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## Structure Reports

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# Bis( $\mu$ -2-hydroxybenzato)- $\kappa^3$ O, $O'$ : $O'$ ; $\kappa^3$ O: $O$ , $O'$ -bis[(2-hydroxybenzato- $\kappa^2$ O, $O'$ )(1,10-phenanthroline- $\kappa^2$ N, $N'$ )- cadmium(II)]

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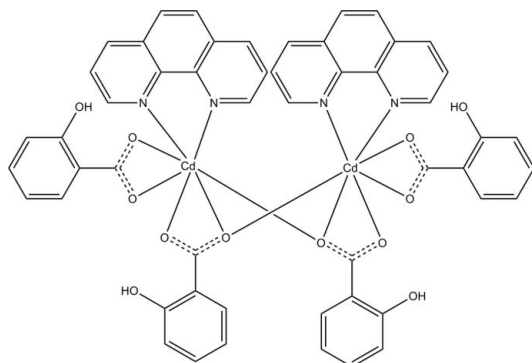
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.067; data-to-parameter ratio = 13.9.

The dinuclear title compound,  $[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ , is located on a crystallographic rotation twofold axis. The two  $\text{Cd}^{\text{II}}$  ions are connected by two tridentate bridging 2-hydroxybenzoate anions. Each  $\text{Cd}^{\text{II}}$  ion is seven-coordinated by five O atoms from three 2-hydroxybenzoate ligands and two N atoms from 1,10-phenanthroline. The 2-hydroxybenzoate molecules adopt two kinds of coordination mode, bidentate chelating and tridentate bridging–chelating. Intramolecular hydrogen bonds between hydroxy and carboxylate groups from 2-hydroxybenzoate groups and  $\pi$ – $\pi$  stacking interactions between parallel 1,10-phenanthroline ligands [centroid–centroid distances = 3.707 (3) and 3.842 (3) Å] are observed. Furthermore, adjacent benzene rings from 2-hydroxybenzoate ligands are involved in  $\pi$ – $\pi$  interactions with interplanar distances of 3.642 (3) Å, thereby forming a chain along the  $a$  axis direction.

## Related literature

For general background, see: Horike *et al.* (2007); Humphrey *et al.* (2007); Sudik *et al.* (2005); Zhang *et al.* (2008). For related structures, see: Du *et al.* (2007); Pan *et al.* (2006); Tomas *et al.* (2006). For related literature, see: Tong *et al.* (1999)



## Experimental

### Crystal data

$[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2]$   
 $M_r = 1133.65$   
Monoclinic,  $C2/c$   
 $a = 27.9391$  (19) Å  
 $b = 10.3078$  (7) Å  
 $c = 20.468$  (2) Å  
 $\beta = 130.770$  (1)°  
 $V = 4464.2$  (6) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 1.03$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
0.30 × 0.25 × 0.18 mm

### Data collection

Bruker APEXII CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.748$ ,  $T_{\text{max}} = 0.837$   
11963 measured reflections  
4390 independent reflections  
3671 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.067$   
 $S = 1.06$   
4390 reflections  
316 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                         | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------------|-------|-------------|-------------|---------------|
| $\text{O6}-\text{H6A}\cdots\text{O4}$ | 0.82  | 1.86        | 2.579 (3)   | 146           |
| $\text{O3}-\text{H3A}\cdots\text{O2}$ | 0.82  | 1.87        | 2.576 (2)   | 143           |

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 1999); 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) and ORTEP-3 (Farrugia, 1997); 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: ZL2145).

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**supplementary materials**

*Acta Cryst.* (2008). E64, m1458 [ doi:10.1107/S1600536808033886 ]

**Bis( $\mu$ -2-hydroxybenzato)- $\kappa^3 O, O': O'; \kappa^3 O: O, O'$ -bis[(2-hydroxybenzato- $\kappa^2 O, O'$ )(1,10-phenanthroline- $\kappa^2 N, N'$ )]cadmium(II)**

**Q.-Y. Shi, Z.-C. Li, Z.-S. Cheng, J.-B. Tan and J.-L. Liu**

**Comment**

Transition metal complexes with substituted benzoate ligands have attracted wide attention in past decades, owing to their variable high-dimensional architectures and potential applications for gas absorption and separation, and catalysis, *etc* [Du *et al.*, 2007; Horike *et al.*, 2007; Humphrey *et al.*, 2007; Pan *et al.*, 2006; Sudik *et al.*, 2005; Tomas *et al.*, 2006; Zhang *et al.*, 2008]. Herein, we report the synthesis and crystal structure of the title compound, obtained by the reaction of  $\text{Sm}(\text{NO}_3)_3$ ,  $\text{Cd}(\text{CH}_3\text{COO})_2$ , 1,10-phenanthroline and 2-hydroxybenzoic acid. No samarium was however incorporated in the crystals isolated and the title compound is a dinuclear  $\text{Cd}^{\text{II}}$  complex of 2-hydroxybenzoic acid and 1,10-phenanthroline. A perspective view of the complex, showing the atomic numbering scheme, is depicted in Fig. 1. Each  $\text{Cd}^{\text{II}}$  is seven-coordinated by five oxygen atoms from three 2-hydroxybenzoate ligands, and two nitrogen atoms from 1,10-phenanthroline, and the coordination geometry around the  $\text{Cd}^{\text{II}}$  ion may be described as a distorted mono-capped trigonal prism. Two adjacent  $\text{Cd}^{\text{II}}$  units are connected by two bridging 2-hydroxybenzoate anions to generate a dinuclear complex. The 2-hydroxybenzoate molecules adopt two kinds of coordination modes, bidentate chelating and tridentate bridging-chelating. The inequivalence between the mono and bidentate bridging oxygen atoms is evident from the Cd—O bond distances: the Cd—O distances of the bridging oxygen atoms are longer than those of the monodentate oxygen atoms: Cd1—O5 is 2.421 (2) Å and Cd1—O5<sup>i</sup> is 2.491 (2) Å, while Cd1—O1, Cd—O2 and Cd—O4 are 2.399 (2), 2.327 (2) and 2.363 (2) Å, respectively (symmetry code: (i):  $-x, y, 1/2 - z$ ).

Intramolecular hydrogen bonds between hydroxyl and carboxylate groups from the 2-hydroxybenzoates [O6 $\cdots$ O4 = 2.579 (3) Å and O3 $\cdots$ O2 = 2.576 (2) Å, Table 1] and  $\pi$ - $\pi$  stacking attractions between parallel 1,10-phenanthroline ligands [centroid to centroid distances: 3.707 (3) and 3.842 (3) Å] are clearly observed in this complex, which may contribute to its stability.

Furthermore, adjacent phenyl rings from 2-hydroxybenzoate ligands are also involved in  $\pi$ - $\pi$  stacking interactions by partial overlap of  $\pi$ -electron densities (Tong *et al.*, 1999). The centroid-centroid separation between rings A (atoms C14—C19) and B<sup>j</sup> [atoms C21—C26; symmetry code: (j):  $1/2 + x, 1/2 - y, 1/2 + z$ ] is 3.642 (3) Å. Considering these  $\pi$ - $\pi$  intermolecular attractions, they imply the formation of a one-dimensional chain along the direction of the a-axis. (Fig. 2).

**Experimental**

A sample of  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.090 g, 0.20 mmol),  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.052 g, 0.20 mmol), 2-hydroxybenzoic acid (0.070 g, 0.50 mmol), 1,10-phenanthroline (0.036 g, 0.20 mmol) and distilled water (8 ml) were mixed in a 15 ml Teflon-lined stainless steel vessel and the pH value was adjusted to about 5 with NaOH. Then, the mixture was heated to 393 K under autogenous pressure for 48 h, and cooled slowly to room temperature. Colorless block-like crystals suitable for X-ray single-crystal diffraction analysis were obtained by filtration and washed with distilled water and ethanol.

## Refinement

All H atoms were placed in calculated positions and were allowed to ride on their parent atoms; C—H = 0.93 (aromatic C—H) and O—H = 0.82 (hydroxyl) Å;  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ .

## Figures



Fig. 1. An *ORTEP-3* (Farrugia, 1997) plot of the title compound with displacement ellipsoids at the 30% probability level. All H atoms are omitted for clarity.

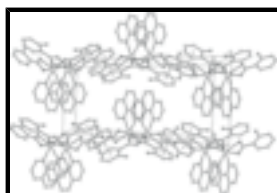


Fig. 2. A packing diagram of the title compound, showing a one-dimensional chain-like structure generated by the intermolecular  $\pi$ - $\pi$  interactions. All H atoms are omitted for clarity. [Symmetry codes: (*j*):  $1/2 + x, 1/2 - y, 1/2 + z$ ].

## Bis( $\mu$ -2-hydroxybenzato)- $\kappa^3\text{O},\text{O}';\text{O}';\kappa^3\text{O}:O,\text{O}'$ - bis[(2-hydroxybenzato- $\kappa^2\text{O},\text{O}'$ )(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$ )]cadmium(II)

### Crystal data

$[\text{Cd}_2(\text{C}_7\text{H}_5\text{O}_3)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2]$

$M_r = 1133.65$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 27.9391(19)\ \text{\AA}$

$b = 10.3078(7)\ \text{\AA}$

$c = 20.468(2)\ \text{\AA}$

$\beta = 130.7700(10)^\circ$

$V = 4464.2(6)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 2272$

$D_x = 1.687\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4082 reflections

$\theta = 1.9\text{--}27.4^\circ$

$\mu = 1.03\ \text{mm}^{-1}$

$T = 298(2)\ \text{K}$

Block, colorless

$0.30 \times 0.25 \times 0.18\ \text{mm}$

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298(2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

4390 independent reflections

3671 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 26.0^\circ$

$\theta_{\text{min}} = 1.9^\circ$

$h = -34 \rightarrow 23$

(SADABS; Sheldrick, 1996)

$T_{\min} = 0.748$ ,  $T_{\max} = 0.837$

11963 measured reflections

$k = -12 \rightarrow 12$

$l = -18 \rightarrow 25$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.067$

$S = 1.06$

4390 reflections

316 parameters

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

$$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 1.2193P]$$

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

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

$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

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

|    | $x$           | $y$        | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|---------------|------------|--------------|----------------------------------|
| C1 | 0.13185 (12)  | 0.5408 (3) | 0.40308 (16) | 0.0477 (6)                       |
| H1 | 0.1436        | 0.4625     | 0.4326       | 0.057*                           |
| C2 | 0.15571 (15)  | 0.6556 (3) | 0.4506 (2)   | 0.0609 (8)                       |
| H2 | 0.1832        | 0.6534     | 0.5105       | 0.073*                           |
| C3 | 0.13835 (14)  | 0.7702 (3) | 0.40838 (19) | 0.0644 (8)                       |
| H3 | 0.1536        | 0.8474     | 0.4394       | 0.077*                           |
| C4 | 0.09731 (13)  | 0.7733 (3) | 0.31771 (18) | 0.0491 (7)                       |
| C5 | 0.07771 (16)  | 0.8903 (3) | 0.2685 (2)   | 0.0652 (9)                       |
| H5 | 0.0920        | 0.9697     | 0.2971       | 0.078*                           |
| C6 | 0.03932 (15)  | 0.8881 (3) | 0.1826 (2)   | 0.0604 (8)                       |
| H6 | 0.0278        | 0.9657     | 0.1524       | 0.072*                           |
| C7 | 0.01567 (12)  | 0.7686 (2) | 0.13628 (17) | 0.0448 (6)                       |
| C8 | -0.02500 (12) | 0.7611 (3) | 0.04561 (18) | 0.0517 (7)                       |
| H8 | -0.0379       | 0.8367     | 0.0131       | 0.062*                           |
| C9 | -0.04538 (13) | 0.6440 (3) | 0.00554 (18) | 0.0510 (7)                       |

## supplementary materials

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|     |               |               |               |             |
|-----|---------------|---------------|---------------|-------------|
| H9  | -0.0719       | 0.6383        | -0.0542       | 0.061*      |
| C10 | -0.02569 (11) | 0.5324 (3)    | 0.05582 (16)  | 0.0438 (6)  |
| H10 | -0.0399       | 0.4524        | 0.0281        | 0.053*      |
| C11 | 0.03313 (11)  | 0.6513 (2)    | 0.18132 (16)  | 0.0352 (5)  |
| C12 | 0.07583 (11)  | 0.6531 (2)    | 0.27488 (16)  | 0.0362 (5)  |
| C13 | 0.16216 (11)  | 0.2707 (2)    | 0.25844 (15)  | 0.0393 (6)  |
| C14 | 0.22134 (11)  | 0.2278 (2)    | 0.27919 (16)  | 0.0407 (6)  |
| C15 | 0.26018 (13)  | 0.1335 (3)    | 0.34283 (19)  | 0.0518 (7)  |
| C16 | 0.31708 (14)  | 0.1016 (3)    | 0.3645 (2)    | 0.0701 (9)  |
| H16 | 0.3431        | 0.0400        | 0.4071        | 0.084*      |
| C17 | 0.33538 (17)  | 0.1594 (4)    | 0.3243 (3)    | 0.0817 (12) |
| H17 | 0.3737        | 0.1362        | 0.3395        | 0.098*      |
| C18 | 0.29839 (16)  | 0.2517 (4)    | 0.2617 (3)    | 0.0750 (10) |
| H18 | 0.3114        | 0.2908        | 0.2346        | 0.090*      |
| C19 | 0.24122 (14)  | 0.2856 (3)    | 0.2392 (2)    | 0.0558 (7)  |
| H19 | 0.2159        | 0.3480        | 0.1969        | 0.067*      |
| C20 | -0.05515 (11) | 0.2173 (2)    | 0.10588 (15)  | 0.0382 (5)  |
| C21 | -0.11314 (11) | 0.1442 (2)    | 0.03654 (15)  | 0.0361 (5)  |
| C22 | -0.11635 (12) | 0.0730 (2)    | -0.02440 (15) | 0.0432 (6)  |
| C23 | -0.17163 (14) | 0.0033 (3)    | -0.08804 (16) | 0.0565 (8)  |
| H23 | -0.1743       | -0.0454       | -0.1285       | 0.068*      |
| C24 | -0.22170 (13) | 0.0073 (3)    | -0.09029 (18) | 0.0607 (8)  |
| H24 | -0.2581       | -0.0396       | -0.1324       | 0.073*      |
| C25 | -0.21937 (13) | 0.0784 (3)    | -0.03221 (18) | 0.0576 (8)  |
| H25 | -0.2541       | 0.0811        | -0.0353       | 0.069*      |
| C26 | -0.16526 (12) | 0.1463 (2)    | 0.03120 (17)  | 0.0451 (6)  |
| H26 | -0.1636       | 0.1944        | 0.0711        | 0.054*      |
| Cd1 | 0.057575 (8)  | 0.350425 (15) | 0.231588 (11) | 0.03562 (7) |
| N1  | 0.09300 (9)   | 0.53845 (19)  | 0.31732 (12)  | 0.0372 (4)  |
| N2  | 0.01241 (8)   | 0.53497 (18)  | 0.14148 (12)  | 0.0361 (4)  |
| O1  | 0.13009 (8)   | 0.36071 (17)  | 0.20625 (12)  | 0.0517 (5)  |
| O2  | 0.14511 (8)   | 0.21631 (18)  | 0.29634 (11)  | 0.0497 (5)  |
| O3  | 0.24496 (10)  | 0.0733 (2)    | 0.38541 (14)  | 0.0733 (6)  |
| H3A | 0.2083        | 0.0907        | 0.3625        | 0.110*      |
| O4  | -0.00846 (8)  | 0.21515 (17)  | 0.10927 (12)  | 0.0527 (5)  |
| O5  | 0.05244 (8)   | 0.28218 (18)  | 0.34009 (12)  | 0.0516 (5)  |
| O6  | -0.06878 (9)  | 0.06944 (18)  | -0.02577 (12) | 0.0582 (5)  |
| H6A | -0.0397       | 0.1157        | 0.0128        | 0.087*      |

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

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.0451 (14) | 0.0544 (16) | 0.0402 (15) | 0.0009 (12)  | 0.0264 (12) | 0.0023 (12)  |
| C2 | 0.0598 (19) | 0.074 (2)   | 0.0388 (15) | -0.0100 (15) | 0.0276 (14) | -0.0083 (14) |
| C3 | 0.075 (2)   | 0.0561 (19) | 0.0585 (19) | -0.0184 (16) | 0.0419 (17) | -0.0227 (15) |
| C4 | 0.0547 (16) | 0.0434 (15) | 0.0540 (17) | -0.0046 (12) | 0.0375 (14) | -0.0069 (12) |
| C5 | 0.083 (2)   | 0.0347 (15) | 0.079 (2)   | -0.0069 (15) | 0.0531 (19) | -0.0092 (15) |
| C6 | 0.081 (2)   | 0.0320 (14) | 0.074 (2)   | 0.0066 (14)  | 0.0534 (19) | 0.0109 (14)  |

|     |              |              |              |              |             |              |
|-----|--------------|--------------|--------------|--------------|-------------|--------------|
| C7  | 0.0488 (14)  | 0.0373 (14)  | 0.0556 (16)  | 0.0067 (11)  | 0.0373 (13) | 0.0082 (12)  |
| C8  | 0.0521 (16)  | 0.0519 (17)  | 0.0555 (17)  | 0.0147 (13)  | 0.0370 (14) | 0.0210 (14)  |
| C9  | 0.0466 (15)  | 0.0615 (19)  | 0.0398 (15)  | 0.0083 (13)  | 0.0260 (13) | 0.0099 (13)  |
| C10 | 0.0407 (13)  | 0.0445 (14)  | 0.0398 (14)  | 0.0001 (11)  | 0.0235 (12) | 0.0003 (11)  |
| C11 | 0.0358 (12)  | 0.0347 (13)  | 0.0438 (14)  | 0.0014 (9)   | 0.0298 (12) | 0.0025 (10)  |
| C12 | 0.0361 (12)  | 0.0362 (13)  | 0.0426 (14)  | -0.0019 (10) | 0.0284 (11) | -0.0020 (10) |
| C13 | 0.0359 (13)  | 0.0407 (14)  | 0.0367 (13)  | -0.0027 (10) | 0.0217 (11) | -0.0052 (11) |
| C14 | 0.0380 (13)  | 0.0415 (14)  | 0.0453 (14)  | -0.0039 (10) | 0.0284 (12) | -0.0091 (11) |
| C15 | 0.0413 (15)  | 0.0504 (17)  | 0.0551 (17)  | 0.0027 (12)  | 0.0277 (14) | -0.0097 (13) |
| C16 | 0.0430 (16)  | 0.072 (2)    | 0.079 (2)    | 0.0128 (15)  | 0.0329 (17) | -0.0067 (18) |
| C17 | 0.052 (2)    | 0.089 (3)    | 0.110 (3)    | -0.0032 (18) | 0.055 (2)   | -0.035 (2)   |
| C18 | 0.080 (2)    | 0.082 (2)    | 0.106 (3)    | -0.026 (2)   | 0.079 (2)   | -0.032 (2)   |
| C19 | 0.0632 (18)  | 0.0562 (18)  | 0.0655 (19)  | -0.0087 (14) | 0.0498 (16) | -0.0096 (14) |
| C20 | 0.0415 (13)  | 0.0274 (12)  | 0.0391 (13)  | -0.0002 (10) | 0.0233 (11) | 0.0027 (10)  |
| C21 | 0.0396 (13)  | 0.0301 (12)  | 0.0340 (12)  | -0.0005 (9)  | 0.0219 (11) | 0.0025 (9)   |
| C22 | 0.0543 (15)  | 0.0336 (14)  | 0.0392 (14)  | 0.0038 (11)  | 0.0295 (12) | 0.0044 (11)  |
| C23 | 0.0702 (19)  | 0.0434 (16)  | 0.0355 (15)  | -0.0025 (13) | 0.0256 (14) | -0.0060 (12) |
| C24 | 0.0474 (17)  | 0.0550 (18)  | 0.0412 (16)  | -0.0091 (13) | 0.0121 (13) | -0.0018 (13) |
| C25 | 0.0417 (15)  | 0.0582 (18)  | 0.0542 (18)  | -0.0056 (13) | 0.0231 (14) | 0.0044 (14)  |
| C26 | 0.0446 (14)  | 0.0438 (15)  | 0.0421 (14)  | 0.0004 (11)  | 0.0261 (12) | 0.0022 (11)  |
| Cd1 | 0.03456 (11) | 0.03147 (11) | 0.03994 (12) | 0.00079 (7)  | 0.02394 (9) | 0.00196 (7)  |
| N1  | 0.0367 (10)  | 0.0370 (11)  | 0.0375 (11)  | 0.0005 (8)   | 0.0240 (9)  | 0.0023 (9)   |
| N2  | 0.0336 (10)  | 0.0365 (11)  | 0.0373 (11)  | 0.0004 (8)   | 0.0228 (9)  | 0.0009 (8)   |
| O1  | 0.0432 (10)  | 0.0568 (12)  | 0.0545 (11)  | 0.0086 (8)   | 0.0316 (9)  | 0.0137 (9)   |
| O2  | 0.0457 (10)  | 0.0594 (12)  | 0.0537 (11)  | 0.0101 (9)   | 0.0367 (9)  | 0.0135 (9)   |
| O3  | 0.0634 (13)  | 0.0808 (16)  | 0.0761 (15)  | 0.0276 (11)  | 0.0457 (12) | 0.0327 (13)  |
| O4  | 0.0434 (10)  | 0.0479 (11)  | 0.0676 (13)  | -0.0064 (8)  | 0.0367 (10) | -0.0098 (9)  |
| O5  | 0.0585 (11)  | 0.0506 (11)  | 0.0498 (11)  | 0.0123 (9)   | 0.0373 (10) | 0.0157 (9)   |
| O6  | 0.0736 (13)  | 0.0545 (12)  | 0.0648 (13)  | -0.0001 (10) | 0.0532 (11) | -0.0074 (10) |

*Geometric parameters (Å, °)*

|        |           |                     |           |
|--------|-----------|---------------------|-----------|
| C1—N1  | 1.331 (3) | C16—H16             | 0.9300    |
| C1—C2  | 1.394 (4) | C17—C18             | 1.373 (5) |
| C1—H1  | 0.9300    | C17—H17             | 0.9300    |
| C2—C3  | 1.353 (4) | C18—C19             | 1.388 (4) |
| C2—H2  | 0.9300    | C18—H18             | 0.9300    |
| C3—C4  | 1.407 (4) | C19—H19             | 0.9300    |
| C3—H3  | 0.9300    | C20—O5 <sup>i</sup> | 1.252 (3) |
| C4—C12 | 1.406 (3) | C20—O4              | 1.260 (3) |
| C4—C5  | 1.432 (4) | C20—C21             | 1.484 (3) |
| C5—C6  | 1.335 (5) | C21—C26             | 1.388 (4) |
| C5—H5  | 0.9300    | C21—C22             | 1.399 (3) |
| C6—C7  | 1.426 (4) | C22—O6              | 1.348 (3) |
| C6—H6  | 0.9300    | C22—C23             | 1.404 (4) |
| C7—C11 | 1.401 (3) | C23—C24             | 1.370 (4) |
| C7—C8  | 1.410 (4) | C23—H23             | 0.9300    |
| C8—C9  | 1.358 (4) | C24—C25             | 1.362 (4) |
| C8—H8  | 0.9300    | C24—H24             | 0.9300    |

## supplementary materials

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|            |           |                          |             |
|------------|-----------|--------------------------|-------------|
| C9—C10     | 1.395 (3) | C25—C26                  | 1.378 (4)   |
| C9—H9      | 0.9300    | C25—H25                  | 0.9300      |
| C10—N2     | 1.331 (3) | C26—H26                  | 0.9300      |
| C10—H10    | 0.9300    | Cd1—O2                   | 2.3271 (16) |
| C11—N2     | 1.349 (3) | Cd1—N1                   | 2.355 (2)   |
| C11—C12    | 1.451 (4) | Cd1—N2                   | 2.3606 (19) |
| C12—N1     | 1.355 (3) | Cd1—O4                   | 2.3630 (18) |
| C13—O1     | 1.247 (3) | Cd1—O1                   | 2.3993 (19) |
| C13—O2     | 1.275 (3) | Cd1—O5                   | 2.4214 (18) |
| C13—C14    | 1.480 (3) | Cd1—O5 <sup>i</sup>      | 2.4911 (18) |
| C14—C19    | 1.388 (4) | O3—H3A                   | 0.8199      |
| C14—C15    | 1.405 (4) | O5—C20 <sup>i</sup>      | 1.252 (3)   |
| C15—O3     | 1.345 (4) | O5—Cd1 <sup>i</sup>      | 2.4911 (18) |
| C15—C16    | 1.382 (4) | O6—H6A                   | 0.8200      |
| C16—C17    | 1.357 (6) |                          |             |
| N1—C1—C2   | 122.8 (3) | O5 <sup>i</sup> —C20—O4  | 119.8 (2)   |
| N1—C1—H1   | 118.6     | O5 <sup>i</sup> —C20—C21 | 121.0 (2)   |
| C2—C1—H1   | 118.6     | O4—C20—C21               | 119.2 (2)   |
| C3—C2—C1   | 119.1 (3) | C26—C21—C22              | 119.0 (2)   |
| C3—C2—H2   | 120.4     | C26—C21—C20              | 120.1 (2)   |
| C1—C2—H2   | 120.4     | C22—C21—C20              | 120.9 (2)   |
| C2—C3—C4   | 120.4 (3) | O6—C22—C21               | 122.9 (2)   |
| C2—C3—H3   | 119.8     | O6—C22—C23               | 118.0 (2)   |
| C4—C3—H3   | 119.8     | C21—C22—C23              | 119.1 (3)   |
| C12—C4—C3  | 116.8 (3) | C24—C23—C22              | 119.8 (3)   |
| C12—C4—C5  | 119.5 (3) | C24—C23—H23              | 120.1       |
| C3—C4—C5   | 123.7 (3) | C22—C23—H23              | 120.1       |
| C6—C5—C4   | 121.4 (3) | C25—C24—C23              | 121.4 (3)   |
| C6—C5—H5   | 119.3     | C25—C24—H24              | 119.3       |
| C4—C5—H5   | 119.3     | C23—C24—H24              | 119.3       |
| C5—C6—C7   | 121.0 (3) | C24—C25—C26              | 119.6 (3)   |
| C5—C6—H6   | 119.5     | C24—C25—H25              | 120.2       |
| C7—C6—H6   | 119.5     | C26—C25—H25              | 120.2       |
| C11—C7—C8  | 117.0 (2) | C25—C26—C21              | 121.1 (3)   |
| C11—C7—C6  | 119.8 (3) | C25—C26—H26              | 119.5       |
| C8—C7—C6   | 123.2 (2) | C21—C26—H26              | 119.5       |
| C9—C8—C7   | 120.2 (2) | O2—Cd1—N1                | 106.89 (7)  |
| C9—C8—H8   | 119.9     | O2—Cd1—N2                | 138.63 (6)  |
| C7—C8—H8   | 119.9     | N1—Cd1—N2                | 70.68 (7)   |
| C8—C9—C10  | 118.7 (3) | O2—Cd1—O4                | 93.20 (6)   |
| C8—C9—H9   | 120.7     | N1—Cd1—O4                | 158.83 (6)  |
| C10—C9—H9  | 120.7     | N2—Cd1—O4                | 89.92 (6)   |
| N2—C10—C9  | 123.1 (2) | O2—Cd1—O1                | 55.09 (6)   |
| N2—C10—H10 | 118.4     | N1—Cd1—O1                | 96.97 (7)   |
| C9—C10—H10 | 118.4     | N2—Cd1—O1                | 83.78 (6)   |
| N2—C11—C7  | 122.8 (2) | O4—Cd1—O1                | 88.99 (7)   |
| N2—C11—C12 | 117.8 (2) | O2—Cd1—O5                | 88.55 (6)   |
| C7—C11—C12 | 119.4 (2) | N1—Cd1—O5                | 78.67 (7)   |

|               |            |                                       |              |
|---------------|------------|---------------------------------------|--------------|
| N1—C12—C4     | 122.7 (2)  | N2—Cd1—O5                             | 128.98 (6)   |
| N1—C12—C11    | 118.5 (2)  | O4—Cd1—O5                             | 109.11 (7)   |
| C4—C12—C11    | 118.8 (2)  | O1—Cd1—O5                             | 140.82 (6)   |
| O1—C13—O2     | 120.2 (2)  | O2—Cd1—O5 <sup>i</sup>                | 126.96 (6)   |
| O1—C13—C14    | 120.7 (2)  | N1—Cd1—O5 <sup>i</sup>                | 115.33 (6)   |
| O2—C13—C14    | 119.0 (2)  | N2—Cd1—O5 <sup>i</sup>                | 86.73 (6)    |
| C19—C14—C15   | 118.7 (3)  | O4—Cd1—O5 <sup>i</sup>                | 53.13 (6)    |
| C19—C14—C13   | 120.3 (2)  | O1—Cd1—O5 <sup>i</sup>                | 140.94 (6)   |
| C15—C14—C13   | 120.9 (2)  | O5—Cd1—O5 <sup>i</sup>                | 70.66 (7)    |
| O3—C15—C16    | 117.8 (3)  | C1—N1—C12                             | 118.2 (2)    |
| O3—C15—C14    | 122.7 (2)  | C1—N1—Cd1                             | 125.56 (17)  |
| C16—C15—C14   | 119.5 (3)  | C12—N1—Cd1                            | 116.05 (15)  |
| C17—C16—C15   | 120.7 (3)  | C10—N2—C11                            | 118.2 (2)    |
| C17—C16—H16   | 119.6      | C10—N2—Cd1                            | 124.98 (16)  |
| C15—C16—H16   | 119.6      | C11—N2—Cd1                            | 116.38 (15)  |
| C16—C17—C18   | 121.2 (3)  | C13—O1—Cd1                            | 91.02 (15)   |
| C16—C17—H17   | 119.4      | C13—O2—Cd1                            | 93.65 (15)   |
| C18—C17—H17   | 119.4      | C15—O3—H3A                            | 109.4        |
| C17—C18—C19   | 119.0 (3)  | C20—O4—Cd1                            | 96.43 (15)   |
| C17—C18—H18   | 120.5      | C20 <sup>i</sup> —O5—Cd1              | 163.72 (17)  |
| C19—C18—H18   | 120.5      | C20 <sup>i</sup> —O5—Cd1 <sup>i</sup> | 90.61 (15)   |
| C14—C19—C18   | 120.9 (3)  | Cd1—O5—Cd1 <sup>i</sup>               | 99.62 (6)    |
| C14—C19—H19   | 119.5      | C22—O6—H6A                            | 109.5        |
| C18—C19—H19   | 119.5      |                                       |              |
| N1—C1—C2—C3   | 0.8 (5)    | O1—Cd1—N1—C1                          | -99.78 (19)  |
| C1—C2—C3—C4   | -0.7 (5)   | O5—Cd1—N1—C1                          | 40.75 (19)   |
| C2—C3—C4—C12  | 0.3 (4)    | O5 <sup>i</sup> —Cd1—N1—C1            | 102.81 (19)  |
| C2—C3—C4—C5   | -178.8 (3) | O2—Cd1—N1—C12                         | 130.28 (16)  |
| C12—C4—C5—C6  | 0.1 (5)    | N2—Cd1—N1—C12                         | -6.16 (15)   |
| C3—C4—C5—C6   | 179.1 (3)  | O4—Cd1—N1—C12                         | -30.7 (3)    |
| C4—C5—C6—C7   | 0.8 (5)    | O1—Cd1—N1—C12                         | 74.72 (16)   |
| C5—C6—C7—C11  | -0.4 (4)   | O5—Cd1—N1—C12                         | -144.75 (17) |
| C5—C6—C7—C8   | 179.9 (3)  | O5 <sup>i</sup> —Cd1—N1—C12           | -82.69 (17)  |
| C11—C7—C8—C9  | -0.2 (4)   | C9—C10—N2—C11                         | -0.4 (4)     |
| C6—C7—C8—C9   | 179.4 (3)  | C9—C10—N2—Cd1                         | -172.1 (2)   |
| C7—C8—C9—C10  | 0.5 (4)    | C7—C11—N2—C10                         | 0.7 (3)      |
| C8—C9—C10—N2  | -0.2 (4)   | C12—C11—N2—C10                        | -178.6 (2)   |
| C8—C7—C11—N2  | -0.4 (4)   | C7—C11—N2—Cd1                         | 173.18 (18)  |
| C6—C7—C11—N2  | 179.9 (2)  | C12—C11—N2—Cd1                        | -6.2 (3)     |
| C8—C7—C11—C12 | 178.9 (2)  | O2—Cd1—N2—C10                         | 84.4 (2)     |
| C6—C7—C11—C12 | -0.7 (4)   | N1—Cd1—N2—C10                         | 178.3 (2)    |
| C3—C4—C12—N1  | 0.1 (4)    | O4—Cd1—N2—C10                         | -10.32 (19)  |
| C5—C4—C12—N1  | 179.3 (2)  | O1—Cd1—N2—C10                         | 78.67 (19)   |
| C3—C4—C12—C11 | 179.7 (2)  | O5—Cd1—N2—C10                         | -125.16 (18) |
| C5—C4—C12—C11 | -1.2 (4)   | O5 <sup>i</sup> —Cd1—N2—C10           | -63.38 (18)  |
| N2—C11—C12—N1 | 0.4 (3)    | O2—Cd1—N2—C11                         | -87.44 (18)  |

## supplementary materials

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|                              |              |  |              |
|------------------------------|--------------|--|--------------|
| C7—C11—C12—N1                | -178.9 (2)   | N1—Cd1—N2—C11                            | 6.44 (15)    |
| N2—C11—C12—C4                | -179.1 (2)   | O4—Cd1—N2—C11                            | 177.81 (16)  |
| C7—C11—C12—C4                | 1.5 (4)      | O1—Cd1—N2—C11                            | -93.21 (16)  |
| O1—C13—C14—C19               | -1.4 (4)     | O5—Cd1—N2—C11                            | 62.97 (18)   |
| O2—C13—C14—C19               | -179.7 (2)   | O5 <sup>i</sup> —Cd1—N2—C11              | 124.74 (16)  |
| O1—C13—C14—C15               | 175.0 (2)    | O2—C13—O1—Cd1                            | 1.5 (2)      |
| O2—C13—C14—C15               | -3.3 (3)     | C14—C13—O1—Cd1                           | -176.72 (19) |
| C19—C14—C15—O3               | 179.4 (3)    | O2—Cd1—O1—C13                            | -0.88 (14)   |
| C13—C14—C15—O3               | 2.9 (4)      | N1—Cd1—O1—C13                            | 104.88 (15)  |
| C19—C14—C15—C16              | 0.6 (4)      | N2—Cd1—O1—C13                            | 174.48 (15)  |
| C13—C14—C15—C16              | -175.9 (2)   | O4—Cd1—O1—C13                            | -95.49 (15)  |
| O3—C15—C16—C17               | -179.6 (3)   | O5—Cd1—O1—C13                            | 24.28 (19)   |
| C14—C15—C16—C17              | -0.8 (5)     | O5 <sup>i</sup> —Cd1—O1—C13              | -108.56 (16) |
| C15—C16—C17—C18              | 0.5 (5)      | O1—C13—O2—Cd1                            | -1.6 (2)     |
| C16—C17—C18—C19              | -0.1 (5)     | C14—C13—O2—Cd1                           | 176.70 (18)  |
| C15—C14—C19—C18              | -0.2 (4)     | N1—Cd1—O2—C13                            | -85.86 (15)  |
| C13—C14—C19—C18              | 176.3 (2)    | N2—Cd1—O2—C13                            | -6.14 (19)   |
| C17—C18—C19—C14              | 0.0 (5)      | O4—Cd1—O2—C13                            | 87.38 (15)   |
| O5 <sup>i</sup> —C20—C21—C26 | -0.5 (3)     | O1—Cd1—O2—C13                            | 0.86 (13)    |
| O4—C20—C21—C26               | -179.4 (2)   | O5—Cd1—O2—C13                            | -163.56 (15) |
| O5 <sup>i</sup> —C20—C21—C22 | 179.2 (2)    | O5 <sup>i</sup> —Cd1—O2—C13              | 132.15 (14)  |
| O4—C20—C21—C22               | 0.3 (3)      | O5 <sup>i</sup> —C20—O4—Cd1              | 0.7 (2)      |
| C26—C21—C22—O6               | 177.6 (2)    | C21—C20—O4—Cd1                           | 179.66 (17)  |
| C20—C21—C22—O6               | -2.1 (3)     | O2—Cd1—O4—C20                            | 134.91 (14)  |
| C26—C21—C22—C23              | -1.4 (3)     | N1—Cd1—O4—C20                            | -63.3 (2)    |
| C20—C21—C22—C23              | 178.9 (2)    | N2—Cd1—O4—C20                            | -86.37 (15)  |
| O6—C22—C23—C24               | -178.3 (2)   | O1—Cd1—O4—C20                            | -170.14 (15) |
| C21—C22—C23—C24              | 0.8 (4)      | O5—Cd1—O4—C20                            | 45.33 (15)   |
| C22—C23—C24—C25              | 0.4 (4)      | O5 <sup>i</sup> —Cd1—O4—C20              | -0.40 (13)   |
| C23—C24—C25—C26              | -1.1 (4)     | O2—Cd1—O5—C20 <sup>i</sup>               | -34.5 (6)    |
| C24—C25—C26—C21              | 0.4 (4)      | N1—Cd1—O5—C20 <sup>i</sup>               | -142.0 (6)   |
| C22—C21—C26—C25              | 0.8 (4)      | N2—Cd1—O5—C20 <sup>i</sup>               | 164.6 (6)    |
| C20—C21—C26—C25              | -179.5 (2)   | O4—Cd1—O5—C20 <sup>i</sup>               | 58.4 (6)     |
| C2—C1—N1—C12                 | -0.4 (4)     | O1—Cd1—O5—C20 <sup>i</sup>               | -54.9 (6)    |
| C2—C1—N1—Cd1                 | 174.0 (2)    | O5 <sup>i</sup> —Cd1—O5—C20 <sup>i</sup> | 95.8 (6)     |
| C4—C12—N1—C1                 | -0.1 (4)     | O2—Cd1—O5—Cd1 <sup>i</sup>               | -162.70 (7)  |
| C11—C12—N1—C1                | -179.6 (2)   | N1—Cd1—O5—Cd1 <sup>i</sup>               | 89.75 (7)    |
| C4—C12—N1—Cd1                | -174.99 (19) | N2—Cd1—O5—Cd1 <sup>i</sup>               | 36.35 (10)   |
| C11—C12—N1—Cd1               | 5.5 (3)      | O4—Cd1—O5—Cd1 <sup>i</sup>               | -69.82 (8)   |
| O2—Cd1—N1—C1                 | -44.2 (2)    | O1—Cd1—O5—Cd1 <sup>i</sup>               | 176.89 (7)   |
| N2—Cd1—N1—C1                 | 179.3 (2)    | O5 <sup>i</sup> —Cd1—O5—Cd1 <sup>i</sup> | -32.44 (8)   |
| O4—Cd1—N1—C1                 | 154.77 (19)  |  |              |

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

*Hydrogen-bond geometry (Å, °)*

| <i>D—H···A</i> | <i>D—H</i> | <i>H···A</i> | <i>D···A</i> | <i>D—H···A</i> |
|----------------|------------|--------------|--------------|----------------|
| O6—H6A···O4    | 0.82       | 1.86         | 2.579 (3)    | 146            |
| O3—H3A···O2    | 0.82       | 1.87         | 2.576 (2)    | 143            |

Fig. 1

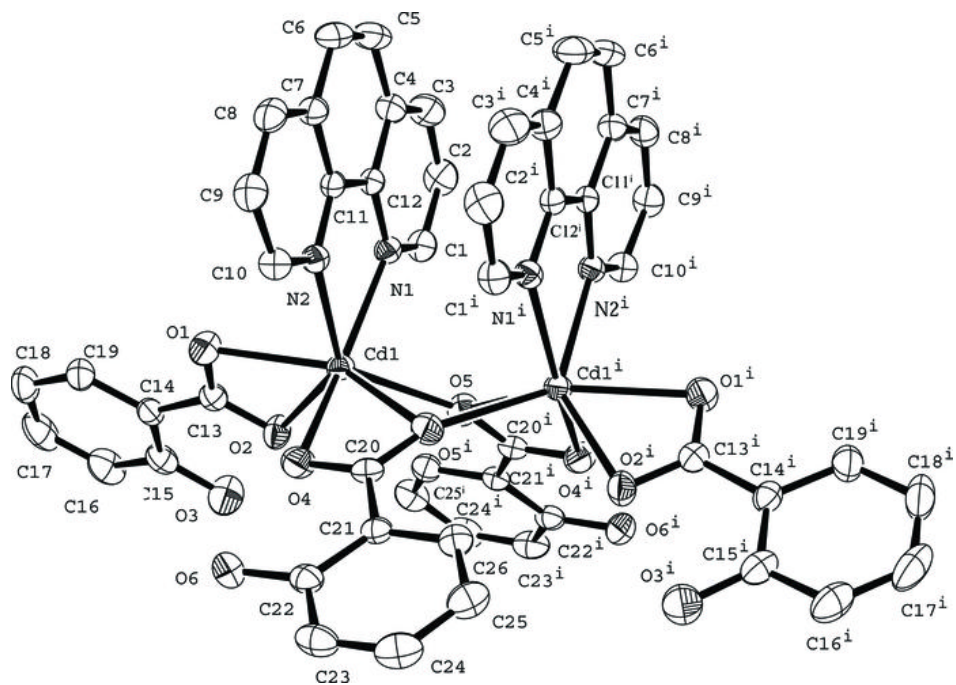


Fig. 2

