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## Structure Reports

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# Bis[2-hydroxy-*N'*-(2-hydroxybenzoyl)-benzohydrazitato]dipyridinecadmium(II)

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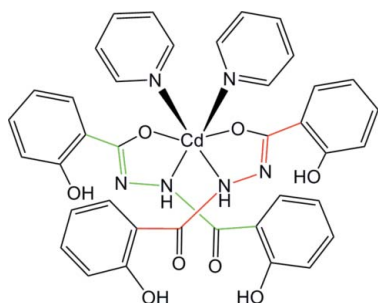
Received 8 August 2008; accepted 22 October 2008

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.027;  $wR$  factor = 0.071; data-to-parameter ratio = 13.1.

The title complex,  $[\text{Cd}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})_2]$ , exhibits crystallographic twofold symmetry. The  $\text{Cd}^{\text{II}}$  atom is located on the twofold rotation axis and reveals a slightly distorted octahedral coordination defined by four atoms ( $\text{N}_2\text{O}_2$ ) from two symmetry-related chelate ligands and two pyridine N atoms. Intramolecular  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds stabilize the molecular conformation while intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding links molecules into a triad, generating a helix along the threefold screw axis.

## Related literature

Three manganese metallacrowns with unsymmetrical aroylhydrazine ligands were synthesized and reported by Dou *et al.* (2006) and John *et al.* (2006). For the crystal structure of an iron compound with *N,N'*-bis-picolinoyl hydrazine, see: Bernhardt *et al.* (2005). For a nickel complex formed by *N,N'*-disalicyloylhydrazine, see: Chen *et al.* (2007).



## Experimental

### Crystal data

$[\text{Cd}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})_2]$   
 $M_r = 813.10$   
 Trigonal,  $P3_121$   
 $a = 13.0380$  (10) Å

$c = 18.069$  (3) Å  
 $V = 2660.0$  (5) Å<sup>3</sup>  
 $Z = 3$   
 Mo  $K\alpha$  radiation

$\mu = 0.68$  mm<sup>-1</sup>  
 $T = 298$  (2) K

0.40 × 0.38 × 0.35 mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.773$ ,  $T_{\text{max}} = 0.797$

13955 measured reflections  
 3146 independent reflections  
 2750 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.071$   
 $S = 1.00$   
 3146 reflections  
 241 parameters  
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.90$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.32$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1353 Friedel pairs  
 Flack parameter:  $-0.06$  (3)

**Table 1**

Selected bond lengths (Å).

|        |           |        |           |
|--------|-----------|--------|-----------|
| Cd1—N1 | 2.331 (3) | Cd1—O1 | 2.389 (2) |
| Cd1—N3 | 2.337 (3) |        |           |

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$            | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---------------------------------|--------------|--------------------|-------------|----------------------|
| O4—H4 $\cdots$ O3               | 0.82         | 1.92               | 2.638 (4)   | 145                  |
| N2—H2 $\cdots$ O2               | 0.86         | 1.94               | 2.624 (4)   | 135                  |
| O2—H2A $\cdots$ O3 <sup>i</sup> | 0.82         | 1.88               | 2.639 (3)   | 153                  |

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); 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); 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: KP2188).

## References

- Bernhardt, P. V., Chin, P., Sharpe, P. C., Wang, J. C. & Richardson, D. R. (2005). *Biol. Inorg. Chem.* **10**, 761–777.  
 Chen, Y.-T., Dou, J.-M., Li, D.-C., Wang, D.-Q. & Zhu, Y.-H. (2007). *Acta Cryst. E63*, m2503–m2504.  
 Dou, J. M., Liu, M. L., Li, D. C. & Wang, D. Q. (2006). *Eur. J. Inorg. Chem.* **23**, 4866–4871.  
 Flack, H. D. (1983). *Acta Cryst. A39*, 876–881.  
 John, R. P., Park, J., Moon, D., Lee, K. & Lah, M. S. (2006). *Chem. Commun.* pp. 3699–3701.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.  
 Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

## supporting information

*Acta Cryst.* (2008). E64, m1466 [doi:10.1107/S1600536808034533]

**Bis[2-hydroxy-*N'*-(2-hydroxybenzoyl)benzohydrazitato]dipyridinecadmium(II)****Yu-Ting Chen and Da-Cheng Li****S1. Comment**

Metal complexes with aroylhydrazine ligands are of increasing attention due to their interesting chemical activities (John *et al.* 2006; Dou *et al.*, 2006). However, the research on the compounds with symmetrical diaroylhydrazine ligands was limited (Bernhardt *et al.*, 2005; Chen *et al.*, 2007). As an extension of our work on the structural characterization of these compounds, the title complex, (I), is synthesized and characterized by X-ray structure analysis. The complex (I) exhibits a twofold rotation symmetry. It comprises of one Cd<sup>II</sup> atom at special position at the twofold rotation axes coordinated by two ligands and two pyridines (Fig. 1 and Table 1). Each ligand acts as the bidentate via the iminoacyl groups forming two five-membered rings around metal ion with the dihedral angle of 59.71 (4)°.

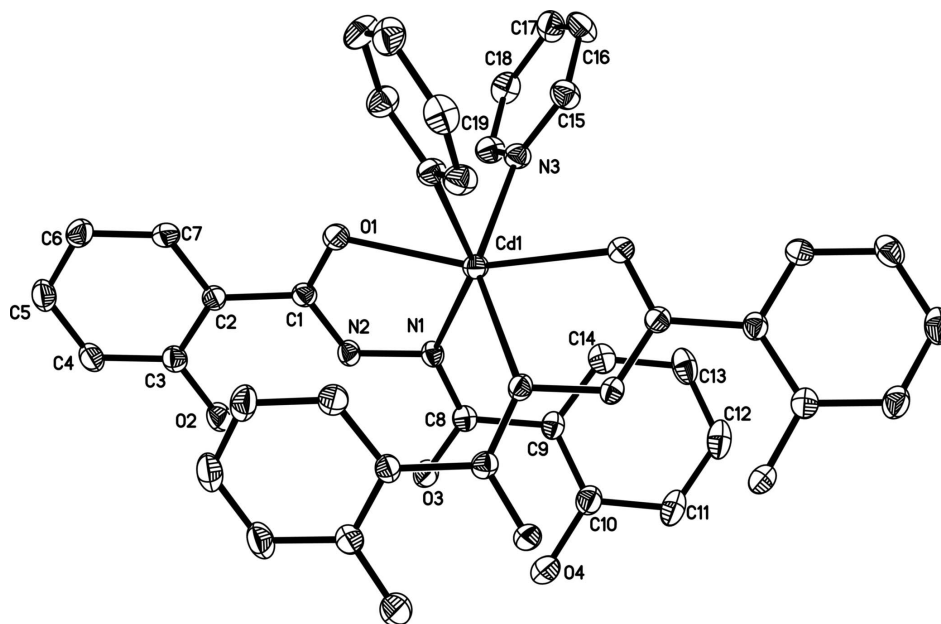
Intramolecular O4—H4···O3 and N2—H2···O2 hydrogen bonds stabilizes the molecular conformation. There is also an intermolecular hydrogen bond O—H···O hydrogen bond [ 2.639 (3) Å] (Table 2) assembling three molecules into a triad, that is a basic structural element of a helix along [0 0 1] direction (Fig. 2).

**S2. Experimental**

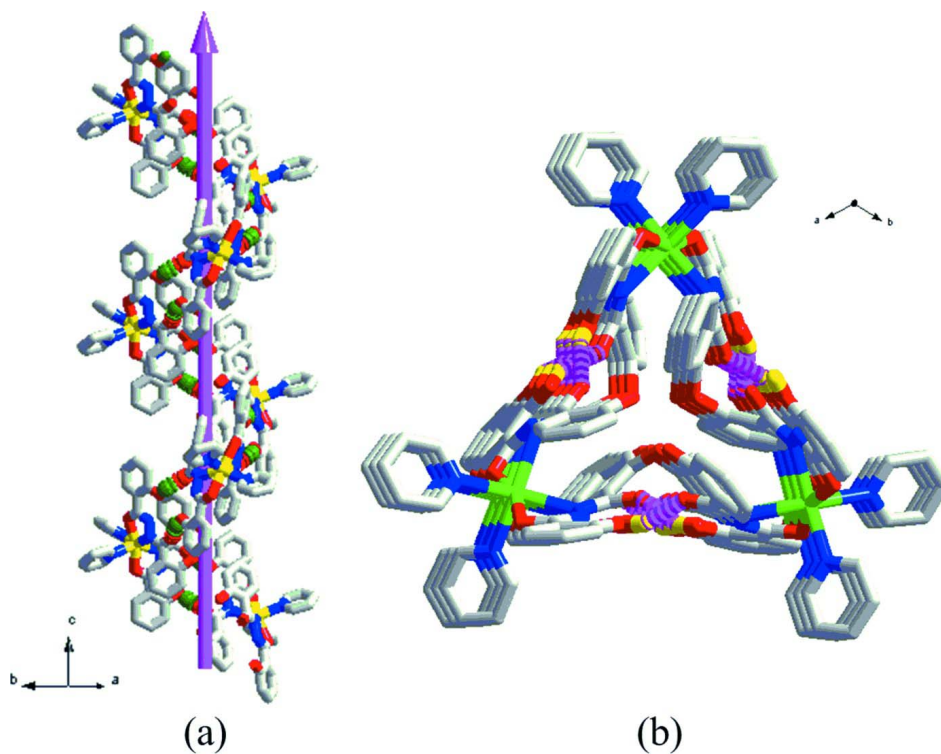
The solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.123 g, 0.4 mmol) in methanol (10 mL) was added to the mixture of 1,2-disalicyloylhydrazine (0.054 g, 0.2 mmol) and sodium hydroxide (0.032 g, 0.8 mmol) in pyridine (10 mL). A colourless solution was generated after stirring for two hours at room temperature. The solution was allowed to stand for 2 weeks, whereupon white block crystals were obtained. Yield: 0.058 g, 77%. m. p. > 573 K. Anal. for C<sub>38</sub>H<sub>32</sub>CdN<sub>6</sub>O<sub>8</sub>: Calc. C, 56.08; H, 3.93; N, 10.33; Found: C, 56.54; H, 3.71; N, 10.54%. The No. of CCDC: 686345.

**S3. Refinement**

All H atoms were placed in geometrically idealized positions and treated as riding on their parent atoms with C(*sp*<sub>2</sub> hybrid)-H distances of 0.93 Å (*U*<sub>iso</sub>(H)=1.2*U*<sub>eq</sub>(C)).

**Figure 1**

The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

Supramolecular structure of the title complex in the direction [001].

**Bis[2-hydroxy-N'-(2-hydroxybenzoyl)benzohydrazitato]dipyridinecadmium(II)***Crystal data*[Cd(C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] $M_r = 813.10$ Trigonal,  $P3_121$  $a = 13.038 (1) \text{ \AA}$  $c = 18.069 (3) \text{ \AA}$  $V = 2660.0 (5) \text{ \AA}^3$  $Z = 3$  $F(000) = 1242$  $D_x = 1.523 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 5141 reflections

 $\theta = 2.9\text{--}22.9^\circ$  $\mu = 0.68 \text{ mm}^{-1}$  $T = 298 \text{ K}$ 

Block, colourless

 $0.40 \times 0.38 \times 0.35 \text{ mm}$ *Data collection*Bruker SMART 1000 CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.773$ ,  $T_{\max} = 0.797$ 

13955 measured reflections

3146 independent reflections

2750 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.033$  $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 1.8^\circ$  $h = -15 \rightarrow 15$  $k = -15 \rightarrow 15$  $l = -21 \rightarrow 10$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.027$  $wR(F^2) = 0.071$  $S = 1.00$ 

3146 reflections

241 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.5675P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.90 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.32 \text{ e \AA}^{-3}$ Absolute structure: Flack (1983), 1353 Friedel  
pairsAbsolute structure parameter:  $-0.06 (3)$ *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 ( $\text{\AA}^2$ )*

|     | $x$        | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|-------------|--------------|----------------------------------|
| Cd1 | 1.0000     | 0.45722 (2) | 0.6667       | 0.04088 (11)                     |
| N1  | 0.8620 (2) | 0.2612 (2)  | 0.69499 (15) | 0.0387 (7)                       |
| N2  | 0.8356 (3) | 0.2467 (3)  | 0.77051 (14) | 0.0406 (6)                       |
| H2  | 0.8005     | 0.1771      | 0.7897       | 0.049*                           |

|     |            |              |              |             |
|-----|------------|--------------|--------------|-------------|
| N3  | 0.8726 (2) | 0.5186 (3)   | 0.61934 (16) | 0.0449 (7)  |
| O1  | 0.9119 (2) | 0.4418 (2)   | 0.78506 (13) | 0.0517 (7)  |
| O2  | 0.7567 (3) | 0.1137 (2)   | 0.88928 (14) | 0.0584 (7)  |
| H2A | 0.7290     | 0.0561       | 0.9170       | 0.088*      |
| O3  | 0.8013 (3) | 0.06392 (19) | 0.69676 (12) | 0.0558 (6)  |
| O4  | 0.9060 (3) | 0.0079 (3)   | 0.59233 (16) | 0.0797 (10) |
| H4  | 0.8760     | 0.0022       | 0.6331       | 0.120*      |
| C1  | 0.8648 (3) | 0.3405 (3)   | 0.81227 (18) | 0.0391 (8)  |
| C2  | 0.8409 (3) | 0.3228 (3)   | 0.89327 (19) | 0.0403 (8)  |
| C3  | 0.7918 (3) | 0.2136 (4)   | 0.9296 (2)   | 0.0454 (9)  |
| C4  | 0.7786 (4) | 0.2086 (4)   | 1.0058 (2)   | 0.0548 (10) |
| H4A | 0.7467     | 0.1360       | 1.0298       | 0.066*      |
| C5  | 0.8122 (4) | 0.3102 (4)   | 1.0464 (2)   | 0.0614 (11) |
| H5  | 0.8012     | 0.3053       | 1.0974       | 0.074*      |
| C6  | 0.8618 (4) | 0.4184 (4)   | 1.0120 (2)   | 0.0556 (10) |
| H6  | 0.8858     | 0.4872       | 1.0393       | 0.067*      |
| C7  | 0.8753 (3) | 0.4233 (3)   | 0.9357 (2)   | 0.0477 (9)  |
| H7  | 0.9085     | 0.4965       | 0.9123       | 0.057*      |
| C8  | 0.8396 (3) | 0.1621 (3)   | 0.66318 (18) | 0.0402 (8)  |
| C9  | 0.8647 (3) | 0.1680 (3)   | 0.58281 (18) | 0.0415 (8)  |
| C10 | 0.9002 (4) | 0.0938 (4)   | 0.5519 (2)   | 0.0547 (10) |
| C11 | 0.9321 (4) | 0.1039 (4)   | 0.4769 (2)   | 0.0687 (13) |
| H11 | 0.9592     | 0.0562       | 0.4568       | 0.082*      |
| C12 | 0.9225 (4) | 0.1852 (4)   | 0.4338 (2)   | 0.0673 (12) |
| H12 | 0.9435     | 0.1926       | 0.3841       | 0.081*      |
| C13 | 0.8832 (4) | 0.2547 (4)   | 0.4624 (2)   | 0.0629 (12) |
| H13 | 0.8754     | 0.3080       | 0.4320       | 0.075*      |
| C14 | 0.8542 (3) | 0.2472 (4)   | 0.5364 (2)   | 0.0516 (9)  |
| H14 | 0.8274     | 0.2958       | 0.5555       | 0.062*      |
| C15 | 0.9145 (4) | 0.6185 (4)   | 0.5806 (2)   | 0.0550 (10) |
| H15 | 0.9942     | 0.6587       | 0.5675       | 0.066*      |
| C16 | 0.8437 (4) | 0.6645 (4)   | 0.5591 (2)   | 0.0636 (12) |
| H16 | 0.8760     | 0.7358       | 0.5334       | 0.076*      |
| C17 | 0.7270 (4) | 0.6045 (4)   | 0.5759 (2)   | 0.0627 (12) |
| H17 | 0.6777     | 0.6335       | 0.5616       | 0.075*      |
| C18 | 0.6827 (3) | 0.5002 (4)   | 0.6144 (2)   | 0.0591 (11) |
| H18 | 0.6026     | 0.4570       | 0.6263       | 0.071*      |
| C19 | 0.7572 (3) | 0.4610 (3)   | 0.6349 (2)   | 0.0535 (9)  |
| H19 | 0.7262     | 0.3903       | 0.6612       | 0.064*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$    |
|-----|-------------|--------------|--------------|--------------|--------------|-------------|
| Cd1 | 0.0445 (2)  | 0.03796 (14) | 0.04239 (18) | 0.02224 (11) | 0.00869 (17) | 0.00434 (9) |
| N1  | 0.0392 (17) | 0.0368 (16)  | 0.0340 (15)  | 0.0144 (14)  | 0.0019 (12)  | 0.0033 (12) |
| N2  | 0.0437 (16) | 0.0396 (16)  | 0.0347 (15)  | 0.0179 (13)  | 0.0072 (13)  | 0.0058 (14) |
| N3  | 0.0448 (18) | 0.0430 (17)  | 0.0494 (17)  | 0.0236 (15)  | 0.0064 (13)  | 0.0045 (14) |
| O1  | 0.0692 (18) | 0.0398 (14)  | 0.0459 (15)  | 0.0271 (13)  | 0.0147 (13)  | 0.0067 (12) |

|     |             |             |             |             |              |              |
|-----|-------------|-------------|-------------|-------------|--------------|--------------|
| O2  | 0.080 (2)   | 0.0438 (15) | 0.0434 (15) | 0.0254 (14) | 0.0077 (13)  | 0.0107 (13)  |
| O3  | 0.0734 (19) | 0.0376 (13) | 0.0493 (14) | 0.0223 (15) | 0.0222 (15)  | 0.0080 (11)  |
| O4  | 0.118 (3)   | 0.081 (2)   | 0.066 (2)   | 0.070 (2)   | 0.0278 (19)  | 0.0082 (17)  |
| C1  | 0.0388 (19) | 0.041 (2)   | 0.041 (2)   | 0.0226 (17) | 0.0035 (16)  | 0.0036 (17)  |
| C2  | 0.042 (2)   | 0.049 (2)   | 0.0364 (18) | 0.0282 (17) | 0.0029 (15)  | 0.0027 (16)  |
| C3  | 0.044 (2)   | 0.056 (2)   | 0.042 (2)   | 0.0290 (18) | 0.0009 (16)  | 0.0031 (18)  |
| C4  | 0.065 (3)   | 0.066 (3)   | 0.042 (2)   | 0.040 (2)   | 0.0030 (19)  | 0.012 (2)    |
| C5  | 0.074 (3)   | 0.092 (4)   | 0.037 (2)   | 0.055 (3)   | 0.005 (2)    | 0.006 (2)    |
| C6  | 0.064 (3)   | 0.073 (3)   | 0.048 (2)   | 0.048 (2)   | -0.0070 (19) | -0.011 (2)   |
| C7  | 0.055 (2)   | 0.049 (2)   | 0.049 (2)   | 0.0344 (19) | 0.0047 (17)  | 0.0020 (17)  |
| C8  | 0.0341 (18) | 0.0382 (17) | 0.0420 (17) | 0.0133 (15) | 0.0033 (15)  | 0.0030 (14)  |
| C9  | 0.038 (2)   | 0.0391 (17) | 0.0363 (16) | 0.0113 (17) | 0.0027 (16)  | -0.0017 (13) |
| C10 | 0.063 (3)   | 0.049 (2)   | 0.047 (2)   | 0.025 (2)   | 0.005 (2)    | -0.0025 (18) |
| C11 | 0.077 (3)   | 0.076 (3)   | 0.046 (2)   | 0.033 (3)   | 0.011 (2)    | -0.011 (2)   |
| C12 | 0.065 (3)   | 0.073 (3)   | 0.039 (2)   | 0.016 (2)   | 0.004 (2)    | -0.006 (2)   |
| C13 | 0.065 (3)   | 0.061 (2)   | 0.040 (2)   | 0.014 (2)   | -0.010 (2)   | 0.0026 (18)  |
| C14 | 0.047 (2)   | 0.044 (2)   | 0.050 (2)   | 0.0129 (17) | -0.0035 (18) | -0.0011 (19) |
| C15 | 0.050 (2)   | 0.056 (2)   | 0.060 (3)   | 0.027 (2)   | 0.0090 (18)  | 0.012 (2)    |
| C16 | 0.069 (3)   | 0.067 (3)   | 0.062 (2)   | 0.040 (2)   | 0.007 (2)    | 0.025 (2)    |
| C17 | 0.065 (3)   | 0.088 (3)   | 0.053 (2)   | 0.051 (3)   | -0.006 (2)   | 0.002 (2)    |
| C18 | 0.041 (2)   | 0.074 (3)   | 0.062 (3)   | 0.028 (2)   | -0.0012 (19) | -0.007 (2)   |
| C19 | 0.048 (2)   | 0.044 (2)   | 0.063 (2)   | 0.0198 (19) | 0.0099 (19)  | 0.0037 (19)  |

*Geometric parameters (Å, °)*

|                     |           |         |           |
|---------------------|-----------|---------|-----------|
| Cd1—N1              | 2.331 (3) | C5—H5   | 0.9300    |
| Cd1—N1 <sup>i</sup> | 2.331 (3) | C6—C7   | 1.387 (5) |
| Cd1—N3 <sup>i</sup> | 2.337 (3) | C6—H6   | 0.9300    |
| Cd1—N3              | 2.337 (3) | C7—H7   | 0.9300    |
| Cd1—O1              | 2.389 (2) | C8—C9   | 1.482 (4) |
| Cd1—O1 <sup>i</sup> | 2.389 (2) | C9—C10  | 1.382 (5) |
| N1—C8               | 1.307 (4) | C9—C14  | 1.389 (5) |
| N1—N2               | 1.397 (4) | C10—C11 | 1.404 (5) |
| N2—C1               | 1.320 (4) | C11—C12 | 1.371 (6) |
| N2—H2               | 0.8600    | C11—H11 | 0.9300    |
| N3—C15              | 1.332 (5) | C12—C13 | 1.346 (6) |
| N3—C19              | 1.333 (5) | C12—H12 | 0.9300    |
| O1—C1               | 1.245 (4) | C13—C14 | 1.380 (5) |
| O2—C3               | 1.357 (4) | C13—H13 | 0.9300    |
| O2—H2A              | 0.8200    | C14—H14 | 0.9300    |
| O3—C8               | 1.271 (4) | C15—C16 | 1.385 (6) |
| O4—C10              | 1.371 (5) | C15—H15 | 0.9300    |
| O4—H4               | 0.8200    | C16—C17 | 1.352 (6) |
| C1—C2               | 1.490 (5) | C16—H16 | 0.9300    |
| C2—C7               | 1.385 (5) | C17—C18 | 1.372 (6) |
| C2—C3               | 1.399 (5) | C17—H17 | 0.9300    |
| C3—C4               | 1.384 (5) | C18—C19 | 1.356 (6) |
| C4—C5               | 1.380 (6) | C18—H18 | 0.9300    |

|                                      |             |             |           |
|--------------------------------------|-------------|-------------|-----------|
| C4—H4A                               | 0.9300      | C19—H19     | 0.9300    |
| C5—C6                                | 1.372 (6)   |             |           |
| N1—Cd1—N1 <sup>i</sup>               | 89.45 (14)  | C5—C6—C7    | 118.8 (4) |
| N1—Cd1—N3 <sup>i</sup>               | 145.80 (9)  | C5—C6—H6    | 120.6     |
| N1 <sup>i</sup> —Cd1—N3 <sup>i</sup> | 99.48 (10)  | C7—C6—H6    | 120.6     |
| N1—Cd1—N3                            | 99.48 (10)  | C2—C7—C6    | 122.2 (4) |
| N1 <sup>i</sup> —Cd1—N3              | 145.80 (9)  | C2—C7—H7    | 118.9     |
| N3 <sup>i</sup> —Cd1—N3              | 91.48 (14)  | C6—C7—H7    | 118.9     |
| N1—Cd1—O1                            | 68.64 (9)   | O3—C8—N1    | 124.5 (3) |
| N1 <sup>i</sup> —Cd1—O1              | 125.88 (9)  | O3—C8—C9    | 119.0 (3) |
| N3 <sup>i</sup> —Cd1—O1              | 79.62 (9)   | N1—C8—C9    | 116.4 (3) |
| N3—Cd1—O1                            | 87.84 (9)   | C10—C9—C14  | 117.9 (3) |
| N1—Cd1—O1 <sup>i</sup>               | 125.88 (9)  | C10—C9—C8   | 120.1 (3) |
| N1 <sup>i</sup> —Cd1—O1 <sup>i</sup> | 68.64 (9)   | C14—C9—C8   | 121.9 (3) |
| N3 <sup>i</sup> —Cd1—O1 <sup>i</sup> | 87.84 (9)   | O4—C10—C9   | 122.1 (3) |
| N3—Cd1—O1 <sup>i</sup>               | 79.62 (9)   | O4—C10—C11  | 117.1 (4) |
| O1—Cd1—O1 <sup>i</sup>               | 162.04 (12) | C9—C10—C11  | 120.7 (4) |
| C8—N1—N2                             | 112.2 (3)   | C12—C11—C10 | 118.9 (4) |
| C8—N1—Cd1                            | 131.0 (2)   | C12—C11—H11 | 120.5     |
| N2—N1—Cd1                            | 111.44 (19) | C10—C11—H11 | 120.5     |
| C1—N2—N1                             | 119.7 (3)   | C13—C12—C11 | 121.0 (4) |
| C1—N2—H2                             | 120.1       | C13—C12—H12 | 119.5     |
| N1—N2—H2                             | 120.1       | C11—C12—H12 | 119.5     |
| C15—N3—C19                           | 117.2 (3)   | C12—C13—C14 | 120.4 (4) |
| C15—N3—Cd1                           | 120.9 (2)   | C12—C13—H13 | 119.8     |
| C19—N3—Cd1                           | 121.7 (2)   | C14—C13—H13 | 119.8     |
| C1—O1—Cd1                            | 113.9 (2)   | C13—C14—C9  | 120.9 (4) |
| C3—O2—H2A                            | 109.5       | C13—C14—H14 | 119.6     |
| C10—O4—H4                            | 109.5       | C9—C14—H14  | 119.6     |
| O1—C1—N2                             | 121.1 (3)   | N3—C15—C16  | 122.3 (4) |
| O1—C1—C2                             | 120.4 (3)   | N3—C15—H15  | 118.8     |
| N2—C1—C2                             | 118.5 (3)   | C16—C15—H15 | 118.8     |
| C7—C2—C3                             | 118.0 (3)   | C17—C16—C15 | 119.2 (4) |
| C7—C2—C1                             | 117.0 (3)   | C17—C16—H16 | 120.4     |
| C3—C2—C1                             | 124.9 (3)   | C15—C16—H16 | 120.4     |
| O2—C3—C4                             | 121.0 (4)   | C16—C17—C18 | 118.8 (4) |
| O2—C3—C2                             | 119.2 (3)   | C16—C17—H17 | 120.6     |
| C4—C3—C2                             | 119.8 (4)   | C18—C17—H17 | 120.6     |
| C5—C4—C3                             | 120.8 (4)   | C19—C18—C17 | 119.1 (4) |
| C5—C4—H4A                            | 119.6       | C19—C18—H18 | 120.5     |
| C3—C4—H4A                            | 119.6       | C17—C18—H18 | 120.5     |
| C6—C5—C4                             | 120.4 (4)   | N3—C19—C18  | 123.3 (4) |
| C6—C5—H5                             | 119.8       | N3—C19—H19  | 118.3     |
| C4—C5—H5                             | 119.8       | C18—C19—H19 | 118.3     |
| N1 <sup>i</sup> —Cd1—N1—C8           | -39.3 (3)   | C7—C2—C3—C4 | 0.2 (5)   |
| N3 <sup>i</sup> —Cd1—N1—C8           | -145.5 (3)  | C1—C2—C3—C4 | 177.0 (4) |

|                             |             |                 |            |
|-----------------------------|-------------|-----------------|------------|
| N3—Cd1—N1—C8                | 107.5 (3)   | O2—C3—C4—C5     | -178.7 (4) |
| O1—Cd1—N1—C8                | -168.6 (3)  | C2—C3—C4—C5     | 0.7 (6)    |
| O1 <sup>i</sup> —Cd1—N1—C8  | 23.6 (3)    | C3—C4—C5—C6     | -1.4 (6)   |
| N1 <sup>i</sup> —Cd1—N1—N2  | 112.3 (2)   | C4—C5—C6—C7     | 1.2 (6)    |
| N3 <sup>i</sup> —Cd1—N1—N2  | 6.1 (3)     | C3—C2—C7—C6     | -0.4 (5)   |
| N3—Cd1—N1—N2                | -100.9 (2)  | C1—C2—C7—C6     | -177.5 (3) |
| O1—Cd1—N1—N2                | -17.02 (19) | C5—C6—C7—C2     | -0.3 (6)   |
| O1 <sup>i</sup> —Cd1—N1—N2  | 175.09 (18) | N2—N1—C8—O3     | -1.8 (5)   |
| C8—N1—N2—C1                 | 172.8 (3)   | Cd1—N1—C8—O3    | 149.6 (3)  |
| Cd1—N1—N2—C1                | 15.7 (3)    | N2—N1—C8—C9     | 180.0 (3)  |
| N1—Cd1—N3—C15               | -164.9 (3)  | Cd1—N1—C8—C9    | -28.6 (4)  |
| N1 <sup>i</sup> —Cd1—N3—C15 | -61.7 (4)   | O3—C8—C9—C10    | -30.0 (5)  |
| N3 <sup>i</sup> —Cd1—N3—C15 | 47.6 (3)    | N1—C8—C9—C10    | 148.3 (3)  |
| O1—Cd1—N3—C15               | 127.1 (3)   | O3—C8—C9—C14    | 150.3 (4)  |
| O1 <sup>i</sup> —Cd1—N3—C15 | -39.9 (3)   | N1—C8—C9—C14    | -31.4 (5)  |
| N1—Cd1—N3—C19               | 20.6 (3)    | C14—C9—C10—O4   | -175.9 (4) |
| N1 <sup>i</sup> —Cd1—N3—C19 | 123.8 (3)   | C8—C9—C10—O4    | 4.4 (6)    |
| N3 <sup>i</sup> —Cd1—N3—C19 | -126.9 (3)  | C14—C9—C10—C11  | 4.1 (6)    |
| O1—Cd1—N3—C19               | -47.3 (3)   | C8—C9—C10—C11   | -175.6 (4) |
| O1 <sup>i</sup> —Cd1—N3—C19 | 145.6 (3)   | O4—C10—C11—C12  | 177.2 (4)  |
| N1—Cd1—O1—C1                | 19.5 (2)    | C9—C10—C11—C12  | -2.9 (7)   |
| N1 <sup>i</sup> —Cd1—O1—C1  | -53.3 (3)   | C10—C11—C12—C13 | -0.1 (7)   |
| N3 <sup>i</sup> —Cd1—O1—C1  | -147.5 (3)  | C11—C12—C13—C14 | 1.6 (7)    |
| N3—Cd1—O1—C1                | 120.5 (2)   | C12—C13—C14—C9  | -0.2 (6)   |
| O1 <sup>i</sup> —Cd1—O1—C1  | 166.0 (2)   | C10—C9—C14—C13  | -2.6 (5)   |
| Cd1—O1—C1—N2                | -19.3 (4)   | C8—C9—C14—C13   | 177.1 (3)  |
| Cd1—O1—C1—C2                | 160.3 (2)   | C19—N3—C15—C16  | 2.3 (6)    |
| N1—N2—C1—O1                 | 2.6 (5)     | Cd1—N3—C15—C16  | -172.4 (3) |
| N1—N2—C1—C2                 | -177.0 (3)  | N3—C15—C16—C17  | -2.1 (6)   |
| O1—C1—C2—C7                 | -1.1 (5)    | C15—C16—C17—C18 | 0.6 (6)    |
| N2—C1—C2—C7                 | 178.5 (3)   | C16—C17—C18—C19 | 0.5 (6)    |
| O1—C1—C2—C3                 | -178.0 (3)  | C15—N3—C19—C18  | -1.2 (6)   |
| N2—C1—C2—C3                 | 1.6 (5)     | Cd1—N3—C19—C18  | 173.5 (3)  |
| C7—C2—C3—O2                 | 179.6 (3)   | C17—C18—C19—N3  | -0.2 (7)   |
| C1—C2—C3—O2                 | -3.5 (5)    |                 |            |

Symmetry code: (i)  $-x+2, -x+y+1, -z+4/3$ .

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H <sup>⋯</sup> <i>A</i>            | <i>D</i> —H | H <sup>⋯</sup> <i>A</i> | <i>D</i> ⋯ <i>A</i> | <i>D</i> —H <sup>⋯</sup> <i>A</i> |
|--|-------------|-------------------------|---------------------|-----------------------------------|
| O4—H4 <sup>⋯</sup> O3                        | 0.82        | 1.92                    | 2.638 (4)           | 145                               |
| N2—H2 <sup>⋯</sup> O2                        | 0.86        | 1.94                    | 2.624 (4)           | 135                               |
| O2—H2 <i>A</i> <sup>⋯</sup> O3 <sup>ii</sup> | 0.82        | 1.88                    | 2.639 (3)           | 153                               |

Symmetry code: (ii)  $x-y, -y, -z+5/3$ .