9300 |
| Cu1—O1 | 2.119 (4) | C6—C7 | 1.379 (7) |
| Cu1—O5 | 2.178 (5) | C6—H6 | 0.9300 |
| Cu1—N1 | 2.187 (4) | C7—N1 | 1.350 (6) |
| C1—O1 | 1.228 (7) | C7—H7 | 0.9300 |
| C1—O2 | 1.258 (6) | O5—H4W | 0.82 (2) |
| C1—C4ⁱ | 1.525 (5) | O5—H3W | 0.82 (9) |
| C2—O4 | 1.227 (5) | O6—H5W | 0.82 (7) |

| | | | |
|---|---|---|---|
| C2—O3 | 1.244 (6) | O6—H6W | 0.83 (7) |
| C2—C3 | 1.552 (6) | O7—H7W | 0.83 (8) |
| C3—N1 | 1.328 (5) | O7—H8W | 0.83 (8) |
| C3—C4 | 1.399 (6) | O8—H1W | 0.84 (8) |
| C4—C5 | 1.349 (6) | O8—H2W | 0.83 (8) |
| | | | |
| O7—Cu1—O6 | 95.00 (16) | C3—C4—C1ⁱⁱ | 123.2 (4) |
| O7—Cu1—O3 | 93.52 (13) | C6—C5—C4 | 117.5 (4) |
| O6—Cu1—O3 | 171.34 (14) | C6—C5—H5 | 121.2 |
| O7—Cu1—O1 | 84.19 (14) | C4—C5—H5 | 121.2 |
| O6—Cu1—O1 | 84.83 (16) | C5—C6—C7 | 121.3 (5) |
| O3—Cu1—O1 | 97.60 (15) | C5—C6—H6 | 119.3 |
| O7—Cu1—O5 | 88.09 (15) | C7—C6—H6 | 119.3 |
| O6—Cu1—O5 | 86.87 (16) | N1—C7—C6 | 121.4 (4) |
| O3—Cu1—O5 | 91.87 (14) | N1—C7—H7 | 119.3 |
| O1—Cu1—O5 | 168.12 (14) | C6—C7—H7 | 119.3 |
| O7—Cu1—N1 | 171.80 (13) | C3—N1—C7 | 118.0 (4) |
| O6—Cu1—N1 | 92.89 (17) | C3—N1—Cu1 | 110.5 (3) |
| O3—Cu1—N1 | 78.54 (13) | C7—N1—Cu1 | 131.3 (3) |
| O1—Cu1—N1 | 98.75 (15) | C1—O1—Cu1 | 145.4 (3) |
| O5—Cu1—N1 | 90.13 (15) | C2—O3—Cu1 | 117.2 (3) |
| O1—C1—O2 | 125.8 (4) | Cu1—O5—H4W | 77 (8) |
| O1—C1—C4ⁱ | 118.0 (4) | Cu1—O5—H3W | 119 (10) |
| O2—C1—C4ⁱ | 116.1 (4) | H4W—O5—H3W | 114 (4) |
| O4—C2—O3 | 126.1 (5) | Cu1—O6—H5W | 118 (7) |
| O4—C2—C3 | 117.0 (5) | Cu1—O6—H6W | 122 (7) |
| O3—C2—C3 | 116.8 (4) | H5W—O6—H6W | 114 (9) |
| N1—C3—C4 | 120.1 (4) | Cu1—O7—H7W | 129 (8) |
| N1—C3—C2 | 115.9 (4) | Cu1—O7—H8W | 92 (8) |
| C4—C3—C2 | 123.9 (4) | H7W—O7—H8W | 112 (9) |
| C5—C4—C3 | 121.5 (4) | H1W—O8—H2W | 111 (4) |
| C5—C4—C1ⁱⁱ | 115.3 (4) | | |

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

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O5—H3*W*···O4ⁱⁱ | 0.82 (9) | 1.93 (8) | 2.735 (6) | 167 (8) |
| O5—H4*W*···O6ⁱⁱⁱ | 0.82 (2) | 2.35 (8) | 2.966 (5) | 132 (10) |
| O6—H5*W*···O5ⁱᵛ | 0.82 (7) | 2.29 (7) | 2.966 (5) | 140 (9) |
| O7—H7*W*···O2ᵛ | 0.83 (8) | 1.90 (9) | 2.720 (5) | 169 (8) |
| O7—H8*W*···O2ⁱⁱⁱ | 0.83 (8) | 2.03 (4) | 2.825 (5) | 162 (11) |

Symmetry codes: (ii) $x+1/2$, $-y+1/2$, $z+1/2$; (iii) $x$, $-y$, $z+1/2$; (iv) $x$, $-y$, $z-1/2$; (v) $x$, $y$, $z+1$.