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## Structure Reports

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Tetraaquabis(3,5-di-4-pyridyl-1*H*-1,2,4-triazolido)cadmium(II) dihydrate

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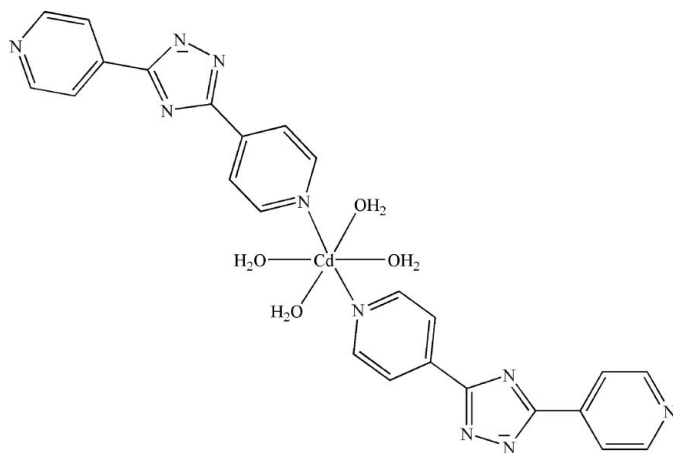
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.030;  $wR$  factor = 0.070; data-to-parameter ratio = 14.7.

In the title compound,  $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_5)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ , the  $\text{Cd}^{\text{II}}$  atom is located on an inversion center and is coordinated by the two N atoms [ $\text{Cd}-\text{N} = 2.278$  (2) Å] and four O atoms [ $\text{Cd}-\text{O} = 2.304$  (2)– $2.322$  (2) Å] in a distorted octahedral geometry. Intermolecular  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds link the complex into a three-dimensional supramolecular framework.

## Related literature

For the properties of hydrogen bonds in biological systems, see: Deisenhofer & Michel (1989). For extended supramolecular structures, see: Beatty (2003); Li *et al.* (2006); Russell & Ward (1996). For comparative bond distances, see: Wen *et al.* (2005); Fu *et al.* (2007).



## Experimental

## Crystal data

 $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_5)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  $M_r = 664.97$ 

Monoclinic,  $P2_1/c$   
 $a = 7.5030$  (15) Å  
 $b = 15.748$  (3) Å  
 $c = 12.009$  (2) Å  
 $\beta = 106.68$  (3)°  
 $V = 1359.2$  (5) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.86$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.40 \times 0.20 \times 0.12$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{\text{min}} = 0.815$ ,  $T_{\text{max}} = 0.911$

9599 measured reflections  
 3101 independent reflections  
 2663 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.070$   
 $S = 1.01$   
 3101 reflections  
 211 parameters  
 9 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.47$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                                      | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| $\text{O1}-\text{H1A}\cdots\text{N2}^{\text{i}}$   | 0.84 (2) | 1.95 (3)    | 2.768 (3)   | 164 (3)       |
| $\text{O1}-\text{H1B}\cdots\text{O3}$              | 0.85 (3) | 1.95 (3)    | 2.786 (3)   | 169 (3)       |
| $\text{O2}-\text{H2A}\cdots\text{N3}^{\text{ii}}$  | 0.85 (3) | 1.98 (3)    | 2.829 (3)   | 171 (3)       |
| $\text{O2}-\text{H2B}\cdots\text{O3}^{\text{iii}}$ | 0.85 (3) | 1.95 (3)    | 2.758 (3)   | 161 (3)       |
| $\text{O3}-\text{H3A}\cdots\text{N4}^{\text{iv}}$  | 0.85 (3) | 2.06 (2)    | 2.895 (3)   | 171 (3)       |
| $\text{O3}-\text{H3B}\cdots\text{N5}^{\text{v}}$   | 0.85 (3) | 1.95 (2)    | 2.796 (3)   | 170 (3)       |

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); 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: BG2273).

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**supplementary materials**

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## Tetraaquabis(3,5-di-4-pyridyl-1*H*-1,2,4-triazolido)cadmium(II) dihydrate

T.-L. Liu and Y.-L. Zhang

### Comment

The hydrogen bond interaction plays an important role in some biological systems (Deisenhofer & Michel, 1989). Supramolecular assembly through hydrogen bonds has been extensively exploited to generate extended one-, two- and three-dimensional structures (Beatty *et al.*, 2003; Li *et al.*, 2006; Russell & Ward, 1996). As part of this ongoing work, we present here the synthesis and structural characterization of the title cadmium complex,  $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_5)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ , (**I**).

The molecule of the title complex, (Fig. 1), is centrosymmetric, so pairs of equivalent ligands lie *trans* to each other in a slightly distorted octahedral coordination geometry, *cis* angles deviating from  $90^\circ$  by less than  $4^\circ$ , with Cd—O bond length in the range 2.304 (2)–2.322 (2) Å and a Cd—N bond length of 2.278 (2) Å. These bond distances compare well with those in the literature (Wen *et al.*, 2005; Fu *et al.*, 2007). Molecules are linked by O—H $\cdots$ O and O—H $\cdots$ N hydrogen bonds (Table 1 and Fig. 2).

### Experimental

$\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.5 mmol, 0.154 g), 1*H*-3,5-di(4-pyridyl)-1,2,4-triazole (0.5 mmol, 0.112 g), and water (12 ml) were placed in a 23-ml Teflon-lined Parr bomb. The bomb was heated at 453 K for 3 d. The colourless block-shaped crystals were filtered off and washed with water and acetone (yield 45%, based on Cd).

### Refinement

Hydrogen atoms of water molecules were located in a difference Fourier map and refined with distance restraints of O—H = 0.85 (2) Å and H $\cdots$ H = 1.39 (2) Å, and free isotropic *U*'s. H atoms on C atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Figures

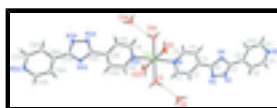


Fig. 1. A view of the molecular structure of (**I**) with the atom-numbering scheme and 30% displacement ellipsoids. Atoms with the suffix A are generated by the symmetry operation ( $-x, -y + 1, -z + 1$ ).

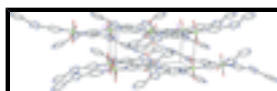


Fig. 2. The 3-D network of (**I**).

## Tetraaquabis(3,5-di-4-pyridyl-1H-1,2,4-triazolido)cadmium(II) dihydrate

### Crystal data

[Cd(C<sub>12</sub>H<sub>8</sub>N<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]:2H<sub>2</sub>O

$M_r = 664.97$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.5030$  (15) Å

$b = 15.748$  (3) Å

$c = 12.009$  (2) Å

$\beta = 106.68$  (3)°

$V = 1359.2$  (5) Å<sup>3</sup>

$Z = 2$

$F_{000} = 676$

$D_x = 1.625$  Mg m<sup>-3</sup>

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

Cell parameters from 2567 reflections

$\theta = 2.6$ – $27.3$ °

$\mu = 0.86$  mm<sup>-1</sup>

$T = 293$  K

Block, colorless

$0.40 \times 0.20 \times 0.12$  mm

### Data collection

Bruker SMART CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$  K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 1998)

$T_{\min} = 0.815$ ,  $T_{\max} = 0.911$

9599 measured reflections

3101 independent reflections

2663 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 9$

$k = -20 \rightarrow 20$

$l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.070$

$S = 1.01$

3101 reflections

211 parameters

9 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H atoms treated by a mixture of  
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.30$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.47$  e Å<sup>-3</sup>

Extinction correction: none

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

|     | <i>x</i>   | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|--------------|----------------------------------|
| Cd1 | 0.0000     | 0.5000       | 0.5000       | 0.02624 (8)                      |
| C1  | 0.0093 (4) | 0.67991 (14) | 0.3780 (2)   | 0.0362 (6)                       |
| H1  | -0.0392    | 0.6476       | 0.3113       | 0.043*                           |
| C2  | 0.0355 (4) | 0.76513 (14) | 0.3660 (2)   | 0.0350 (5)                       |
| H2  | 0.0038     | 0.7894       | 0.2923       | 0.042*                           |
| C3  | 0.1089 (3) | 0.81536 (13) | 0.46302 (19) | 0.0260 (5)                       |
| C4  | 0.1464 (4) | 0.77542 (14) | 0.5700 (2)   | 0.0371 (6)                       |
| H4  | 0.1919     | 0.8065       | 0.6382       | 0.045*                           |
| C5  | 0.1161 (4) | 0.68949 (15) | 0.5749 (2)   | 0.0380 (6)                       |
| H5  | 0.1430     | 0.6638       | 0.6476       | 0.046*                           |
| C6  | 0.1502 (3) | 0.90502 (13) | 0.45109 (18) | 0.0265 (5)                       |
| C7  | 0.2512 (3) | 1.02895 (14) | 0.4805 (2)   | 0.0274 (5)                       |
| C8  | 0.3340 (3) | 1.10850 (13) | 0.53511 (19) | 0.0276 (5)                       |
| C9  | 0.3496 (4) | 1.17874 (16) | 0.4689 (2)   | 0.0472 (7)                       |
| H9  | 0.3127     | 1.1754       | 0.3882       | 0.057*                           |
| C10 | 0.4202 (5) | 1.25321 (16) | 0.5236 (2)   | 0.0515 (8)                       |
| H10 | 0.4285     | 1.2995       | 0.4772       | 0.062*                           |
| C11 | 0.4620 (4) | 1.19586 (16) | 0.7006 (2)   | 0.0423 (6)                       |
| H11 | 0.5012     | 1.2010       | 0.7811       | 0.051*                           |
| C12 | 0.3919 (4) | 1.11875 (15) | 0.6541 (2)   | 0.0376 (6)                       |
| H12 | 0.3837     | 1.0738       | 0.7027       | 0.045*                           |
| H1A | 0.081 (4)  | 0.4477 (19)  | 0.303 (2)    | 0.065 (11)*                      |
| H2A | 0.251 (5)  | 0.487 (2)    | 0.722 (2)    | 0.076 (12)*                      |
| H3A | 0.333 (4)  | 0.5708 (17)  | 0.2136 (15)  | 0.057 (10)*                      |
| H1B | 0.225 (4)  | 0.5023 (14)  | 0.349 (3)    | 0.050 (9)*                       |
| H2B | 0.371 (3)  | 0.474 (2)    | 0.656 (3)    | 0.071 (11)*                      |
| H3B | 0.419 (4)  | 0.6266 (12)  | 0.301 (2)    | 0.059 (9)*                       |
| N1  | 0.0504 (3) | 0.64121 (11) | 0.48107 (16) | 0.0309 (4)                       |
| N2  | 0.1075 (3) | 0.94209 (12) | 0.34725 (16) | 0.0338 (5)                       |
| N3  | 0.1745 (3) | 1.02282 (12) | 0.36636 (17) | 0.0351 (5)                       |
| N4  | 0.2401 (3) | 0.95673 (11) | 0.53920 (16) | 0.0269 (4)                       |
| N5  | 0.4772 (3) | 1.26344 (13) | 0.6379 (2)   | 0.0413 (5)                       |
| O1  | 0.1563 (3) | 0.46448 (12) | 0.36541 (15) | 0.0358 (4)                       |

## supplementary materials

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|    |            |              |              |            |
|----|------------|--------------|--------------|------------|
| O2 | 0.2657 (3) | 0.49379 (12) | 0.65460 (16) | 0.0416 (4) |
| O3 | 0.3821 (3) | 0.57563 (10) | 0.28626 (15) | 0.0349 (4) |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Cd1 | 0.03522 (14) | 0.01796 (11) | 0.02429 (13) | -0.00424 (9) | 0.00655 (10) | -0.00067 (8) |
| C1  | 0.0537 (16)  | 0.0256 (11)  | 0.0261 (12)  | -0.0094 (11) | 0.0063 (11)  | -0.0044 (9)  |
| C2  | 0.0516 (15)  | 0.0269 (11)  | 0.0240 (11)  | -0.0059 (11) | 0.0067 (11)  | 0.0028 (9)   |
| C3  | 0.0296 (11)  | 0.0208 (10)  | 0.0275 (11)  | -0.0013 (8)  | 0.0079 (9)   | 0.0014 (8)   |
| C4  | 0.0577 (16)  | 0.0233 (11)  | 0.0255 (12)  | -0.0090 (11) | 0.0042 (12)  | -0.0027 (9)  |
| C5  | 0.0596 (17)  | 0.0254 (11)  | 0.0249 (12)  | -0.0073 (11) | 0.0057 (12)  | 0.0031 (9)   |
| C6  | 0.0331 (12)  | 0.0206 (10)  | 0.0241 (11)  | -0.0013 (9)  | 0.0056 (9)   | 0.0011 (8)   |
| C7  | 0.0333 (12)  | 0.0205 (9)   | 0.0295 (12)  | -0.0024 (9)  | 0.0106 (10)  | 0.0006 (9)   |
| C8  | 0.0302 (12)  | 0.0204 (10)  | 0.0314 (12)  | -0.0019 (9)  | 0.0075 (10)  | -0.0006 (9)  |
| C9  | 0.078 (2)    | 0.0311 (13)  | 0.0308 (13)  | -0.0176 (13) | 0.0137 (14)  | -0.0018 (10) |
| C10 | 0.084 (2)    | 0.0276 (12)  | 0.0446 (16)  | -0.0188 (14) | 0.0214 (16)  | 0.0009 (11)  |
| C11 | 0.0532 (16)  | 0.0364 (13)  | 0.0303 (13)  | -0.0066 (12) | 0.0010 (12)  | -0.0046 (10) |
| C12 | 0.0496 (15)  | 0.0260 (11)  | 0.0327 (13)  | -0.0042 (10) | 0.0046 (12)  | 0.0042 (9)   |
| N1  | 0.0435 (11)  | 0.0199 (9)   | 0.0278 (10)  | -0.0049 (8)  | 0.0077 (9)   | 0.0005 (7)   |
| N2  | 0.0487 (13)  | 0.0241 (9)   | 0.0258 (10)  | -0.0087 (9)  | 0.0066 (9)   | 0.0016 (7)   |
| N3  | 0.0523 (13)  | 0.0239 (9)   | 0.0265 (10)  | -0.0089 (9)  | 0.0073 (10)  | 0.0020 (8)   |
| N4  | 0.0348 (10)  | 0.0192 (9)   | 0.0261 (10)  | -0.0021 (7)  | 0.0078 (8)   | 0.0005 (7)   |
| N5  | 0.0488 (13)  | 0.0280 (10)  | 0.0458 (13)  | -0.0092 (9)  | 0.0112 (11)  | -0.0087 (9)  |
| O1  | 0.0405 (10)  | 0.0387 (10)  | 0.0295 (9)   | -0.0055 (8)  | 0.0120 (8)   | -0.0026 (8)  |
| O2  | 0.0349 (10)  | 0.0577 (12)  | 0.0288 (9)   | 0.0058 (9)   | 0.0035 (8)   | -0.0038 (8)  |
| O3  | 0.0458 (10)  | 0.0258 (8)   | 0.0299 (9)   | -0.0037 (7)  | 0.0060 (8)   | -0.0015 (7)  |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|                     |           |         |            |
|---------------------|-----------|---------|------------|
| Cd1—N1 <sup>i</sup> | 2.278 (2) | C7—N4   | 1.353 (3)  |
| Cd1—N1              | 2.278 (2) | C7—C8   | 1.467 (3)  |
| Cd1—O2              | 2.304 (2) | C8—C12  | 1.379 (3)  |
| Cd1—O2 <sup>i</sup> | 2.304 (2) | C8—C9   | 1.386 (3)  |
| Cd1—O1 <sup>i</sup> | 2.322 (2) | C9—C10  | 1.373 (3)  |
| Cd1—O1              | 2.322 (2) | C9—H9   | 0.9300     |
| C1—N1               | 1.334 (3) | C10—N5  | 1.325 (3)  |
| C1—C2               | 1.370 (3) | C10—H10 | 0.9300     |
| C1—H1               | 0.9300    | C11—N5  | 1.327 (3)  |
| C2—C3               | 1.385 (3) | C11—C12 | 1.376 (3)  |
| C2—H2               | 0.9300    | C11—H11 | 0.9300     |
| C3—C4               | 1.385 (3) | C12—H12 | 0.9300     |
| C3—C6               | 1.461 (3) | N2—N3   | 1.362 (3)  |
| C4—C5               | 1.376 (3) | O1—H1A  | 0.844 (17) |
| C4—H4               | 0.9300    | O1—H1B  | 0.845 (17) |
| C5—N1               | 1.331 (3) | O2—H2A  | 0.857 (17) |
| C5—H5               | 0.9300    | O2—H2B  | 0.847 (17) |
| C6—N2               | 1.330 (3) | O3—H3A  | 0.848 (16) |

|                                      |             |                            |             |
|--------------------------------------|-------------|----------------------------|-------------|
| C6—N4                                | 1.352 (3)   | O3—H3B                     | 0.850 (17)  |
| C7—N3                                | 1.329 (3)   |                            |             |
| N1 <sup>i</sup> —Cd1—N1              | 180.0       | N3—C7—N4                   | 113.8 (2)   |
| N1 <sup>i</sup> —Cd1—O2              | 90.47 (7)   | N3—C7—C8                   | 121.7 (2)   |
| N1—Cd1—O2                            | 89.53 (7)   | N4—C7—C8                   | 124.5 (2)   |
| N1 <sup>i</sup> —Cd1—O2 <sup>i</sup> | 89.53 (7)   | C12—C8—C9                  | 116.6 (2)   |
| N1—Cd1—O2 <sup>i</sup>               | 90.47 (7)   | C12—C8—C7                  | 122.1 (2)   |
| O2—Cd1—O2 <sup>i</sup>               | 180.0       | C9—C8—C7                   | 121.3 (2)   |
| N1 <sup>i</sup> —Cd1—O1 <sup>i</sup> | 91.96 (7)   | C10—C9—C8                  | 119.5 (2)   |
| N1—Cd1—O1 <sup>i</sup>               | 88.04 (7)   | C10—C9—H9                  | 120.3       |
| O2—Cd1—O1 <sup>i</sup>               | 86.71 (7)   | C8—C9—H9                   | 120.3       |
| O2 <sup>i</sup> —Cd1—O1 <sup>i</sup> | 93.29 (7)   | N5—C10—C9                  | 124.3 (2)   |
| N1 <sup>i</sup> —Cd1—O1              | 88.04 (7)   | N5—C10—H10                 | 117.8       |
| N1—Cd1—O1                            | 91.96 (7)   | C9—C10—H10                 | 117.8       |
| O2—Cd1—O1                            | 93.29 (7)   | N5—C11—C12                 | 124.3 (2)   |
| O2 <sup>i</sup> —Cd1—O1              | 86.71 (7)   | N5—C11—H11                 | 117.9       |
| O1 <sup>i</sup> —Cd1—O1              | 180.0       | C12—C11—H11                | 117.9       |
| N1—C1—C2                             | 122.9 (2)   | C11—C12—C8                 | 119.6 (2)   |
| N1—C1—H1                             | 118.5       | C11—C12—H12                | 120.2       |
| C2—C1—H1                             | 118.5       | C8—C12—H12                 | 120.2       |
| C1—C2—C3                             | 120.4 (2)   | C5—N1—C1                   | 117.07 (19) |
| C1—C2—H2                             | 119.8       | C5—N1—Cd1                  | 120.33 (15) |
| C3—C2—H2                             | 119.8       | C1—N1—Cd1                  | 122.54 (15) |
| C2—C3—C4                             | 116.5 (2)   | C6—N2—N3                   | 105.89 (18) |
| C2—C3—C6                             | 120.91 (19) | C7—N3—N2                   | 105.73 (18) |
| C4—C3—C6                             | 122.5 (2)   | C6—N4—C7                   | 100.94 (18) |
| C5—C4—C3                             | 119.6 (2)   | C10—N5—C11                 | 115.8 (2)   |
| C5—C4—H4                             | 120.2       | Cd1—O1—H1A                 | 111 (2)     |
| C3—C4—H4                             | 120.2       | Cd1—O1—H1B                 | 117 (2)     |
| N1—C5—C4                             | 123.5 (2)   | H1A—O1—H1B                 | 108 (2)     |
| N1—C5—H5                             | 118.3       | Cd1—O2—H2A                 | 117 (2)     |
| C4—C5—H5                             | 118.3       | Cd1—O2—H2B                 | 128 (2)     |
| N2—C6—N4                             | 113.65 (19) | H2A—O2—H2B                 | 108 (2)     |
| N2—C6—C3                             | 121.01 (19) | H3A—O3—H3B                 | 108 (2)     |
| N4—C6—C3                             | 125.27 (19) |                            |             |
| N1—C1—C2—C3                          | 0.6 (4)     | C2—C1—N1—C5                | 1.3 (4)     |
| C1—C2—C3—C4                          | -2.3 (4)    | C2—C1—N1—Cd1               | 178.6 (2)   |
| C1—C2—C3—C6                          | 175.5 (2)   | O2—Cd1—N1—C5               | -38.2 (2)   |
| C2—C3—C4—C5                          | 2.2 (4)     | O2 <sup>i</sup> —Cd1—N1—C5 | 141.8 (2)   |
| C6—C3—C4—C5                          | -175.5 (2)  | O1 <sup>i</sup> —Cd1—N1—C5 | 48.5 (2)    |
| C3—C4—C5—N1                          | -0.4 (4)    | O1—Cd1—N1—C5               | -131.5 (2)  |
| C2—C3—C6—N2                          | 4.4 (3)     | O2—Cd1—N1—C1               | 144.6 (2)   |
| C4—C3—C6—N2                          | -178.0 (2)  | O2 <sup>i</sup> —Cd1—N1—C1 | -35.4 (2)   |
| C2—C3—C6—N4                          | -172.4 (2)  | O1 <sup>i</sup> —Cd1—N1—C1 | -128.6 (2)  |
| C4—C3—C6—N4                          | 5.2 (4)     | O1—Cd1—N1—C1               | 51.4 (2)    |

## supplementary materials

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|               |            |                |            |
|---------------|------------|----------------|------------|
| N3—C7—C8—C12  | 171.4 (2)  | N4—C6—N2—N3    | 0.9 (3)    |
| N4—C7—C8—C12  | -6.7 (4)   | C3—C6—N2—N3    | -176.3 (2) |
| N3—C7—C8—C9   | -5.4 (4)   | N4—C7—N3—N2    | 0.3 (3)    |
| N4—C7—C8—C9   | 176.4 (2)  | C8—C7—N3—N2    | -178.0 (2) |
| C12—C8—C9—C10 | 0.0 (4)    | C6—N2—N3—C7    | -0.6 (3)   |
| C7—C8—C9—C10  | 177.0 (3)  | N2—C6—N4—C7    | -0.7 (3)   |
| C8—C9—C10—N5  | 0.4 (5)    | C3—C6—N4—C7    | 176.3 (2)  |
| N5—C11—C12—C8 | 0.6 (4)    | N3—C7—N4—C6    | 0.2 (3)    |
| C9—C8—C12—C11 | -0.4 (4)   | C8—C7—N4—C6    | 178.5 (2)  |
| C7—C8—C12—C11 | -177.5 (2) | C9—C10—N5—C11  | -0.3 (5)   |
| C4—C5—N1—C1   | -1.4 (4)   | C12—C11—N5—C10 | -0.2 (4)   |
| C4—C5—N1—Cd1  | -178.7 (2) |                |            |

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

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

| $D-H\cdots A$                     | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| O1—H1A $\cdots$ N2 <sup>ii</sup>  | 0.84 (2) | 1.95 (3)    | 2.768 (3)   | 164 (3)       |
| O1—H1B $\cdots$ O3                | 0.85 (3) | 1.95 (3)    | 2.786 (3)   | 169 (3)       |
| O2—H2A $\cdots$ N3 <sup>iii</sup> | 0.85 (3) | 1.98 (3)    | 2.829 (3)   | 171 (3)       |
| O2—H2B $\cdots$ O3 <sup>iv</sup>  | 0.85 (3) | 1.95 (3)    | 2.758 (3)   | 161 (3)       |
| O3—H3A $\cdots$ N4 <sup>v</sup>   | 0.85 (3) | 2.06 (2)    | 2.895 (3)   | 171 (3)       |
| O3—H3B $\cdots$ N5 <sup>vi</sup>  | 0.85 (3) | 1.95 (2)    | 2.796 (3)   | 170 (3)       |

Symmetry codes: (ii)  $-x, y-1/2, -z+1/2$ ; (iii)  $x, -y+3/2, z+1/2$ ; (iv)  $-x+1, -y+1, -z+1$ ; (v)  $x, -y+3/2, z-1/2$ ; (vi)  $-x+1, -y+2, -z+1$ .



Fig. 1

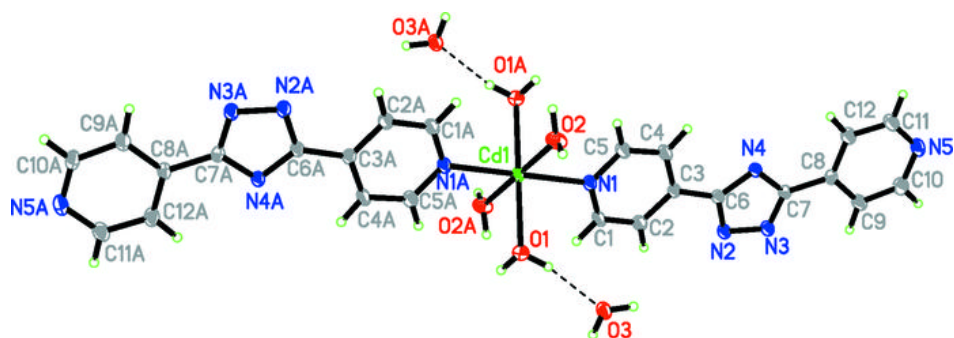


Fig. 2

