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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in solvent or counterion
 R factor = 0.033
 wR factor = 0.108
Data-to-parameter ratio = 17.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(4-hydroxybenzoato- κO)bis(1,10-phenanthroline- $\kappa^2\text{N},\text{N}'$)cadmium(II) dihydrate

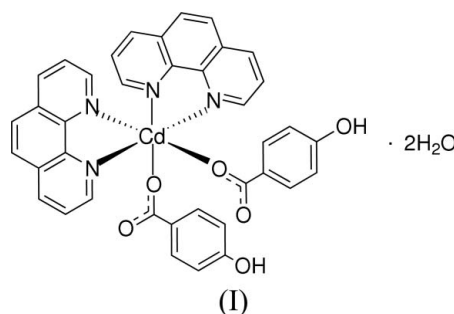
In the title compound, $[\text{Cd}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$, the Cd^{II} ion is located on a twofold axis and assumes a distorted octahedral CdN_4O_2 coordination geometry, formed by two phenanthroline (phen) ligands and two 4-hydroxybenzoate (HBA) anions. π - π stacking is observed between the parallel phen ligands of adjacent Cd^{II} complexes. One water O atom is located on a twofold axis. The other water molecule is disordered over two sites.

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Comment

As part of our ongoing investigation of π - π stacking interactions in metal complexes (Chen *et al.*, 2003), the title compound, (I), has been prepared and its X-ray crystal structure is presented here.



The crystal structure of (I) consists of Cd^{II} complexes and solvent water molecules. The Cd^{II} ion is located on a twofold axis and is coordinated by two phenanthroline (phen) ligands and two 4-hydroxybenzoate (HBA) anions with a distorted CdN_4O_2 octahedral geometry (Fig. 1). The monodentate HBA anions coordinate to the Cd^{II} ion in a *cis* configuration, their benzene rings being nearly perpendicular to each other [the dihedral angle is $73.50(7)^\circ$]. The two phen ligands are also nearly perpendicular to each other, the dihedral angle being $85.52(6)^\circ$.

A partially overlapped arrangement between parallel phen ligands is observed in the crystal structure of (I) (Figs. 2 and 3]. The face-to-face separations between the $\text{N}2$ -phen and $\text{N}2^{\text{iii}}$ -phen ligands [symmetry code: (iii) $1 - x, 1 - y, 1 - z$] and between the $\text{N}2$ -phen and $\text{N}2^{\text{iv}}$ -phen ligands [symmetry code: (iv) $1 - x, 2 - y, 1 - z$] are $3.49(2)$ and $3.512(18)$ Å, respectively, indicating the existence of π - π stacking between neighbouring Cd^{II} complexes.

The hydroxy group forms an intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond with the uncoordinated carboxylate atom O2 of a neighbouring complex (Table 2). The solvent water molecule O1W is located on a twofold axis and is hydrogen

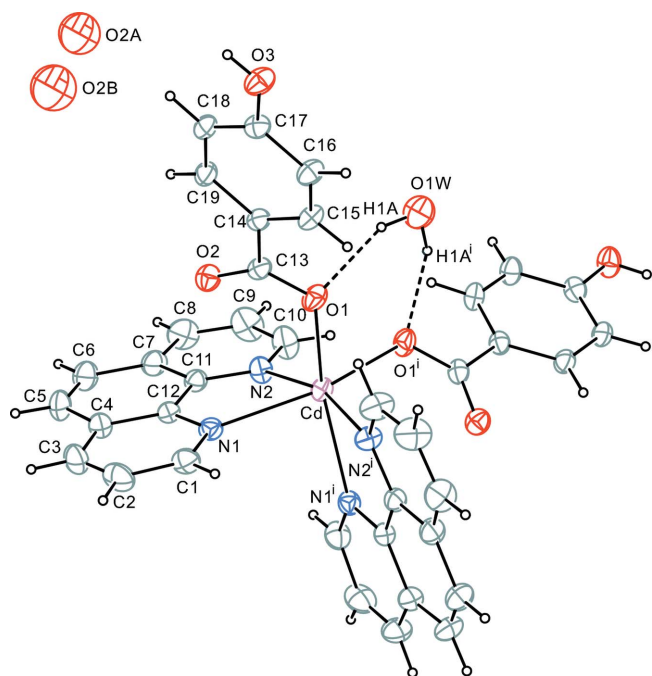


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). The H atoms of the disordered water molecules have been omitted for clarity. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

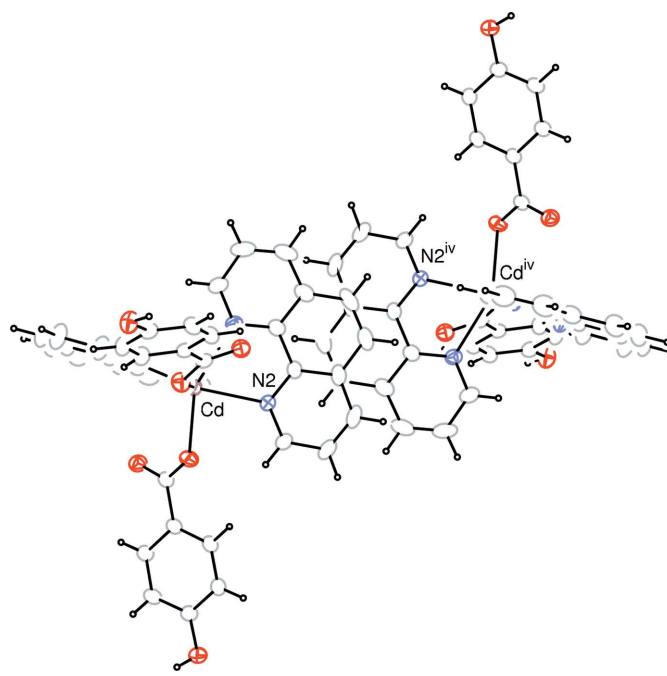


Figure 3
 π - π stacking between parallel N2-phen and N2^{iv}-phen ligands of neighbouring Cd^{II} complexes. [Symmetry code: (iv) $1 - x, 2 - y, 1 - z$.]

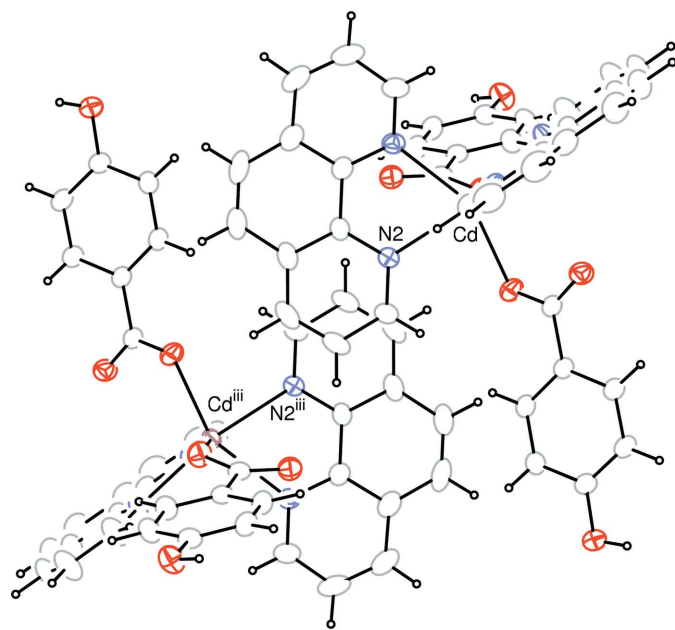


Figure 2
 π - π stacking between parallel N2-phen and N2ⁱⁱⁱ-phen ligands of neighbouring Cd^{II} complexes. [Symmetry code: (iii) $1 - x, 1 - y, 1 - z$.]

bonded to the carboxylate groups of the complex (Fig. 1). The other water molecule, located close to a twofold axis, is disordered over two sites (O2A and O2B), with a separation of 1.22 (2) Å between them. The disordered water molecule is not involved in the hydrogen-bond network.

Experimental

Cd(NO₃)₂·4H₂O (0.62 g, 2 mmol), 4-hydroxybenzoic acid (0.32 g, 2 mmol) and Na₂CO₃ (0.21 g, 2 mmol) were dissolved in a water-ethanol solution (20 ml, 3:1), and then phen (0.40 g, 2 mmol) was added to the solution. The mixture was refluxed for 5 h, and then filtered after cooling to room temperature. Single crystals of (I) were obtained after three months.

Crystal data

[Cd(C₇H₅O₃)₂(C₁₂H₈N₂)₂].2H₂O
M_r = 783.06
 Monoclinic, C2/c
a = 23.158 (11) Å
b = 9.399 (3) Å
c = 16.802 (5) Å
 β = 99.416 (2)°
V = 3608 (2) Å³

Z = 4
D_x = 1.442 Mg m⁻³
 Mo K α radiation
 μ = 0.66 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.53 × 0.32 × 0.20 mm

Data collection

Rigaku R-Axis RAPID
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.702, *T_{max}* = 0.875

17121 measured reflections
 4123 independent reflections
 3771 reflections with *I* > 2 σ (*I*)
R_{int} = 0.025
 θ_{max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.033
wR(*F*²) = 0.108
S = 1.09
 4123 reflections
 235 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 1.9122P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.89 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.45 \text{ e \AA}^{-3}$

Table 1Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-----------------------|------------|-----------------------|-------------|
| Cd—O1 | 2.257 (2) | Cd—N2 | 2.378 (2) |
| Cd—N1 | 2.389 (2) | | |
| O1—Cd—O1 ⁱ | 90.47 (11) | N1—Cd—N1 ⁱ | 85.02 (11) |
| O1—Cd—N1 | 98.61 (8) | N1—Cd—N2 | 69.59 (8) |
| O1—Cd—N1 ⁱ | 152.69 (8) | N1—Cd—N2 ⁱ | 98.27 (8) |
| O1—Cd—N2 | 108.40 (8) | N2—Cd—N2 ⁱ | 164.01 (12) |
| O1—Cd—N2 ⁱ | 83.12 (8) | | |

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.**Table 2**Hydrogen-bond geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|-------|-------------|-------------|---------------|
| O1W—H1A \cdots O1 | 0.99 | 2.04 | 2.952 (5) | 152 |
| O3—H3 \cdots O2 ⁱⁱ | 0.82 | 1.81 | 2.629 (3) | 170 |

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

The solvent water molecule located close to a twofold axis is disordered over two sites, O2A and O2B. The occupancies were refined and converged to 0.273 (5) and 0.227 (5), respectively. They were fixed at 0.25 in the final cycles of refinement. The aromatic H atoms were placed in calculated positions with C—H = 0.93 \AA and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Water and hydroxy

H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ for the disordered water molecule and $U_{\text{iso}}(\text{H}) = 0.08 \text{\AA}^2$ for the other water molecule and the hydroxy group.

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, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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