# metal-organic compounds

# Poly[[tetraaquabis($\mu$-hydroxyacetato-$\kappa^4O^1,O^2$:$O^1,O^{1'}$)-$\mu_2$-sulfato-$\kappa^2O$:$O'$-dicadmium(II)] monohydrate]

**Urszula Rychlewska,$^{a*}$ Beata Warzajtis,$^a$ Mirjana Dj. Dimitrijević,$^b$ Nenad S. Draskovic$^b$ and Miloš I. Djuran$^b$**

$^a$Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and $^b$Department of Chemistry, Faculty of Science, University of Kragujevac, R. Domanovića 12, PO Box 60, 34000 Kragujevac, Serbia
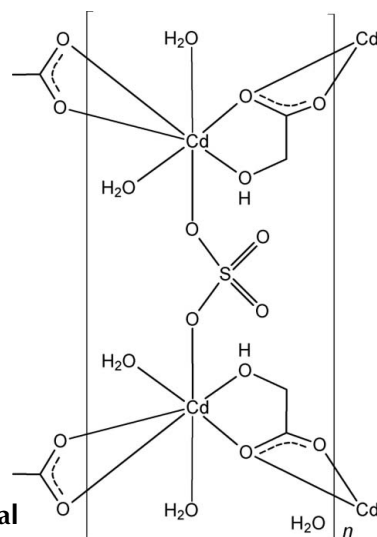Correspondence e-mail: urszular@amu.edu.pl

The title compound, $\{[Cd_2(C_2H_3O_3)_2(SO_4)(H_2O)_4]\cdot H_2O\}_n$, was obtained unintentionally in a transmetallation reaction. The crystal structure contains a two-dimensional metal–organic framework based on $Cd^{II}$–($\mu$-hydroxyacetato-$\kappa^4O^1,O^2$:$O^1,O^{1'}$)–$Cd^{II}$ zigzag chains joined together by bridging $SO_4$ anions. The resulting layers are shifted with respect to each other and are stacked along the $c$ axis. Their construction is supported by hydrogen bonds between water molecules and between water molecules and carboxylate or sulfate groups. Neighbouring layers are bridged by hydrogen bonds between the hydroxyl substituent and a sulfate anion. The sulfate anion and solvent water molecule are located on twofold axes. The results demonstrate that care must be taken when preparing ethylenediaminetetraacetic acid-type complexes by transmetallation, in order to avoid precipitation of metal complexes with the $\alpha$-hydroxyacetate ligand.

## Related literature

For examples of the successful application of transmetallation reactions in the synthesis of metal(II) complexes with hexadentate 1,3-propanediaminetetraacetate and 1,4-butanediaminetetraacetate ligands, see: Radanović et al. (2003, 2004, 2007); Rychlewska et al. (2000, 2005, 2007).



## Experimental

### Crystal data

| | |
|---|---|
| $[Cd_2(C_2H_3O_3)_2(SO_4)(H_2O)_4]\cdot H_2O$ | $V$ = 1529.34 (5) Å$^3$ |
| $M_r$ = 561.03 | $Z$ = 4 |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a$ = 13.5750 (3) Å | $\mu$ = 2.99 mm$^{-1}$ |
| $b$ = 8.5777 (1) Å | $T$ = 295 K |
| $c$ = 13.7734 (3) Å | $0.30 \times 0.30 \times 0.20$ mm |
| $\beta$ = 107.528 (2)° | |

### Data collection

| | |
|---|---|
| Kuma KM4 CCD $\kappa$-geometry diffractometer | 8842 measured reflections |
| | 1710 independent reflections |
| Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007) | 1602 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.018 |
| $T_{min}$ = 0.388, $T_{max}$ = 0.550 | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.015 | 102 parameters |
| $wR(F^2)$ = 0.038 | H-atom parameters constrained |
| $S$ = 1.13 | $\Delta\rho_{max}$ = 0.46 e Å$^{-3}$ |
| 1710 reflections | $\Delta\rho_{min}$ = $-0.31$ e Å$^{-3}$ |

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

| | | | |
|---|---|---|---|
| Cd1—O1 | 2.3584 (14) | Cd1—O2W | 2.3245 (14) |
| Cd1—O2 | 2.3013 (14) | Cd1—O2$^i$ | 2.5937 (14) |
| Cd1—O4 | 2.2386 (16) | Cd1—O3$^i$ | 2.3379 (17) |
| Cd1—O1W | 2.2731 (15) | | |

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

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1W—H1W$\cdots$O2W$^{ii}$ | 0.85 | 1.94 | 2.784 (2) | 170 |
| O1W—H2w$\cdots$O3$^{iii}$ | 0.85 | 1.88 | 2.723 (2) | 172 |
| O2W—H3W$\cdots$O3W | 0.85 | 1.88 | 2.720 (2) | 172 |
| O2W—H4W$\cdots$O5$^i$ | 0.85 | 1.82 | 2.648 (2) | 162 |
| O1—H1O$\cdots$O5$^{iv}$ | 0.85 | 1.81 | 2.659 (2) | 175 |
| O3W—H5W$\cdots$O4$^v$ | 0.85 | 2.25 | 2.813 (3) | 124 |

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$; (iii) $x, y-1, z$; (iv) $x, -y+2, z-\frac{1}{2}$; (v) $x+\frac{1}{2}, y+\frac{1}{2}, z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1989) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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# supporting information

# Poly[[tetraaquabis(*μ*-hydroxyacetato-*κ*⁴*O*¹,*O*²:*O*¹,*O*¹′)-*μ*₂-sulfato-*κ*²*O*:*O*′-dicadmium(II)] monohydrate]

**Urszula Rychlewska, Beata Warzajtis, Mirjana Dj. Dimitrijević, Nenad S. Draskovic and Miloš I. Djuran**

### S1. Comment

Research concerning metal–organic frameworks (MOF) has recently become important due to their potential application in a number of areas, including gas storage and catalysis. Prominent in this class of materials are frameworks that involve *α*-hydroxycarboxylate ligands spanning network nodes. We have recently obtained one such MOF by serendipity, when trying to synthesize cadmium(II) homometallic complex with 1,4-bdta ligand (1,4-bdta stands for 1,4-butanediaminetetraactetate) by the process of transmetallation. So far we have successfully used this strategy for obtaining *M*(II) complexes with both 1,3-pdta (1,3-propanediaminetetraacetate) (Rychlewska *et al.*, 2000; Radanović *et al.*, 2003; Radanović *et al.*, 2004; Rychlewska *et al.*, 2005, 2007) and 1,4-bdta ligands (Radanović *et al.*, 2007). In this procedure, barium(II) cations, forming the homometallic barium 1,3-pdta or 1,4-bdta complex, are being exchanged by much smaller in size metal(II) cations. At the very first step of this reaction we synthesize the ligands by reacting 1,3-propanediamine (or 1,4-butanediamine) with sodium chloracetate. It turned out that, when trying to synthesize 1,4-bdta ligand, we have obtained, in the reaction mixture, besides the expected $H_4$-1,4-bdta, some amount of *α*-hydroxycarboxylic acid. Most probably, this *α*-hydroxycarboxylic acid has originated from the chloracetic acid when heated at pH > 10. Consequent addition of $BaCl_2$ to the solution resulted in formation of two types of barium(II) salts, one formed by $H_4$-1,4-bdta and the other by $HOCH_2COOH$. An attempt to exchange barium(II) by cadmium(II) cations by addition of $CdSO_4$ resulted in percipitation of two-dimensional homometallic MOF formed by Cd$^{II}$ cations, hydroxyacetate and sulfate anions, instead of the expected Cd$^{II}$ 1,4-bdta complex. This has been unequivocally established by the X-ray crystal structure analysis, the results of which are reported in this paper. We next attempted to verify this hypothetical synthetic route by synthesizing the very same Cd$^{II}$ complex starting from $(HOCH_2COO)_2Ba$ salt. For both samples we have performed elemental microanalyses and NMR measurements which confirmed their identity.

In the crystal the Cd$^{II}$ nodes bind together by a singly deprotonated hydroxyacetate and doubly deprotonated sulfate linkers. The hydroxyacetate acts as a tetradentate ligand with *α*-hydroxyacetate group O1–C1–C2–O2 acting as a bidentate chelate to Cd1, and carboxylate group O2–C2–O3 acting as a bidentate chelate to Cd1 at *1/2 - x, 1/2 + y, 1/2 - z*. The two Cd$^{II}$ centers sharing the same (O2) carboxylate oxygen and bridged by the O2–C2–O3 carboxylate group are 4.736 (1) Å apart, and extend in a *zigzag* manner along the *b*-direction. Each Cd$^{II}$ cation is chelated by a hydroxyacetate residue and a carboxylate group, and is coordinated by two water molecules, and one sulfate anion, resulting in a sevenfold coordination mode (Fig. 1). The hydroxyacetate anions and one coordinated water molecule (O1W) lie in the equatorial plane while the other water molecule (O2W) and the sulfate anion take the axial positions. Hence, the coordination polyhedron formed around Cd1 is a distorted pentagonal bipyramid with the in-plane *cis* bond angles in the range 52.37 (4)–83.68 (5)°, the smallest angle reflecting chelation by the carboxylate ligand, and with the out-of-plane

*trans* angle of 170.76 (6)°. Sulfate anions lie on the twofold axis and connect the neighbouring $Cd^{II}$ centers, related by this symmetry axis *via* O4 oxygen atoms. Separation of the two $Cd^{II}$ metal centers bridged by the sulfate group measures 6.773 (1) Å. The sulfate bridges help to extend the basic structural motif in the *a*-direction, thus forming a (001) layer (Fig. 2). This polymeric two-dimensional construction is additionally supported by hydrogen bonds (Table 2) that involve crystalline water molecule, which also occupies the twofold axis (O3w). This water molecule acts as a double hydrogen bond donor to two coordinated sulfate O atoms (O4 and its symmetry equivalent) and a double hydrogen bond acceptor from the axially coordinated water molecule (O2W and its twofold equivalent). The equatorially coordinated water molecule (O1W) acts as a hydrogen bond donor to carboxylate O3 and the axially coordinated water O2W. The neighbouring two-dimensional layers are bridged by a hydrogen bond formed between a hydroxyl group (O1) acting as a hydrogen-bond donor and the uncoordinated oxygen atom (O5) from the sulfate anion. The hydrogen bond parameters are provided in Table 2.

The reported X-ray analysis allowed us to identify and structurally characterize the unintentionally synthesized two-dimensional MOF and to demonstrate that care must be taken when preparing the edta-type complexes by transmetallation to avoid precipitation of metal complexes with *α*-hydroxyacetate bridges. To remove the excess of Ba(II) *α*-hydroxyacetate, a water washing procedure should be repeated several times.

## S2. Experimental

2.56 g (0.003 mol) of $CdSO_4.8H_2O$ were dissolved in 50 cm$^3$ of distilled water at 70°C. To this solution, 6.27 g of solid Ba[Ba(1,4-bdta)].2H$_2$O containing Ba(HOCH$_2$COO)$_2$ in ratio 3:1, respectively, was added and the reaction mixture was heated at 90°C with stirring for 6 h. The precipitated BaSO$_4$ was removed by filtration and the filtrate was evaporated to *ca* 10 cm$^3$ and then left in a refrigerator for several days. Colorless crystals of the title compound were collected, washed with ethanol, and air-dried. Yield 0.98 g (59.5%). The complex was recrystallized from hot water while cooling in a refrigerator. Analysis calculated for C$_4$H$_{14}$Cd$_2$O$_{14}$S.H$_2$O (FW = 561.03; m. p. 416 K): C 8.84, H 2.87, S 5.90%; found: C 8.93, H 2.83, S 6.28%.

## S3. Refinement

All H atoms attached to C atoms were placed in their idealized positions, the hydroxyl and water H atoms were located on difference Fourier maps. All H atoms were refined as riding on their carrier atoms with constraints imposed on the bond lengths and displacement parameters, *i.e.* C—H = 0.96 Å O—H = 0.85 Å with $U_{iso}(H)$ 20% higher than $U_{eq}$ of the carrier atom.
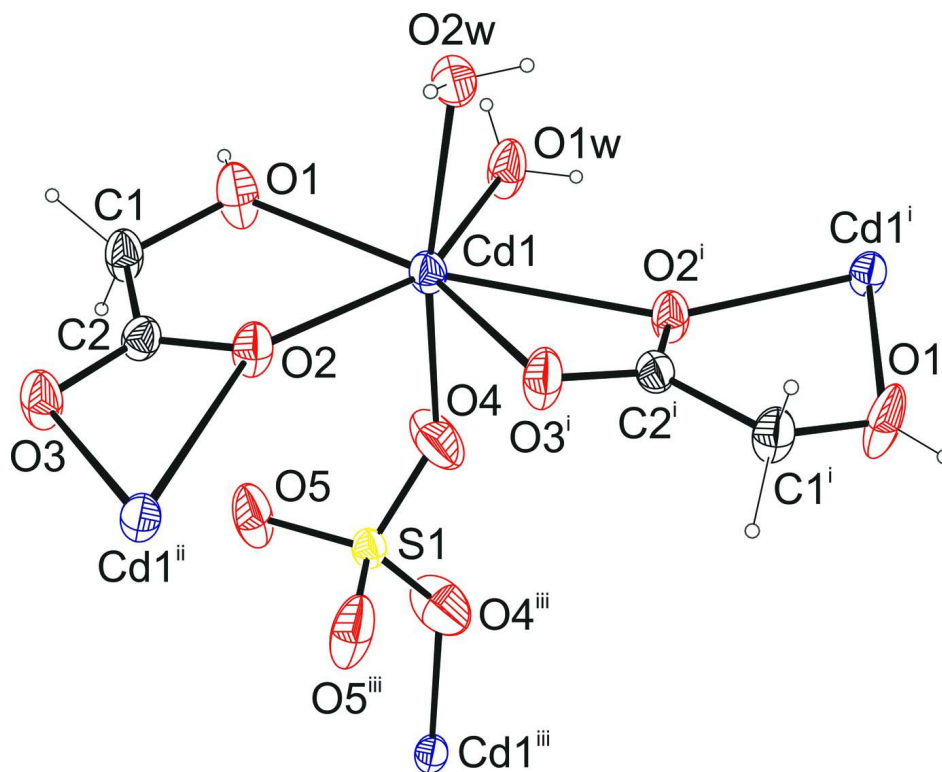
**Figure 1**

Basic supramolecular motif showing pentagonal bipyramidal coordination around Cd$^{II}$. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes: *i = -x + 1/2, y - 1/2, -z + 1/2; ii= -x + 1/2, y + 1/2, -z + 1/2; iii= -x, y, -z + 1/2.*
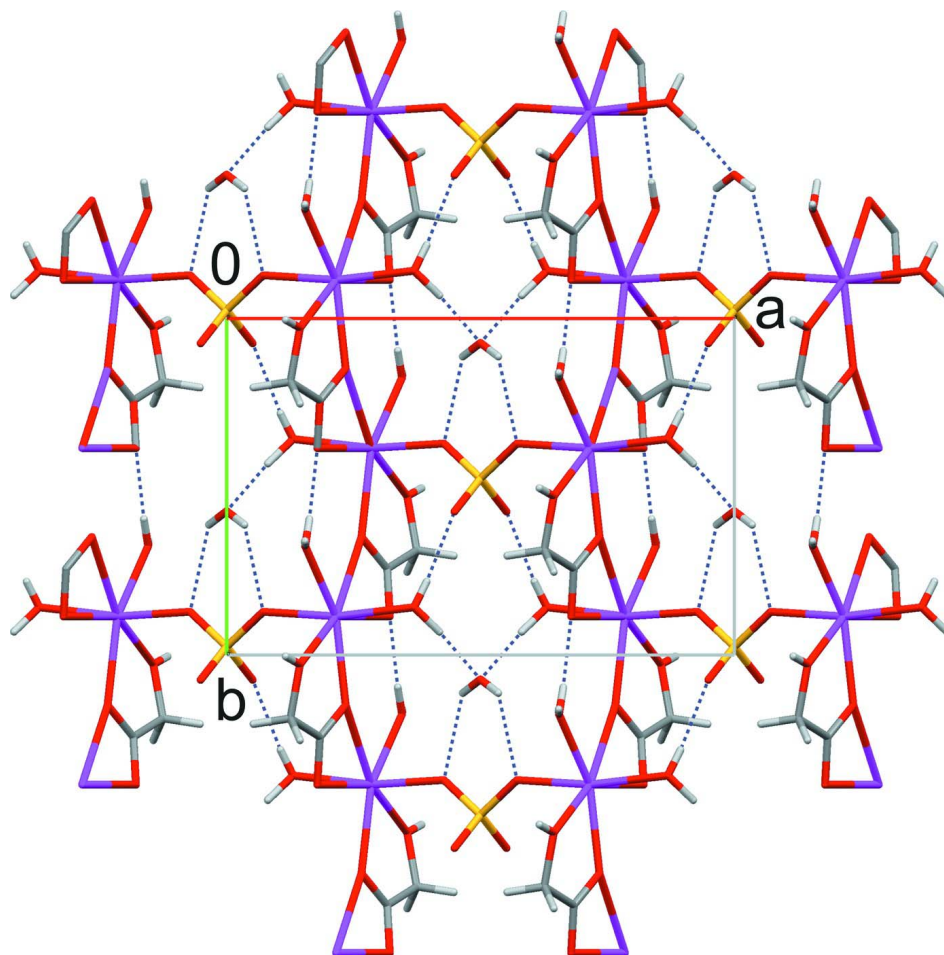
**Figure 2**

View down the monoclinic *c*-direction showing hydrogen bonding (dashed lines), water channels and two-dimensional structure of the complex.

**Poly[[tetraaquabis(*μ₂*-hydroxyacetato- *κ⁴O¹,O²:O¹,O¹′*)-*μ₂*-sulfato- *κ²O:O′*-dicadmium(II)] monohydrate]**

*Crystal data*

$[Cd_2(C_2H_3O_3)_2(SO_4)(H_2O)_4]\cdot H_2O$
$M_r = 561.03$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 13.5750\ (3)$ Å
$b = 8.5777\ (1)$ Å
$c = 13.7734\ (3)$ Å
$\beta = 107.528\ (2)°$
$V = 1529.34\ (5)$ Å$^3$
$Z = 4$

$F(000) = 1088$
$D_x = 2.437$ Mg m$^{-3}$
Melting point: 416 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5972 reflections
$\theta = 2.9–28.0°$
$\mu = 2.99$ mm$^{-1}$
$T = 295$ K
Prismatic, colourless
$0.30 \times 0.30 \times 0.20$ mm

*Data collection*

Kuma KM4 CCD *κ*-geometry
   diffractometer
Radiation source: fine-focus sealed tube

Graphite monochromator
*ω* and *φ* scans

Absorption correction: multi-scan
  (*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min} = 0.388$, $T_{max} = 0.550$
8842 measured reflections
1710 independent reflections
1602 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.9°$
$h = -17\rightarrow17$
$k = -10\rightarrow10$
$l = -17\rightarrow17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.038$
$S = 1.13$
1710 reflections
102 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 0.9781P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å$^{-3}$
$\Delta\rho_{min} = -0.31$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
  2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$
Extinction coefficient: 0.00703 (18)

*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.

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

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Cd1 | 0.215433 (10) | 0.885016 (14) | 0.174423 (9) | 0.02516 (7) |
| O1W | 0.15455 (14) | 0.67573 (17) | 0.07284 (12) | 0.0463 (4) |
| H1W | 0.1546 | 0.6610 | 0.0118 | 0.056* |
| H2W | 0.1641 | 0.5894 | 0.1046 | 0.056* |
| O2W | 0.36889 (11) | 0.85773 (16) | 0.13399 (12) | 0.0344 (3) |
| H3W | 0.4134 | 0.9233 | 0.1669 | 0.041* |
| H4W | 0.3970 | 0.7714 | 0.1573 | 0.041* |
| O1 | 0.14443 (14) | 1.02774 (17) | 0.02309 (11) | 0.0499 (4) |
| H1O | 0.1128 | 1.0004 | −0.0376 | 0.060* |
| C1 | 0.12548 (16) | 1.1879 (2) | 0.03179 (14) | 0.0323 (4) |
| H1A | 0.0528 | 1.2052 | 0.0191 | 0.039* |
| H1B | 0.1474 | 1.2454 | −0.0178 | 0.039* |
| C2 | 0.18369 (14) | 1.2435 (2) | 0.13702 (13) | 0.0254 (4) |
| O2 | 0.23446 (11) | 1.14930 (16) | 0.20257 (11) | 0.0310 (3) |
| O4 | 0.07190 (15) | 0.87150 (18) | 0.22208 (19) | 0.0617 (6) |
| S1 | 0.0000 | 0.97501 (7) | 0.2500 | 0.02325 (13) |
| O5 | 0.05131 (16) | 1.0737 (2) | 0.33543 (12) | 0.0570 (5) |
| O3W | 0.5000 | 1.0723 (3) | 0.2500 | 0.0749 (10) |
| H5W | 0.5380 | 1.1144 | 0.2183 | 0.090* |
| O3 | 0.17860 (15) | 1.38542 (15) | 0.15667 (12) | 0.0396 (3) |

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

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cd1 | 0.03149 (10) | 0.02054 (9) | 0.02099 (9) | 0.00182 (4) | 0.00418 (6) | −0.00095 (5) |
| O1W | 0.0858 (12) | 0.0209 (7) | 0.0251 (7) | −0.0006 (7) | 0.0062 (7) | −0.0006 (6) |
| O2W | 0.0402 (8) | 0.0289 (7) | 0.0334 (8) | 0.0051 (6) | 0.0098 (6) | 0.0019 (6) |
| O1 | 0.0872 (12) | 0.0260 (8) | 0.0193 (7) | 0.0107 (7) | −0.0098 (7) | −0.0061 (6) |
| C1 | 0.0445 (11) | 0.0231 (9) | 0.0224 (9) | 0.0022 (8) | −0.0001 (8) | 0.0011 (7) |
| C2 | 0.0323 (9) | 0.0211 (9) | 0.0218 (8) | −0.0040 (7) | 0.0067 (7) | 0.0000 (7) |
| O2 | 0.0416 (7) | 0.0226 (6) | 0.0214 (6) | −0.0032 (5) | −0.0018 (6) | 0.0001 (5) |
| O3 | 0.0629 (10) | 0.0208 (7) | 0.0274 (8) | −0.0011 (6) | 0.0021 (7) | −0.0030 (5) |
| O4 | 0.0565 (11) | 0.0353 (9) | 0.1112 (18) | 0.0121 (7) | 0.0524 (13) | 0.0067 (9) |
| S1 | 0.0263 (3) | 0.0186 (3) | 0.0233 (3) | 0.000 | 0.0051 (2) | 0.000 |
| O5 | 0.0940 (15) | 0.0310 (8) | 0.0250 (8) | −0.0193 (8) | −0.0139 (8) | 0.0032 (7) |
| O3W | 0.0500 (15) | 0.0271 (12) | 0.140 (3) | 0.000 | 0.0168 (17) | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cd1—O1 | 2.3584 (14) | O1—H1O | 0.8500 |
| Cd1—O2 | 2.3013 (14) | C1—C2 | 1.504 (3) |
| Cd1—O4 | 2.2386 (16) | C1—H1A | 0.9601 |
| Cd1—O1W | 2.2731 (15) | C1—H1B | 0.9599 |
| Cd1—O2W | 2.3245 (14) | C2—O2 | 1.252 (2) |
| Cd1—O2$^i$ | 2.5937 (14) | C2—O3 | 1.253 (2) |
| Cd1—O3$^i$ | 2.3379 (17) | O2—Cd1$^{ii}$ | 2.5937 (14) |
| O1W—H1W | 0.8500 | O4—S1 | 1.4543 (16) |
| O1W—H2W | 0.8500 | S1—O5 | 1.4468 (16) |
| O2W—H3W | 0.8500 | O3W—H5W | 0.8500 |
| O2W—H4W | 0.8500 | O3—Cd1$^{ii}$ | 2.3379 (17) |
| O1—C1 | 1.410 (2) | | |
| | | | |
| O4—Cd1—O1W | 87.27 (7) | Cd1—O2W—H3W | 110.5 |
| O4—Cd1—O2 | 93.73 (5) | H4W—O2W—H3W | 102.0 |
| O1W—Cd1—O2 | 152.03 (5) | C1—O1—Cd1 | 117.86 (11) |
| O4—Cd1—O2W | 170.76 (6) | C1—O1—H1O | 107.6 |
| O1W—Cd1—O2W | 87.65 (6) | Cd1—O1—H1O | 132.6 |
| O2—Cd1—O2W | 94.38 (5) | O1—C1—C2 | 109.54 (15) |
| O4—Cd1—O3$^i$ | 92.14 (8) | O1—C1—H1A | 109.8 |
| O1W—Cd1—O3$^i$ | 127.91 (5) | C2—C1—H1A | 109.8 |
| O2—Cd1—O3$^i$ | 80.02 (5) | O1—C1—H1B | 109.7 |
| O2W—Cd1—O3$^i$ | 84.91 (6) | C2—C1—H1B | 109.8 |
| O4—Cd1—O1 | 97.23 (7) | H1A—C1—H1B | 108.2 |
| O1W—Cd1—O1 | 83.68 (5) | O2—C2—O3 | 121.68 (18) |
| O2—Cd1—O1 | 68.45 (5) | O2—C2—C1 | 120.37 (17) |
| O2W—Cd1—O1 | 89.87 (6) | O3—C2—C1 | 117.95 (17) |
| O3$^i$—Cd1—O1 | 147.55 (5) | C2—O2—Cd1 | 120.32 (12) |
| O4—Cd1—O2$^i$ | 81.27 (6) | C2—O2—Cd1$^{ii}$ | 86.96 (11) |
| O1W—Cd1—O2$^i$ | 76.21 (5) | Cd1—O2—Cd1$^{ii}$ | 150.69 (6) |

| | | | |
|---|---|---|---|
| O2—Cd1—O2$^i$ | 131.594 (18) | S1—O4—Cd1 | 139.34 (10) |
| O2W—Cd1—O2$^i$ | 90.02 (5) | O5—S1—O5$^{iii}$ | 108.34 (13) |
| O3$^i$—Cd1—O2$^i$ | 52.37 (4) | O5—S1—O4$^{iii}$ | 109.84 (12) |
| O1—Cd1—O2$^i$ | 159.88 (5) | O5$^{iii}$—S1—O4$^{iii}$ | 112.05 (13) |
| Cd1—O1W—H2W | 113.6 | O5—S1—O4 | 112.05 (13) |
| Cd1—O1W—H1W | 128.1 | O5$^{iii}$—S1—O4 | 109.84 (12) |
| H2W—O1W—H1W | 109.5 | O4$^{iii}$—S1—O4 | 104.74 (14) |
| Cd1—O2W—H4W | 109.2 | C2—O3—Cd1$^{ii}$ | 98.98 (12) |
| | | | |
| O4—Cd1—O1—C1 | 74.77 (15) | O2$^i$—Cd1—O2—C2 | −163.19 (14) |
| O1W—Cd1—O1—C1 | 161.19 (16) | O4—Cd1—O2—Cd1$^{ii}$ | 74.85 (14) |
| O2—Cd1—O1—C1 | −16.41 (14) | O1W—Cd1—O2—Cd1$^{ii}$ | 166.05 (11) |
| O2W—Cd1—O1—C1 | −111.16 (15) | O2W—Cd1—O2—Cd1$^{ii}$ | −100.72 (13) |
| O3$^i$—Cd1—O1—C1 | −30.9 (2) | O3$^i$—Cd1—O2—Cd1$^{ii}$ | −16.67 (13) |
| O2$^i$—Cd1—O1—C1 | 159.13 (13) | O1—Cd1—O2—Cd1$^{ii}$ | 171.15 (15) |
| Cd1—O1—C1—C2 | 16.3 (2) | O2$^i$—Cd1—O2—Cd1$^{ii}$ | −6.79 (12) |
| O1—C1—C2—O2 | −3.4 (2) | O1W—Cd1—O4—S1 | −144.9 (2) |
| O1—C1—C2—O3 | 177.33 (17) | O2—Cd1—O4—S1 | 7.1 (2) |
| O3—C2—O2—Cd1 | 167.52 (14) | O3$^i$—Cd1—O4—S1 | 87.2 (2) |
| C1—C2—O2—Cd1 | −11.7 (2) | O1—Cd1—O4—S1 | −61.6 (2) |
| O3—C2—O2—Cd1$^{ii}$ | −1.16 (18) | O2$^i$—Cd1—O4—S1 | 138.6 (2) |
| C1—C2—O2—Cd1$^{ii}$ | 179.64 (15) | Cd1—O4—S1—O5 | −57.4 (2) |
| O4—Cd1—O2—C2 | −81.55 (15) | Cd1—O4—S1—O5$^{iii}$ | 63.0 (2) |
| O1W—Cd1—O2—C2 | 9.6 (2) | Cd1—O4—S1—O4$^{iii}$ | −176.5 (3) |
| O2W—Cd1—O2—C2 | 102.89 (14) | O2—C2—O3—Cd1$^{ii}$ | 1.3 (2) |
| O3$^i$—Cd1—O2—C2 | −173.07 (15) | C1—C2—O3—Cd1$^{ii}$ | −179.48 (13) |
| O1—Cd1—O2—C2 | 14.76 (13) | | |

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*, *y*, −*z*+1/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*···O2*W*$^{iv}$ | 0.85 | 1.94 | 2.784 (2) | 170 |
| O1*W*—H2w···O3$^v$ | 0.85 | 1.88 | 2.723 (2) | 172 |
| O2*W*—H3*W*···O3*W* | 0.85 | 1.88 | 2.720 (2) | 172 |
| O2*W*—H4*W*···O5$^i$ | 0.85 | 1.82 | 2.648 (2) | 162 |
| O1—H1*O*···O5$^{vi}$ | 0.85 | 1.81 | 2.659 (2) | 175 |
| O3*W*—H5*W*···O4$^{vii}$ | 0.85 | 2.25 | 2.813 (3) | 124 |

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1/2, −*y*+3/2, −*z*; (v) *x*, *y*−1, *z*; (vi) *x*, −*y*+2, *z*−1/2; (vii) *x*+1/2, *y*+1/2, *z*.