# metal-organic compounds

# Poly[diaqua-1κ²*O*-bis[μ₃-2-(1*H*-tetrazol-5-yl)benzoato(2−)]dicadmium(II)]

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The title compound, $[Cd_2(C_8H_4N_4O_2)_2(H_2O)_2]_n$, is a coordination polymer prepared by the hydrothermal reaction of cadmium(II) chloride and 2-(1*H*-tetrazol-5-yl)benzoic acid. Two types of coordinated cadmium cations exist in the structure. One is located on a twofold axis and is coordinated by four O and two N atoms from four symmetry-related ligands, forming a trigonal-prismatic coordination polyhedron. The other is located on an inversion center and is octahedrally coordinated by two N and two O atoms from two ligands in equatorial sites, and two water molecules in axial sites. The organic ligand bridges three Cd atoms, through a carboxylate group and two N atoms of the tetrazolate unit. This mode of coordination results in a two-dimensional framework. The crystal structure is stabilized by intermolecular O—H···O and O—H···N hydrogen bonds.

## Related literature

For the chemistry of tetrazole derivatives, see: Xiong *et al.* (2002); Xue *et al.* (2002); Dunica *et al.* (1991); Wang *et al.* (2005); Wittenberger *et al.* (1993); Hu *et al.* (2007).
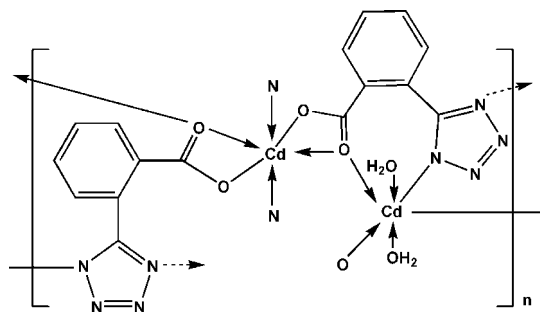


## Experimental

### Crystal data

$[Cd_2(C_8H_4N_4O_2)_2(H_2O)_2]$
$M_r = 637.16$
Monoclinic, $C2/c$
$a = 19.886$ (4) Å
$b = 7.3522$ (15) Å
$c = 15.409$ (3) Å
$\beta = 115.97$ (3)°

$V = 2025.4$ (7) Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.15$ mm⁻¹
$T = 293$ (2) K
$0.35 \times 0.30 \times 0.10$ mm

### Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.473$, $T_{max} = 0.809$

8913 measured reflections
1976 independent reflections
1922 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
$S = 1.13$
1976 reflections
156 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.36$ e Å⁻³
$\Delta\rho_{min} = -0.42$ e Å⁻³

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
| --- | --- | --- | --- | --- |
| O1W—H1W···O2ⁱ | 0.75 (4) | 2.06 (4) | 2.758 (2) | 156 (4) |
| O1W—H2W···N2ⁱⁱ | 0.87 (4) | 2.14 (4) | 2.961 (3) | 155 (3) |

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *PRPKAPPA* (Ferguson, 1999).

## References

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# supporting information

## Poly[diaqua-1$\kappa^2$*O*-bis[$\mu_3$-2-(1*H*-tetrazol-5-yl)benzoato(2−)]dicadmium(II)]

### Xiu-Zhi Li, Bao-Zhen Wu and Zhi-Rong Qu

### S1. Comment

Coordination frameworks have received much attention over the past decade because of their potential applications. Multifunctional organic ligands are necessary to construct such frameworks. 2-(1*H*-tetrazol-5-yl)benzoic acid is a ligand with two functional groups, one carboxylate group and one tetrazole ring. Tetrazole compounds have a wide range of applications in coordination chemistry, medicinal chemistry and material science (Hu *et al.*, 2007; Xiong *et al.*, 2002; Xue *et al.*, 2002; Wang *et al.*, 2005; Dunica *et al.*, 1991; Wittenberger *et al.*, 1993). We report here the crystal structure of the title compound, which was obtained by the hydrothermal reaction of cadmium chloride and 2-(1*H*-tetrazol-5-yl)benzoic acid.

   In the structure of this compound, two types of coordinated cadmium cations exist (Fig. 1). Cd1 is located on a 2-fold rotation axis, and is trigonal prismatically coordinated by two O and two N from four different ligands. While Cd2 is loacated on an inversion center, and is octahedrally coordinated by two N and two O from two ligands at equatorial sites, and two O atoms of $H_2O$ at axial sites. The organic ligand bridges three Cd atoms by coordinating one Cd atom through one N atom from the tetrazole unit, by coordinating the other Cd atom through one O atom and one $\mu_3$-O from the carboxylate unit, and by coordinating a third Cd atom through a N atom from the tetrazole unit and one $\mu_3$-O from the carboxylate unit. Such an arrangement makes Cd1 and Cd2 bridged by one $\mu_3$-O carboxylate group and the tetrazole unit, resulting in a two-dimensional framework (Fig. 2). The crystal structure is stabilized by intermolecular O—H···O and O—H···N hydrogen bonds (Table 1).

### S2. Experimental

A mixture of $CdCl_2$ (0.2 mmol) and 2-(1*H*-tetrazol-5-yl)benzoic acid (0.2 mmol) in $H_2O$ (4 ml) was heated in a Pyrex tube at 373 K for two days. After slowly cooling down to room temperature over a period of 12 h., colourless crystals of the title compound suitable for diffraction were isolated.

### S3. Refinement

Water H atoms were found in a difference map and refined freely. Other H atoms positions were calculated geometrically and these H atoms were allowed to ride on their carrier C atoms with C—H = 0.93 Å, and $U_{iso}$(H) = 1.2 $U_{eq}$(C).
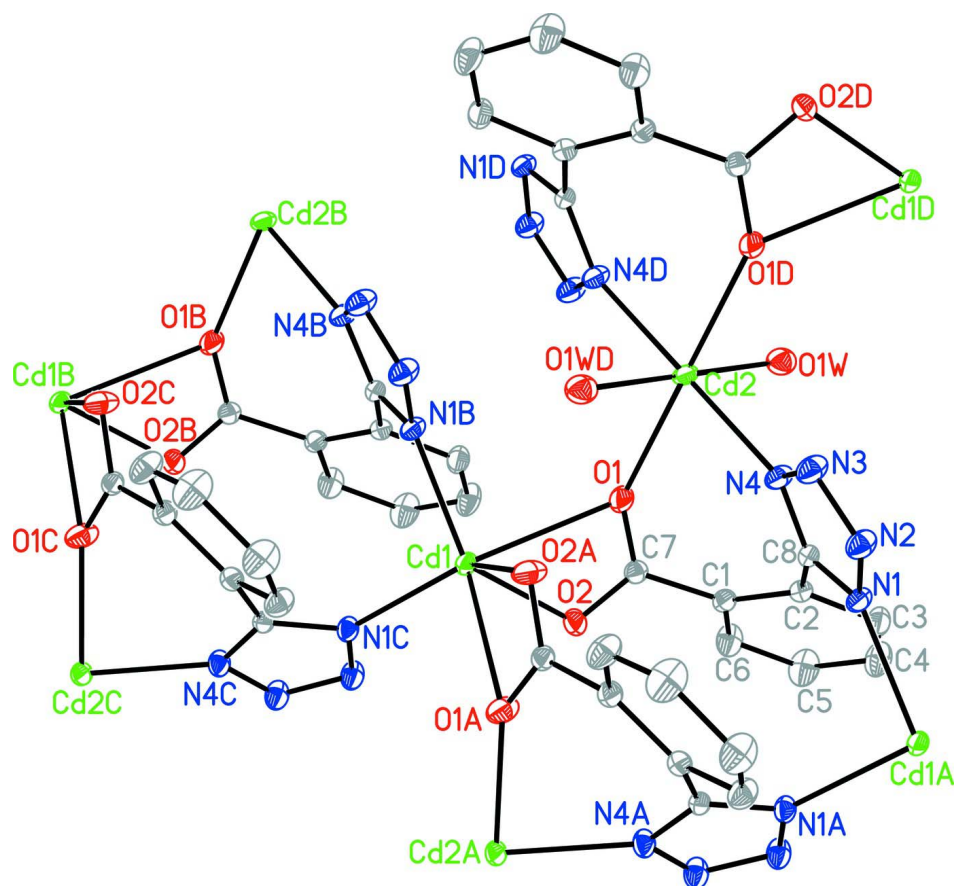
**Figure 1**

A partial packing diagram of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) -*x*, -*y* + 1, -*z*; (B) -*x*, +*y*, *1/2* - *z*; (C) +*x*, +*y* - 1, +*z*; (D) -*x*, +*y* - 1, *1/2* - *z*.]
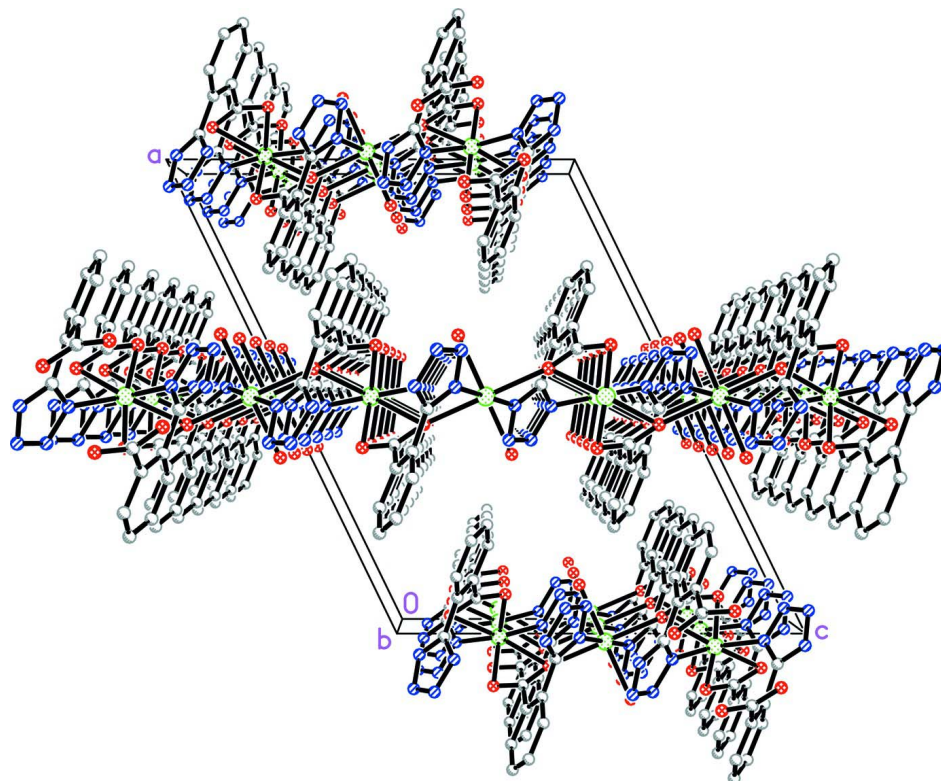
**Figure 2**

Packing diagram of the title compound, showing the structure along the *b* axis. No displacement parameters are displayed and H atoms have been omitted for clarity.

**(I)**

*Crystal data*

| | |
|---|---|
| $[Cd_2(C_8H_4N_4O_2)_2(H_2O)_2]$ | $F(000) = 1232$ |
| $M_r = 637.16$ | $D_x = 2.090$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -C 2yc | Cell parameters from 0 reflections |
| $a = 19.886$ (4) Å | $\theta = 3.1$–27.5° |
| $b = 7.3522$ (15) Å | $\mu = 2.15$ mm$^{-1}$ |
| $c = 15.409$ (3) Å | $T = 293$ K |
| $\beta = 115.97$ (3)° | Block, colourless |
| $V = 2025.4$ (7) Å$^3$ | $0.35 \times 0.30 \times 0.10$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Rigaku SCXmini diffractometer | 8913 measured reflections |
| Radiation source: fine-focus sealed tube | 1976 independent reflections |
| Graphite monochromator | 1922 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 13.6612 pixels mm$^{-1}$ | $R_{int} = 0.029$ |
| CCD Profile fitting scans | $\theta_{max} = 26.0°$, $\theta_{min} = 3.0°$ |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) | $h = -24 \rightarrow 24$ |
| $T_{min} = 0.473$, $T_{max} = 0.809$ | $k = -9 \rightarrow 9$ |
| | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.018$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.046$ | |
| $S = 1.13$ | $w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 3.1517P]$ |
| 1976 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 156 parameters | $(\Delta/\sigma)_{max} = 0.001$ |
| 0 restraints | $\Delta\rho_{max} = 0.36$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{min} = -0.42$ e Å$^{-3}$ |
| | Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| Secondary atom site location: difference Fourier map | |
| | Extinction coefficient: 0.00235 (14) |

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cd1 | 0.0000 | 0.21274 (3) | 0.2500 | 0.02355 (9) |
| Cd2 | 0.0000 | 0.5000 | 0.0000 | 0.02567 (9) |
| O1 | 0.05131 (10) | 0.4374 (2) | 0.16197 (11) | 0.0376 (4) |
| O1W | 0.11318 (10) | 0.6113 (3) | 0.00533 (13) | 0.0352 (4) |
| H1W | 0.115 (2) | 0.579 (5) | −0.040 (3) | 0.063 (11)* |
| H2W | 0.115 (2) | 0.730 (6) | 0.006 (3) | 0.071 (11)* |
| O2 | 0.09395 (10) | 0.4136 (2) | 0.31727 (11) | 0.0361 (4) |
| N1 | −0.01798 (10) | 1.0095 (2) | 0.13491 (13) | 0.0239 (4) |
| N2 | −0.08259 (11) | 1.0024 (2) | 0.05335 (14) | 0.0303 (4) |
| N3 | −0.08190 (11) | 0.8588 (3) | 0.00480 (13) | 0.0319 (4) |
| N4 | −0.01705 (10) | 0.7689 (2) | 0.05357 (13) | 0.0264 (4) |
| C1 | 0.12913 (12) | 0.6784 (3) | 0.26098 (15) | 0.0235 (4) |
| C2 | 0.09950 (11) | 0.8385 (3) | 0.20847 (14) | 0.0223 (4) |
| C3 | 0.14406 (14) | 0.9941 (3) | 0.23224 (17) | 0.0308 (5) |
| H3 | 0.1253 | 1.1003 | 0.1971 | 0.037* |
| C4 | 0.21556 (14) | 0.9938 (3) | 0.3061 (2) | 0.0409 (6) |
| H4 | 0.2444 | 1.0989 | 0.3208 | 0.049* |
| C5 | 0.24392 (14) | 0.8370 (4) | 0.3581 (2) | 0.0450 (6) |
| H5 | 0.2921 | 0.8361 | 0.4082 | 0.054* |
| C6 | 0.20091 (13) | 0.6821 (3) | 0.33610 (17) | 0.0361 (5) |
| H6 | 0.2203 | 0.5772 | 0.3722 | 0.043* |
| C7 | 0.08845 (12) | 0.5008 (3) | 0.24438 (16) | 0.0225 (4) |
| C8 | 0.02201 (11) | 0.8642 (3) | 0.13370 (14) | 0.0204 (4) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cd1 | 0.03345 (14) | 0.01501 (12) | 0.01947 (13) | 0.000 | 0.00909 (9) | 0.000 |
| Cd2 | 0.03771 (15) | 0.01834 (13) | 0.01698 (13) | 0.00252 (8) | 0.00830 (10) | −0.00369 (7) |
| O1 | 0.0559 (11) | 0.0246 (8) | 0.0209 (8) | −0.0100 (8) | 0.0062 (7) | −0.0002 (6) |
| O1W | 0.0392 (10) | 0.0341 (10) | 0.0287 (9) | 0.0054 (7) | 0.0116 (7) | 0.0008 (7) |
| O2 | 0.0511 (10) | 0.0304 (9) | 0.0210 (7) | −0.0135 (8) | 0.0105 (7) | 0.0019 (6) |

| | | | | | |
|---|---|---|---|---|---|
| N1 | 0.0276 (9) | 0.0179 (8) | 0.0205 (9) | 0.0017 (7) | 0.0052 (7) | −0.0029 (6) |
| N2 | 0.0298 (10) | 0.0247 (10) | 0.0277 (10) | 0.0045 (7) | 0.0047 (8) | −0.0028 (7) |
| N3 | 0.0328 (10) | 0.0261 (10) | 0.0259 (9) | 0.0037 (8) | 0.0028 (8) | −0.0050 (8) |
| N4 | 0.0298 (9) | 0.0218 (9) | 0.0214 (9) | 0.0027 (7) | 0.0053 (7) | −0.0048 (7) |
| C1 | 0.0256 (10) | 0.0215 (10) | 0.0223 (10) | −0.0005 (8) | 0.0095 (8) | −0.0014 (8) |
| C2 | 0.0256 (10) | 0.0211 (10) | 0.0204 (10) | −0.0008 (8) | 0.0102 (8) | −0.0019 (8) |
| C3 | 0.0334 (13) | 0.0233 (11) | 0.0325 (13) | −0.0042 (9) | 0.0113 (10) | 0.0011 (8) |
| C4 | 0.0319 (13) | 0.0332 (13) | 0.0482 (16) | −0.0132 (10) | 0.0090 (11) | −0.0041 (10) |
| C5 | 0.0262 (12) | 0.0430 (14) | 0.0456 (15) | −0.0062 (11) | −0.0029 (10) | 0.0007 (12) |
| C6 | 0.0295 (12) | 0.0306 (12) | 0.0352 (13) | 0.0011 (10) | 0.0022 (10) | 0.0063 (10) |
| C7 | 0.0242 (11) | 0.0199 (10) | 0.0212 (11) | 0.0029 (7) | 0.0077 (9) | 0.0006 (7) |
| C8 | 0.0264 (10) | 0.0156 (9) | 0.0195 (9) | −0.0017 (8) | 0.0102 (8) | −0.0010 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cd1—N1[i] | 2.2251 (17) | N1—N2 | 1.349 (3) |
| Cd1—N1[ii] | 2.2251 (17) | N1—Cd1[v] | 2.2251 (17) |
| Cd1—O2 | 2.2473 (16) | N2—N3 | 1.298 (3) |
| Cd1—O2[iii] | 2.2473 (16) | N3—N4 | 1.347 (3) |
| Cd1—O1 | 2.6117 (17) | N4—C8 | 1.333 (3) |
| Cd1—O1[iii] | 2.6118 (17) | C1—C6 | 1.390 (3) |
| Cd1—C7[iii] | 2.779 (2) | C1—C2 | 1.404 (3) |
| Cd2—N4[iv] | 2.2251 (18) | C1—C7 | 1.498 (3) |
| Cd2—N4 | 2.2251 (18) | C2—C3 | 1.394 (3) |
| Cd2—O1 | 2.2916 (16) | C2—C8 | 1.477 (3) |
| Cd2—O1[iv] | 2.2916 (16) | C3—C4 | 1.378 (4) |
| Cd2—O1W | 2.3623 (19) | C3—H3 | 0.9300 |
| Cd2—O1W[iv] | 2.3623 (19) | C4—C5 | 1.376 (4) |
| O1—C7 | 1.247 (3) | C4—H4 | 0.9300 |
| O1W—H1W | 0.75 (4) | C5—C6 | 1.375 (3) |
| O1W—H2W | 0.87 (4) | C5—H5 | 0.9300 |
| O2—C7 | 1.256 (3) | C6—H6 | 0.9300 |
| N1—C8 | 1.337 (3) | | |
| | | | |
| N1[i]—Cd1—N1[ii] | 95.61 (9) | Cd2—O1—Cd1 | 127.14 (7) |
| N1[i]—Cd1—O2 | 128.32 (7) | Cd2—O1W—H1W | 107 (3) |
| N1[ii]—Cd1—O2 | 105.23 (6) | Cd2—O1W—H2W | 112 (2) |
| N1[i]—Cd1—O2[iii] | 105.23 (6) | H1W—O1W—H2W | 108 (4) |
| N1[ii]—Cd1—O2[iii] | 128.32 (7) | C7—O2—Cd1 | 101.17 (13) |
| O2—Cd1—O2[iii] | 97.83 (9) | C8—N1—N2 | 106.63 (16) |
| N1[i]—Cd1—O1 | 88.50 (6) | C8—N1—Cd1[v] | 131.21 (14) |
| N1[ii]—Cd1—O1 | 151.13 (6) | N2—N1—Cd1[v] | 121.56 (13) |
| O2—Cd1—O1 | 52.34 (5) | N3—N2—N1 | 108.79 (17) |
| O2[iii]—Cd1—O1 | 77.28 (6) | N2—N3—N4 | 109.07 (17) |
| N1[i]—Cd1—O1[iii] | 151.13 (6) | C8—N4—N3 | 106.63 (17) |
| N1[ii]—Cd1—O1[iii] | 88.50 (6) | C8—N4—Cd2 | 133.51 (14) |
| O2—Cd1—O1[iii] | 77.28 (6) | N3—N4—Cd2 | 119.53 (13) |
| O2[iii]—Cd1—O1[iii] | 52.34 (5) | C6—C1—C2 | 118.9 (2) |

| | | | |
|---|---|---|---|
| O1—Cd1—O1ⁱ | 101.55 (8) | C6—C1—C7 | 116.11 (19) |
| N1ⁱ—Cd1—C7ⁱ | 130.83 (7) | C2—C1—C7 | 125.01 (19) |
| N1ⁱⁱ—Cd1—C7ⁱ | 111.72 (7) | C3—C2—C1 | 118.60 (19) |
| O2—Cd1—C7ⁱ | 83.94 (7) | C3—C2—C8 | 115.22 (19) |
| O2ⁱ—Cd1—C7ⁱ | 26.32 (6) | C1—C2—C8 | 126.00 (18) |
| O1—Cd1—C7ⁱ | 86.03 (6) | C4—C3—C2 | 121.5 (2) |
| O1ⁱ—Cd1—C7ⁱ | 26.51 (6) | C4—C3—H3 | 119.2 |
| N4ⁱᵛ—Cd2—N4 | 180.00 (10) | C2—C3—H3 | 119.3 |
| N4ⁱᵛ—Cd2—O1 | 99.09 (6) | C5—C4—C3 | 119.6 (2) |
| N4—Cd2—O1 | 80.91 (6) | C5—C4—H4 | 120.2 |
| N4ⁱᵛ—Cd2—O1ⁱᵛ | 80.91 (6) | C3—C4—H4 | 120.2 |
| N4—Cd2—O1ⁱᵛ | 99.09 (6) | C6—C5—C4 | 119.9 (2) |
| O1—Cd2—O1ⁱᵛ | 180.0 | C6—C5—H5 | 120.1 |
| N4ⁱᵛ—Cd2—O1W | 91.33 (7) | C4—C5—H5 | 120.0 |
| N4—Cd2—O1W | 88.67 (7) | C5—C6—C1 | 121.5 (2) |
| O1—Cd2—O1W | 93.94 (7) | C5—C6—H6 | 119.3 |
| O1ⁱᵛ—Cd2—O1W | 86.06 (7) | C1—C6—H6 | 119.2 |
| N4ⁱᵛ—Cd2—O1Wⁱᵛ | 88.67 (7) | O1—C7—O2 | 120.06 (19) |
| N4—Cd2—O1Wⁱᵛ | 91.33 (7) | O1—C7—C1 | 122.33 (19) |
| O1—Cd2—O1Wⁱᵛ | 86.06 (7) | O2—C7—C1 | 117.60 (19) |
| O1ⁱᵛ—Cd2—O1Wⁱᵛ | 93.94 (7) | N4—C8—N1 | 108.88 (18) |
| O1W—Cd2—O1Wⁱᵛ | 180.00 (9) | N4—C8—C2 | 129.86 (18) |
| C7—O1—Cd2 | 144.77 (14) | N1—C8—C2 | 120.98 (17) |
| C7—O1—Cd1 | 84.22 (13) | | |

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

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$W$—H1$W$···O2ᵛⁱ | 0.75 (4) | 2.06 (4) | 2.758 (2) | 156 (4) |
| O1$W$—H2$W$···N2ᵛⁱⁱ | 0.87 (4) | 2.14 (4) | 2.961 (3) | 155 (3) |

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