

## Bis( $\mu$ -2,4-dihydroxybenzoato- $\kappa^2$ O:O')-bis[aqua(2,4-dihydroxybenzoato- $\kappa$ O)-(1,10-phenanthroline- $\kappa^2$ N,N')-cadmium(II)]

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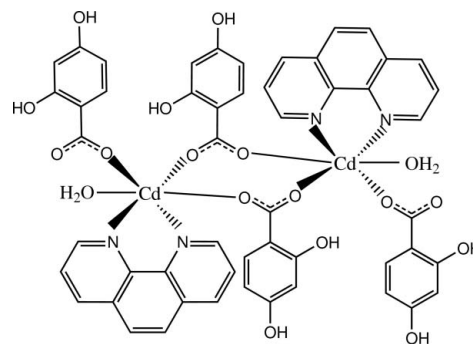
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; disorder in main residue;  $R$  factor = 0.028;  $wR$  factor = 0.067; data-to-parameter ratio = 13.0.

In the title centrosymmetric dimeric  $\text{Cd}^{\text{II}}$  complex,  $[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_4)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$ , the  $\text{Cd}^{\text{II}}$  cation is coordinated by a bidentate phenanthroline (phen) ligand, three dihydroxybenzoate (dhba) anions and one water molecule in a distorted  $\text{CdN}_2\text{O}_4$  octahedral geometry. Among the dhba anions, two anions bridge two  $\text{Cd}^{\text{II}}$  cations to form the dimeric complex with significant different  $\text{Cd}-\text{O}$  bond distances of 2.2215 (19) and 2.406 (2) Å. The centroid-centroid distance of 3.4615 (19) Å between two nearly parallel benzene rings of the dhba and phen ligands coordinating to the same  $\text{Cd}^{\text{II}}$  cation indicates the existence of intramolecular  $\pi-\pi$  stacking in the complex. Extensive  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding and intermolecular weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding help to stabilize the crystal structure. One hydroxy group of the monodentate dhba ligand is disordered over two sites with a site-occupancy ratio of 0.9:0.1.

### Related literature

For the correlation between  $\pi-\pi$  stacking and electron-transfer processes in some biological systems, see: Deisenhofer & Michel (1989). For general background to  $\pi-\pi$  stacking, see: Li *et al.* (2005). For  $\pi-\pi$  stacking involving a dihydroxybenzoate ligand in an Ni complex, see: Yang *et al.* (2006). Intramolecular  $\pi-\pi$  stacking was previously observed in a Sr complex with a hydroxybenzoate ligand, see: Su *et al.* (2005).



### Experimental

#### Crystal data

$[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_4)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$	$V = 2331.4$ (11) Å <sup>3</sup>
$M_r = 1233.68$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.899$ (4) Å	$\mu = 1.00$ mm <sup>-1</sup>
$b = 6.874$ (2) Å	$T = 296$ K
$c = 23.400$ (6) Å	$0.26 \times 0.17 \times 0.11$ mm
$\beta = 103.378$ (2)°	

#### Data collection

Rigaku R-Axis RAPID diffractometer	19273 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	4654 independent reflections
$T_{\text{min}} = 0.758$ , $T_{\text{max}} = 0.890$	4015 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.067$	$\Delta\rho_{\text{max}} = 0.66$ e Å <sup>-3</sup>
$S = 1.11$	$\Delta\rho_{\text{min}} = -0.38$ e Å <sup>-3</sup>
4654 reflections	
358 parameters	
3 restraints	

**Table 1**

Selected bond lengths (Å).

Cd—N1	2.326 (2)	Cd—O5	2.406 (2)
Cd—N2	2.324 (2)	Cd—O6 <sup>i</sup>	2.2215 (19)
Cd—O1	2.215 (2)	Cd—O9	2.361 (2)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H3A <sup>ii</sup> ···O2	0.82	1.81	2.540 (3)	148
O3'—H3B <sup>iii</sup> ···O1	0.82	1.56	2.332 (19)	156
O4—H4A <sup>iii</sup> ···O7 <sup>iii</sup>	0.82	1.91	2.719 (3)	172
O7—H7A <sup>iii</sup> ···O6	0.82	1.80	2.523 (3)	147
O8—H8A <sup>iii</sup> ···O3 <sup>iii</sup>	0.82	1.94	2.752 (3)	169
O9—H9A <sup>iii</sup> ···O2	0.86 (1)	1.97 (2)	2.738 (3)	148 (3)
O9—H9B <sup>iii</sup> ···O5 <sup>iv</sup>	0.86 (1)	2.03 (2)	2.842 (3)	158 (3)
C24—H24 <sup>iii</sup> ···O5 <sup>i</sup>	0.93	2.58	3.433 (4)	152

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2775).

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**supplementary materials**

*Acta Cryst.* (2010). E66, m760-m761 [ doi:10.1107/S1600536810021252 ]

**Bis( $\mu$ -2,4-dihydroxybenzoato- $\kappa^2O:O'$ )bis[aqua(2,4-dihydroxybenzoato- $\kappa O$ )(1,10-phenanthroline- $\kappa^2N,N'$ )cadmium(II)]**

**J.-J. Nie, T.-T. Pan, J.-R. Su and D.-J. Xu**

**Comment**

The  $\pi$ - $\pi$  stacking between aromatic rings is an important non-covalent interaction and correlated with the electron transfer process in some biological systems (Deisenhofer & Michel, 1989). As a continuous work of the series investigation on the nature of  $\pi$ - $\pi$  stacking (Li *et al.*, 2005), we prepared the title Cd<sup>II</sup> complex which contains a double-hydroxy substituted benzoate ligand. We present here its crystal structure to compare with those incorporating monohydroxybenzoate ligand and to show the effect of hydroxy substitution on the benzene ring to  $\pi$ - $\pi$  stacking between aromatic rings.

The molecular structure of the title compound is shown in Fig. 1. The dimeric Cd<sup>II</sup> complex locates across on an inversion center. Each Cd<sup>II</sup> atom is coordinated by one phenanthroline (phen), one water molecule and three dihydroxybenzoate (dhba) dianions in a distorted octahedral geometry (Table 1). The C1-containing dhba is monodentately coordinated to a Cd<sup>II</sup> atom and is well coplanar with the Cd atom [the maximum atomic deviation 0.071 (3) Å (Cd)] while the C8-containing dhba bridges two Cd atoms to form the dimeric complex.

It is notable that intra-molecular  $\pi$ - $\pi$  stacking exists in the dimeric complex. Partially overlapped arrangement between nearly parallel C9-containing benzene ring and phen ring system [dihedral angle 6.56°] is observed in the molecular structure; the shorter centroids distance of 3.4615 (19) Å between C9-benzene and C19-benzene rings suggests the existence of intramolecular  $\pi$ - $\pi$  stacking. The perpendicular distance of centroid of C9-benzene ring on C19-benzene ring and perpendicular distance of centroid of C19-benzene ring on C9-benzene ring are 3.365 and 3.388 Å. Intra-molecular  $\pi$ - $\pi$  stacking was previously observed in a Sr<sup>II</sup> complex with hydroxybenzoate ligand (Su *et al.*, 2007).  $\pi$ - $\pi$  stacking involving dhba ligand in a Ni<sup>II</sup> complex was reported by Yang *et al.* (2006).

Intermolecular  $\pi$ - $\pi$  stacking is also present in the crystal structure; the centroid distance between C9-ring and C19<sup>i</sup>-ring is 3.754 (2) Å [symmetry code: (i)  $x, -1 + y, z$ ] (Fig. 2).

Extensive O—H $\cdots$ O hydrogen bonding and intermolecular weak C—H $\cdots$ O hydrogen bonding (Table 2) help to stabilize the crystal structure.

**Experimental**

CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.46 g, 2 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.21 g, 2 mmol) and 2,4-dihydroxybenzoic acid (0.31 g, 2 mmol) was dissolved in a water/ethanol solution (20 ml, 1:3); then phenanthroline (0.36 g, 2 mmol) was added to above solution. The mixture was refluxed for 3 h, and then filtered after cooling to room temperature. Colorless single crystals of the title compound were obtained after one week.

## Refinement

One hydroxy group of C1-containing dhba ligand is disordered, site occupancies for O3 and O3' atoms were initially refined and converged to 0.895 (3) and 0.105 (3), they were fixed as 0.9 and 0.1 respectively in the final refinement. Water H atoms were located in a difference Fourier map and refined with O—H distance restrains,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . Other H atoms were placed in calculated positions with O—H = 0.82 and C—H = 0.93 Å, and refined in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O}, \text{C})$ . In the final refinement the C6—C7 distance was constrained to be 1.38±0.01 Å.

## Figures

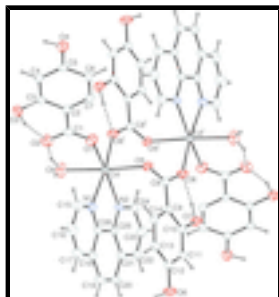


Fig. 1. The dimeric molecular structure of the title complex with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). The minor disordered component is omitted for clarity. Dashed lines indicate intramolecular hydrogen bonding [symmetry code: (i) 1 - x, 1 - y, 1 - z].

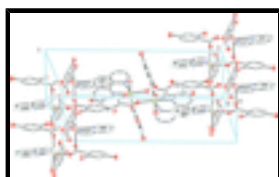


Fig. 2. The unit cell packing showing intermolecular  $\pi$ - $\pi$  stacking between dhba and phen rings.

## Bis( $\mu$ -2,4-dihydroxybenzoato- $\kappa^2\text{O}:\text{O}'$ )bis[aqua(2,4-dihydroxybenzoato- $\kappa\text{O}$ )(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$ )]cadmium(II)

### Crystal data

$[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_4)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]$

$M_r = 1233.68$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 14.899$  (4) Å

$b = 6.874$  (2) Å

$c = 23.400$  (6) Å

$\beta = 103.378$  (2)°

$V = 2331.4$  (11) Å<sup>3</sup>

$Z = 2$

$F(000) = 1240$

$D_x = 1.757$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 15860 reflections

$\theta = 3.1$ – $26.0$ °

$\mu = 1.00$  mm<sup>-1</sup>

$T = 296$  K

Prism, colorless

$0.26 \times 0.17 \times 0.11$  mm

### Data collection

Rigaku R-Axis RAPID  
diffractometer

4654 independent reflections

Radiation source: fine-focus sealed tube graphite	4015 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.031$
Detector resolution: 10.0 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 26.1^\circ$ , $\theta_{\text{min}} = 3.1^\circ$
$\omega$ scans	$h = -18 \rightarrow 18$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -8 \rightarrow 8$
$T_{\text{min}} = 0.758$ , $T_{\text{max}} = 0.890$	$l = -29 \rightarrow 29$
19273 measured reflections	

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.067$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.11$	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 1.5199P]$ where $P = (F_o^2 + 2F_c^2)/3$
4654 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
358 parameters	$\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cd	0.397190 (12)	0.67327 (3)	0.425111 (8)	0.03048 (7)	
N1	0.37208 (16)	0.6779 (3)	0.32325 (9)	0.0369 (5)	
N2	0.53505 (15)	0.7623 (3)	0.40192 (9)	0.0329 (5)	
O1	0.25877 (13)	0.5555 (3)	0.42507 (10)	0.0534 (6)	
O2	0.16636 (15)	0.8085 (3)	0.39648 (12)	0.0592 (6)	
O3	-0.00646 (15)	0.7698 (3)	0.38480 (10)	0.0421 (5)	0.90
H3A	0.0419	0.8218	0.3821	0.063*	0.90
O3'	0.2006 (13)	0.254 (3)	0.4445 (9)	0.040 (4)	0.10
H3B	0.2343	0.3426	0.4388	0.060*	0.10

## supplementary materials

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O4	-0.11493 (14)	0.1736 (3)	0.44782 (11)	0.0531 (5)	
H4A	-0.1643	0.2313	0.4387	0.080*	
O5	0.44142 (12)	0.3360 (3)	0.43181 (8)	0.0376 (4)	
O6	0.58823 (14)	0.2947 (3)	0.47871 (8)	0.0465 (5)	
O7	0.71417 (12)	0.3368 (3)	0.42386 (8)	0.0453 (5)	
H7A	0.6910	0.3342	0.4524	0.068*	
O8	0.63878 (16)	0.2938 (4)	0.21875 (9)	0.0554 (6)	
H8A	0.5953	0.2774	0.1905	0.083*	
O9	0.33412 (15)	0.9899 (3)	0.41432 (12)	0.0584 (6)	
H9A	0.2763 (6)	0.977 (6)	0.4129 (16)	0.070*	
H9B	0.353 (3)	1.1085 (18)	0.4142 (16)	0.070*	
C1	0.18095 (18)	0.6359 (5)	0.41415 (12)	0.0408 (7)	
C2	0.10138 (17)	0.5164 (4)	0.42243 (10)	0.0324 (5)	
C3	0.01181 (18)	0.5888 (4)	0.40876 (11)	0.0330 (6)	
H3	0.0011	0.7142	0.3939	0.040*	0.10
C4	-0.06174 (17)	0.4778 (4)	0.41683 (11)	0.0350 (6)	
H4	-0.1212	0.5289	0.4077	0.042*	
C5	-0.04658 (18)	0.2906 (4)	0.43854 (12)	0.0349 (6)	
C6	0.04272 (16)	0.2132 (4)	0.45253 (13)	0.0386 (6)	
H6	0.0532	0.0874	0.4672	0.046*	
C7	0.11485 (15)	0.3269 (4)	0.44412 (11)	0.0366 (6)	
H7	0.1742	0.2758	0.4532	0.044*	0.90
C8	0.52452 (18)	0.3071 (4)	0.43170 (11)	0.0314 (5)	
C9	0.55409 (17)	0.2915 (3)	0.37581 (11)	0.0295 (5)	
C10	0.64719 (18)	0.3133 (4)	0.37392 (11)	0.0338 (5)	
C11	0.67359 (19)	0.3138 (4)	0.32113 (12)	0.0412 (6)	
H11	0.7354	0.3295	0.3206	0.049*	
C12	0.6079 (2)	0.2908 (4)	0.26885 (12)	0.0384 (6)	
C13	0.5157 (2)	0.2642 (4)	0.26956 (12)	0.0378 (6)	
H13	0.4717	0.2452	0.2347	0.045*	
C14	0.49017 (18)	0.2662 (4)	0.32251 (12)	0.0343 (6)	
H14	0.4283	0.2501	0.3227	0.041*	
C15	0.2934 (2)	0.6307 (5)	0.28578 (13)	0.0469 (7)	
H15	0.2427	0.5985	0.3007	0.056*	
C16	0.2839 (3)	0.6274 (5)	0.22552 (14)	0.0568 (9)	
H16	0.2281	0.5924	0.2006	0.068*	
C17	0.3582 (3)	0.6768 (5)	0.20315 (13)	0.0541 (8)	
H17	0.3529	0.6768	0.1628	0.065*	
C18	0.4424 (2)	0.7273 (4)	0.24132 (12)	0.0425 (7)	
C19	0.5236 (3)	0.7702 (5)	0.22142 (14)	0.0523 (8)	
H19	0.5212	0.7717	0.1813	0.063*	
C20	0.6036 (3)	0.8083 (5)	0.25983 (15)	0.0525 (8)	
H20	0.6557	0.8362	0.2458	0.063*	
C21	0.6106 (2)	0.8070 (4)	0.32217 (13)	0.0404 (6)	
C22	0.6939 (2)	0.8440 (5)	0.36345 (15)	0.0512 (8)	
H22	0.7474	0.8713	0.3509	0.061*	
C23	0.6955 (2)	0.8396 (5)	0.42162 (15)	0.0502 (8)	
H23	0.7498	0.8653	0.4493	0.060*	
C24	0.6148 (2)	0.7962 (4)	0.43937 (13)	0.0420 (7)	

H24	0.6170	0.7908	0.4794	0.050*
C25	0.53247 (19)	0.7677 (4)	0.34348 (11)	0.0325 (6)
C26	0.4460 (2)	0.7251 (4)	0.30205 (11)	0.0337 (6)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd	0.02787 (10)	0.03859 (11)	0.02644 (10)	-0.00149 (8)	0.00929 (7)	0.00251 (8)
N1	0.0418 (12)	0.0401 (12)	0.0289 (11)	-0.0037 (11)	0.0084 (9)	-0.0006 (10)
N2	0.0353 (12)	0.0348 (11)	0.0296 (11)	-0.0047 (9)	0.0100 (9)	0.0011 (9)
O1	0.0253 (10)	0.0670 (14)	0.0680 (14)	-0.0048 (10)	0.0112 (9)	0.0102 (12)
O2	0.0403 (12)	0.0583 (14)	0.0801 (16)	-0.0100 (10)	0.0161 (11)	0.0206 (13)
O3	0.0364 (12)	0.0399 (12)	0.0486 (13)	-0.0017 (9)	0.0067 (10)	0.0083 (10)
O3'	0.029 (9)	0.031 (9)	0.064 (13)	0.004 (8)	0.016 (9)	0.006 (9)
O4	0.0311 (10)	0.0518 (12)	0.0791 (15)	-0.0038 (9)	0.0182 (10)	0.0162 (12)
O5	0.0328 (10)	0.0374 (10)	0.0479 (11)	-0.0010 (8)	0.0202 (8)	0.0007 (9)
O6	0.0390 (11)	0.0724 (15)	0.0296 (10)	0.0036 (10)	0.0107 (8)	-0.0020 (10)
O7	0.0266 (9)	0.0754 (14)	0.0338 (10)	-0.0018 (10)	0.0067 (8)	-0.0044 (10)
O8	0.0514 (13)	0.0872 (17)	0.0321 (10)	-0.0028 (12)	0.0187 (9)	-0.0037 (11)
O9	0.0403 (12)	0.0381 (11)	0.0909 (17)	-0.0028 (10)	0.0029 (12)	0.0015 (12)
C1	0.0298 (14)	0.0571 (19)	0.0354 (14)	-0.0078 (13)	0.0073 (11)	0.0004 (13)
C2	0.0264 (12)	0.0460 (15)	0.0249 (11)	-0.0032 (11)	0.0062 (10)	-0.0005 (11)
C3	0.0326 (13)	0.0366 (13)	0.0290 (12)	0.0004 (11)	0.0054 (10)	0.0004 (11)
C4	0.0230 (12)	0.0472 (16)	0.0351 (13)	0.0031 (11)	0.0077 (10)	0.0008 (12)
C5	0.0297 (13)	0.0415 (15)	0.0352 (13)	-0.0050 (11)	0.0112 (11)	-0.0012 (12)
C6	0.0342 (14)	0.0377 (16)	0.0445 (15)	0.0029 (11)	0.0103 (12)	0.0067 (12)
C7	0.0238 (12)	0.0508 (16)	0.0348 (13)	0.0049 (12)	0.0057 (10)	0.0010 (13)
C8	0.0352 (14)	0.0268 (12)	0.0344 (13)	-0.0023 (11)	0.0127 (11)	0.0006 (10)
C9	0.0302 (13)	0.0291 (13)	0.0303 (12)	0.0017 (10)	0.0095 (10)	0.0008 (10)
C10	0.0299 (13)	0.0385 (14)	0.0329 (13)	-0.0012 (11)	0.0073 (10)	0.0013 (11)
C11	0.0332 (14)	0.0554 (17)	0.0382 (14)	-0.0019 (13)	0.0151 (12)	-0.0014 (13)
C12	0.0438 (16)	0.0425 (16)	0.0328 (14)	0.0027 (12)	0.0166 (12)	0.0010 (12)
C13	0.0397 (15)	0.0419 (15)	0.0291 (13)	0.0041 (12)	0.0026 (11)	-0.0043 (12)
C14	0.0290 (13)	0.0365 (14)	0.0367 (14)	0.0006 (11)	0.0061 (11)	-0.0024 (11)
C15	0.0464 (17)	0.0512 (18)	0.0398 (15)	-0.0067 (14)	0.0027 (13)	-0.0059 (14)
C16	0.061 (2)	0.063 (2)	0.0383 (16)	-0.0058 (17)	-0.0045 (15)	-0.0064 (15)
C17	0.081 (2)	0.0488 (17)	0.0279 (14)	0.0025 (17)	0.0036 (15)	-0.0025 (13)
C18	0.069 (2)	0.0309 (14)	0.0298 (14)	0.0020 (13)	0.0174 (14)	0.0001 (11)
C19	0.083 (3)	0.0474 (18)	0.0335 (15)	0.0018 (17)	0.0284 (16)	0.0039 (13)
C20	0.068 (2)	0.0501 (18)	0.0532 (19)	0.0054 (16)	0.0422 (18)	0.0091 (15)
C21	0.0474 (16)	0.0354 (14)	0.0449 (16)	0.0050 (13)	0.0239 (13)	0.0077 (12)
C22	0.0439 (17)	0.0514 (18)	0.065 (2)	0.0025 (14)	0.0273 (15)	0.0150 (16)
C23	0.0346 (15)	0.0570 (19)	0.0565 (19)	-0.0060 (14)	0.0057 (13)	0.0112 (16)
C24	0.0410 (15)	0.0470 (17)	0.0367 (14)	-0.0058 (13)	0.0063 (12)	0.0069 (13)
C25	0.0439 (15)	0.0260 (12)	0.0311 (13)	0.0001 (11)	0.0162 (12)	0.0037 (10)
C26	0.0464 (16)	0.0259 (13)	0.0295 (13)	0.0000 (11)	0.0100 (11)	0.0012 (10)



## supplementary materials

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### *Geometric parameters (Å, °)*

Cd—N1	2.326 (2)	C5—C6	1.400 (4)
Cd—N2	2.324 (2)	C6—C7	1.379 (4)
Cd—O1	2.215 (2)	C6—H6	0.9300
Cd—O5	2.406 (2)	C7—H7	0.9300
Cd—O6 <sup>i</sup>	2.2215 (19)	C8—C9	1.477 (3)
Cd—O9	2.361 (2)	C9—C14	1.394 (4)
N1—C15	1.331 (4)	C9—C10	1.406 (4)
N1—C26	1.348 (4)	C10—C11	1.380 (4)
N2—C24	1.324 (3)	C11—C12	1.388 (4)
N2—C25	1.360 (3)	C11—H11	0.9300
O1—C1	1.256 (3)	C12—C13	1.390 (4)
O2—C1	1.258 (4)	C13—C14	1.378 (4)
O3—C3	1.366 (3)	C13—H13	0.9300
O3—H3A	0.8200	C14—H14	0.9300
O3'—C7	1.370 (18)	C15—C16	1.384 (4)
O3'—H3B	0.8200	C15—H15	0.9300
O4—C5	1.354 (3)	C16—C17	1.373 (5)
O4—H4A	0.8200	C16—H16	0.9300
O5—C8	1.254 (3)	C17—C18	1.404 (5)
O6—C8	1.279 (3)	C17—H17	0.9300
O6—Cd <sup>i</sup>	2.222 (2)	C18—C26	1.410 (4)
O7—C10	1.359 (3)	C18—C19	1.425 (5)
O7—H7A	0.8200	C19—C20	1.342 (5)
O8—C12	1.355 (3)	C19—H19	0.9300
O8—H8A	0.8200	C20—C21	1.438 (4)
O9—H9A	0.860 (11)	C20—H20	0.9300
O9—H9B	0.862 (14)	C21—C25	1.395 (4)
C1—C2	1.491 (4)	C21—C22	1.407 (4)
C2—C3	1.390 (4)	C22—C23	1.356 (5)
C2—C7	1.395 (4)	C22—H22	0.9300
C3—C4	1.384 (4)	C23—C24	1.392 (4)
C3—H3	0.9300	C23—H23	0.9300
C4—C5	1.382 (4)	C24—H24	0.9300
C4—H4	0.9300	C25—C26	1.452 (4)
O1—Cd—O6 <sup>i</sup>	84.81 (8)	O5—C8—O6	123.0 (2)
O1—Cd—N2	165.66 (8)	O5—C8—C9	120.7 (2)
O6 <sup>i</sup> —Cd—N2	109.02 (8)	O6—C8—C9	116.3 (2)
O1—Cd—N1	94.34 (8)	C14—C9—C10	117.4 (2)
O6 <sup>i</sup> —Cd—N1	172.63 (8)	C14—C9—C8	121.3 (2)
N2—Cd—N1	72.45 (8)	C10—C9—C8	121.2 (2)
O1—Cd—O9	89.40 (8)	O7—C10—C11	117.7 (2)
O6 <sup>i</sup> —Cd—O9	87.72 (9)	O7—C10—C9	121.3 (2)
N2—Cd—O9	94.81 (8)	C11—C10—C9	121.1 (2)
N1—Cd—O9	84.96 (9)	C10—C11—C12	120.0 (3)
O1—Cd—O5	83.61 (8)	C10—C11—H11	120.0

O6 <sup>i</sup> —Cd—O5	93.93 (7)	C12—C11—H11	120.0
N2—Cd—O5	91.45 (7)	O8—C12—C11	116.7 (3)
N1—Cd—O5	93.25 (7)	O8—C12—C13	123.1 (3)
O9—Cd—O5	172.64 (7)	C11—C12—C13	120.1 (2)
C15—N1—C26	119.1 (2)	C14—C13—C12	119.2 (2)
C15—N1—Cd	125.4 (2)	C14—C13—H13	120.4
C26—N1—Cd	115.42 (17)	C12—C13—H13	120.4
C24—N2—C25	118.2 (2)	C13—C14—C9	122.2 (2)
C24—N2—Cd	126.73 (18)	C13—C14—H14	118.9
C25—N2—Cd	114.91 (17)	C9—C14—H14	118.9
C1—O1—Cd	130.9 (2)	N1—C15—C16	122.8 (3)
C3—O3—H3A	109.5	N1—C15—H15	118.6
C7—O3'—H3B	109.5	C16—C15—H15	118.6
C5—O4—H4A	109.5	C17—C16—C15	118.9 (3)
C8—O5—Cd	114.07 (16)	C17—C16—H16	120.6
C8—O6—Cd <sup>i</sup>	138.08 (18)	C15—C16—H16	120.6
C10—O7—H7A	109.5	C16—C17—C18	119.9 (3)
C12—O8—H8A	109.5	C16—C17—H17	120.0
Cd—O9—H9A	106 (3)	C18—C17—H17	120.0
Cd—O9—H9B	139 (3)	C17—C18—C26	117.3 (3)
H9A—O9—H9B	115 (4)	C17—C18—C19	123.0 (3)
O1—C1—O2	124.3 (3)	C26—C18—C19	119.6 (3)
O1—C1—C2	117.0 (3)	C20—C19—C18	120.8 (3)
O2—C1—C2	118.7 (3)	C20—C19—H19	119.6
C3—C2—C7	117.9 (2)	C18—C19—H19	119.6
C3—C2—C1	121.5 (3)	C19—C20—C21	121.5 (3)
C7—C2—C1	120.7 (2)	C19—C20—H20	119.2
O3—C3—C4	118.0 (2)	C21—C20—H20	119.2
O3—C3—C2	120.7 (2)	C25—C21—C22	117.7 (3)
C4—C3—C2	121.3 (2)	C25—C21—C20	119.5 (3)
C4—C3—H3	119.3	C22—C21—C20	122.7 (3)
C2—C3—H3	119.3	C23—C22—C21	119.5 (3)
C5—C4—C3	119.7 (2)	C23—C22—H22	120.2
C5—C4—H4	120.1	C21—C22—H22	120.2
C3—C4—H4	120.1	C22—C23—C24	119.2 (3)
O4—C5—C4	123.1 (2)	C22—C23—H23	120.4
O4—C5—C6	116.5 (2)	C24—C23—H23	120.4
C4—C5—C6	120.4 (2)	N2—C24—C23	123.0 (3)
C7—C6—C5	118.7 (2)	N2—C24—H24	118.5
C7—C6—H6	120.6	C23—C24—H24	118.5
C5—C6—H6	120.6	N2—C25—C21	122.2 (3)
O3'—C7—C6	123.2 (8)	N2—C25—C26	118.7 (2)
O3'—C7—C2	113.5 (8)	C21—C25—C26	119.1 (2)
C6—C7—C2	122.0 (2)	N1—C26—C18	122.0 (3)
C6—C7—H7	119.0	N1—C26—C25	118.5 (2)
C2—C7—H7	119.0	C18—C26—C25	119.5 (3)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ .

## supplementary materials

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### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A $\cdots$ O2	0.82	1.81	2.540 (3)	148
O3'—H3B $\cdots$ O1	0.82	1.56	2.332 (19)	156
O4—H4A $\cdots$ O7 <sup>ii</sup>	0.82	1.91	2.719 (3)	172
O7—H7A $\cdots$ O6	0.82	1.80	2.523 (3)	147
O8—H8A $\cdots$ O3 <sup>iii</sup>	0.82	1.94	2.752 (3)	169
O9—H9A $\cdots$ O2	0.86 (1)	1.97 (2)	2.738 (3)	148 (3)
O9—H9B $\cdots$ O5 <sup>iv</sup>	0.86 (1)	2.03 (2)	2.842 (3)	158 (3)
C24—H24 $\cdots$ O5 <sup>i</sup>	0.93	2.58	3.433 (4)	152

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



Fig. 2

