

Diaquadibenzimidazolebis(5-fluoro-2,4-dioxo-1,2,3,4-tetrahydropyrimidine-1-acetato)-cadmium(II)

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In the title centrosymmetric compound, $[\text{Cd}(\text{C}_6\text{H}_4\text{FN}_2\text{O}_4)_2(\text{C}_7\text{H}_6\text{N}_2)_2(\text{H}_2\text{O})_2]$, the cadmium(II) cation is coordinated by one O atom from each 5-fluoro-2,4-dioxo-1,2,3,4-tetrahydropyrimidine-1-acetate anion, one N atom from each benzimidazole ligand and two water molecules. The geometry around the cadmium(II) cation, which is located on a center of inversion, is distorted octahedral. Molecules, which function as supramolecular blocks, are linked by intermolecular N—H...O and O—H...O hydrogen bonds into a three-dimensional supramolecular network, which is reinforced by π – π interactions.

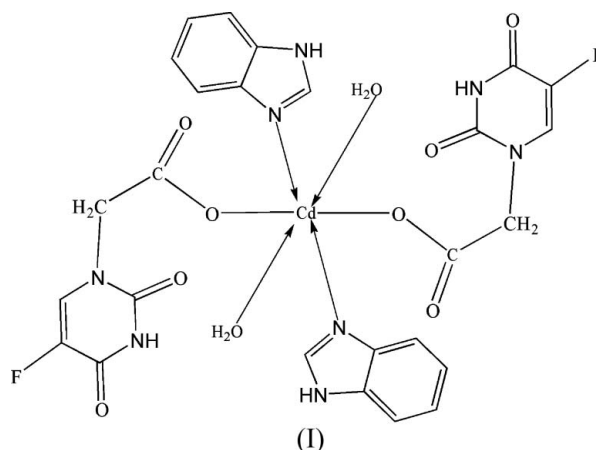
Key indicators

Single-crystal X-ray study
 $T = 298 \text{ K}$
 Mean $\sigma(\text{C}—\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.025
 wR factor = 0.067
 Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Recently, attention has been paid to N—H...O and O—H...O hydrogen-bond interactions owing to their biological relevance (Aakeröy *et al.*, 2005). 5-Fluoro-2,4-dioxo-1,2,3,4-tetrahydropyrimidine-1-acetate (5-FUAA) is a good candidate for the development of supramolecular networks by the above interactions in crystals; it has good antimicrobial and antitumor activity (Beall & Sloan, 2001, 2002), with both carboxylate and carbonyl as potential coordinating groups. We report the structure of the title compound, $[\text{Cd}(\text{C}_6\text{H}_4\text{FN}_2\text{O}_4)_2(\text{C}_7\text{H}_6\text{N}_2)_2(\text{H}_2\text{O})_2]$, (I).



The mononuclear unit of (I) consists of a Cd^{II} ion, two coordinated water molecules, two benzimidazole (BIM) molecules and two 5-FUAA anions binding through their carboxylate O atoms in monodentate mode. This pattern is similar to that found in $[\text{Zn}(\text{C}_6\text{H}_4\text{N}_2\text{O}_4\text{F})_2(\text{H}_2\text{O})_4](\text{H}_2\text{O})_4$ (Huang *et al.*, 2000). The Cd atom lies on an inversion center with distorted octahedral coordination geometry (Fig. 1 and Table 1). The equatorial plane $[\text{O}1/\text{O}1^1/\text{N}3/\text{N}3^1]$; symmetry code: (i) $-x, -y + 2, -z$] consists of two carboxylate O atoms

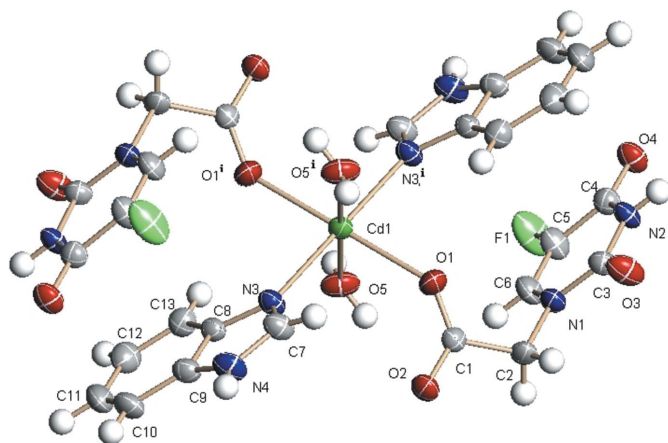


Figure 1
The mononuclear unit of (I), showing displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $-x, -y + 2, -z$].

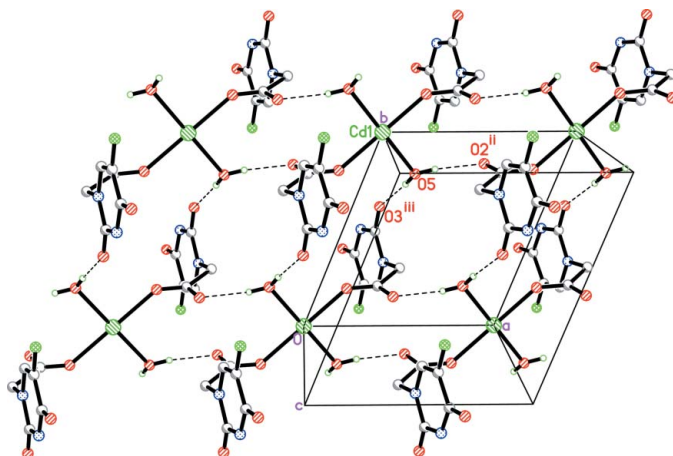


Figure 2
Part of a (001) O—H...O hydrogen-bonded (dashed lines) sheet. The benzimidazole molecules and H atoms not involved in these interactions have been omitted for clarity [symmetry codes: (ii) $-x + 1, -y + 2, -z$; (iii) $x, y - 1, z$].

from 5-FUAA and two N atoms from two BIM molecules. The two axial positions are filled by two O atoms from two water molecules. The Cd—N3 and Cd—O1 distances are in good agreement with the sum of covalent radii (2.23 and 2.21 Å, respectively), while the Cd—O5 distance is a little longer than the sum of covalent radii but clearly smaller than the sum of van de Waals radii (2.90 Å) (March *et al.*, 2003). Distortion in (I) from ideal octahedral coordination, which has 12 90° and three 180° angles (Seppelt, 2003), is mainly reflected in the N—Cd—O angles [ranging from 85.68 (7) to 94.32 (7)°].

All ligands, including 5-FUAA, BIM and water molecules, of the mononuclear units are involved in directional intermolecular hydrogen-bond interactions (Table 2), which are the primary tools in assembling intriguing supramolecular structures (Zaworotko, 1997; Braga & Grepioni, 2000). Figs. 2 and 3 show the hydrogen-bonding network, which can be described in graph-set motifs (Etter, 1990; Grell *et al.*, 2000). Fig. 2 shows part of a (001) O—H...O hydrogen-bonded sheet with water molecules as donors and carboxylate O (O_2^{ii} ; see Table 2 for symmetry codes) and the carbonyl O atoms (O_3^{iii})

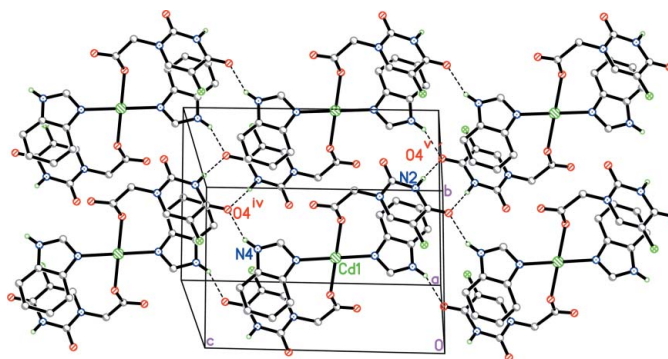


Figure 3
Part of a (100) N—H...O hydrogen-bonded (dashed lines) sheet. The water molecules and H atoms not involved in these interactions have been omitted for clarity [symmetry codes: (iv) $x, y, z + 1$; (v) $-x, -y + 3, -z - 1$].

as acceptors. Around each $R_4^4(18)$ motif there are two $R_2^2(12)$ motifs and two $R_2^2(18)$ motifs. All of the above-mentioned motifs form a tetranuclear unit, which may be described as an $R_4^4(30)$ motif, and two neighboring tetranuclear units share an $R_2^2(18)$ motif. Fig. 3 shows a (100) N—H...O hydrogen-bonded sheet with two atoms (N2 from 5-FUAA and N4 from BIM) as hydrogen-bond donors *via* atoms H2 and H4, respectively, to carbonyl O atoms (O_4^{iv} and O_4^v) forming N—H...O hydrogen-bond networks of $R_2^2(8)$, $R_2^2(26)$ and $R_4^4(26)$ motifs (Fig. 3). Each $R_2^2(8)$ motif is constructed by a pair of 5-FUAA anions, bordering with the $R_4^4(26)$ motif located in the center of Fig. 3. Moreover, there are $R_2^2(26)$ motifs, overlapping partially with the $R_4^4(26)$ motifs. A three-dimensional network is formed by the combination of the (001) and (100) sheets.

The hydrogen-bonded supramolecular network is reinforced by π — π interactions (Fig. 4). The 5-FUAA and BIM ligands are overlapped mutually by different π — π interactions between the uracil ring and the imidazole ring at $(-x, -y + 2, -z)$, and between the uracil ring and the benzene ring at $(-x, -y + 2, -z)$, with centroid—centroid distances of 3.88 (8) and 3.63 (6) Å, respectively.

Experimental

The title compound was synthesized in a hydrothermal process from a mixture of benzimidazole (2 mmol, 0.24 g), cadmium sulfate (1 mmol, 0.22 g), 5-fluoro-2,4-dioxo-1,2,3,4-tetrahydropyrimidine-1-acetic acid (2 mmol, 0.75 g) and water (20 ml). The reaction was carried out in a 30 ml Teflon-lined stainless steel reactor. The reactor was heated to 418 K for 4 d. The reactor was cooled slowly to room temperature to yield colorless crystals that were collected and washed with water.

Crystal data

[Cd(C₆H₄FN₂O₄)₂(C₇H₆N₂)₂·(H₂O)₂]
 $M_r = 758.93$
 Triclinic, $P\bar{1}$
 $a = 7.5216$ (5) Å
 $b = 8.3323$ (5) Å
 $c = 12.2228$ (7) Å
 $\alpha = 88.287$ (1)°
 $\beta = 89.114$ (1)°
 $\gamma = 68.041$ (1)°
 $V = 710.13$ (8) Å³

$Z = 1$
 $D_x = 1.775$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4153 reflections
 $\theta = 2.6$ – 25.0 °
 $\mu = 0.86$ mm⁻¹
 $T = 298$ (2) K
 Block, colorless
 0.29 × 0.24 × 0.14 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.789$, $T_{\max} = 0.890$
 5125 measured reflections

2470 independent reflections
 2438 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.067$
 $S = 1.20$
 2470 reflections
 220 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.1722P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.67 \text{ e } \text{\AA}^{-3}$

Table 1

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

Cd1—N3 ⁱ	2.2630 (19)	N1—C2	1.466 (3)
Cd1—N3	2.2630 (19)	N2—C4	1.368 (3)
Cd1—O1	2.2658 (17)	N2—C3	1.387 (3)
Cd1—O1 ⁱ	2.2658 (17)	N3—C7	1.302 (3)
Cd1—O5 ⁱ	2.3794 (18)	N3—C8	1.399 (3)
Cd1—O5	2.3794 (18)	N4—C7	1.342 (3)
O3—C3	1.215 (3)	N4—C9	1.382 (3)
O4—C4	1.233 (3)	C4—C5	1.434 (3)
N1—C6	1.365 (3)	C5—C6	1.331 (4)
N1—C3	1.369 (3)		
N3 ⁱ —Cd1—N3	180	O1—Cd1—O5 ⁱ	90.32 (7)
N3—Cd1—O1	94.32 (7)	N3—Cd1—O5	91.64 (7)
N3—Cd1—O1 ⁱ	85.68 (7)	O1—Cd1—O5	89.68 (7)
O1—Cd1—O1 ⁱ	180	O5 ⁱ —Cd1—O5	180
N3—Cd1—O5 ⁱ	88.36 (7)	N3—C7—N4	113.2 (2)

Symmetry code: (i) $-x, -y + 2, -z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5B \cdots O2 ⁱⁱ	0.81 (2)	1.95 (2)	2.752 (3)	171 (3)
O5—H5A \cdots O3 ⁱⁱⁱ	0.79 (2)	2.05 (2)	2.839 (2)	175 (3)
N4—H4 \cdots O4 ^{iv}	0.86	2.10	2.884 (3)	152
N2—H2 \cdots O4 ^v	0.86	2.21	3.062 (3)	172

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

H atoms of the water molecule were located in difference density maps and refined with O—H and H \cdots H distances restrained to 0.82 (2) and 1.39 (1) \AA , respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $Csp^2-H = 0.93 \text{ \AA}$ with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$, $Csp^3-H = 0.97 \text{ \AA}$ with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{parent atom})$ and $N-H = 0.86 \text{ \AA}$ with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

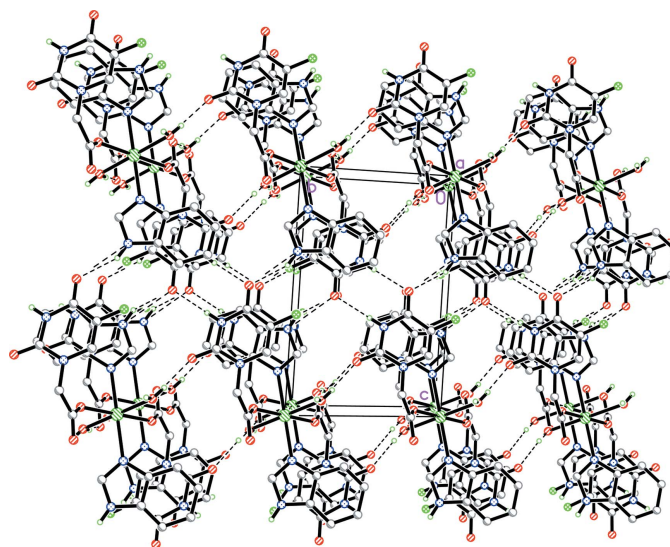


Figure 4

A perspective view of the three-dimensional supramolecular network of (I) along the a axis. The hydrogen-bonding interactions are shown as dashed lines and the H atoms not involved in these interactions have been omitted for clarity.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2002); software used to prepare material for publication: SHELXL97.

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