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Poly[*diaqua*(μ_4 -3-fluorophthalato- κ^4 O:O:O':O')cadmium(II)]

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Poly[*diaqua*(μ_4 -3-fluorophthalato- κ^4 O:O:O':O'')-cadmium(II)]

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Key indicators

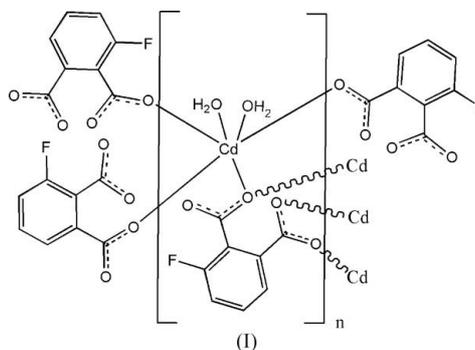
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.017
 wR factor = 0.042
Data-to-parameter ratio = 12.0

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

The crystal structure of the title compound, $[\text{Cd}(\text{C}_8\text{H}_3\text{FO}_4)(\text{H}_2\text{O})_2]_n$, consists of polymeric sheets formed by the bridging of octahedrally coordinated Cd^{II} by carboxylate O atoms of the 3-fluorophthalate (3-fpt^{2-}) ligand. The layers exhibit hydrogen bonding between each of two coordinated water molecules and two O atoms of the ligand. Adjacent sheets are connected through π - π interactions.

Comment

Polycarboxylates represent a versatile class of ligands for the construction of metal-organic coordination polymers (Ye *et al.*, 2005). Their versatility stems from the variety of bridging modes of the carboxylate group (Mehrotra & Bohra, 1983). Many of these solids exhibit properties such as gas absorption, catalytic activity, and luminescence (Rowell *et al.*, 2004; Wasuke *et al.*, 2005; Kim *et al.*, 2004). With this in mind, the title compound, (I), was prepared as a part of our ongoing efforts to construct new coordination polymers employing polycarboxylate ligands.



The asymmetric unit consists of one Cd^{II} ion, a 3-fluorophthalate (3-fpt^{2-}) dianion, and two coordinated water molecules. The Cd^{II} ion exhibits an all-oxygen coordination in a distorted octahedral environment (Fig. 1). The axial sites are defined by a water O atom and a 3-fpt^{2-} O atom, while the equatorial sites are defined by a water O atom and three carboxylate O atoms from three equivalent 3-fpt^{2-} ligands.

The Cd—O bond distances are normal (Table 1), with an average value of 2.3031 (18) Å. All other distances and angles are comparable with those in a similar Cd^{II} -phthalate coordination polymer (Vaz *et al.*, 1996).

In (I) there are O—H...O hydrogen bonds involving three H atoms of the two water molecules and two O acceptor atoms of the 3-fpt^{2-} ligand (Table 2). The remaining water H atom along with the other two 3-fpt^{2-} O atoms are not involved in hydrogen bonding.

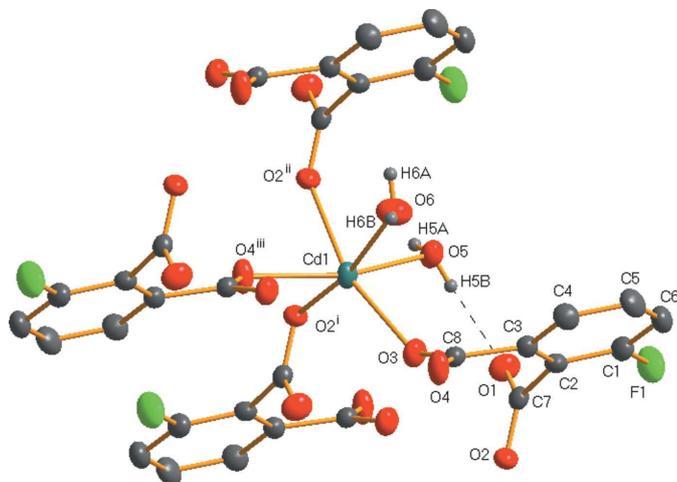


Figure 1
The coordination environment of the Cd^{II} atom in (I), showing the atom-labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 2, -z + 1$.]

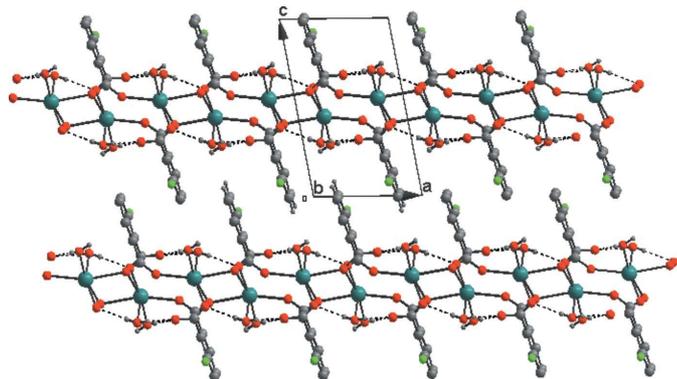


Figure 2
View of the crystal packing in (I). All H atoms, except for those of water, have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

As is typical for metal phthalate-type complexes, the two carboxylate groups in (I) are not coplanar with the aromatic ring (Vaz *et al.*, 1996). One of the carboxylate groups makes a dihedral angle of $72.7(1)^\circ$, while the other is twisted at an angle of $31.5(1)^\circ$.

The 3-ftp²⁻ ligand acts in a μ_4 -bridging fashion that links four symmetrically related Cd^{II} centers. The result is the formation of a 14-membered ring, an eight-membered ring, and a four-membered ring with Cd...Cd distances of $5.6292(4)$, $4.2213(3)$, and $3.7270(3)$ Å, respectively. The center of each ring corresponds to a crystallographic inversion center.

The aforementioned bridging of Cd^{II} centers in (I) results in the formation of thick polymeric sheets that are stacked along the *c* axis, with the benzene rings of the 3-ftp²⁻ ligands projecting outward from each side (Fig. 2). Adjacent sheets are connected through π - π interactions involving the protruding aromatic rings of 3-ftp²⁻ from successive layers, with a centroid-centroid distance of $3.67(2)$ Å between rings.

Experimental

All chemicals and solvents were purchased from commercial sources and used without further purification. 3-Fluorophthalic acid (3 mmol) was added to 100 ml of water and subsequently brought to pH 6.5 by the addition of 3 M NaOH with constant stirring. To this solution was added 10 ml of a 0.10 M solution of Cd(NO₃)₂·4H₂O. Single crystals of (I) were obtained in two weeks after slow evaporation of this solution.

Crystal data

[Cd(C₈H₃FO₄)(H₂O)₂]
 $M_r = 330.54$
 Triclinic, $P\bar{1}$
 $a = 6.9460(5)$ Å
 $b = 7.2330(5)$ Å
 $c = 10.8199(8)$ Å
 $\alpha = 103.217(1)^\circ$
 $\beta = 93.351(1)^\circ$
 $\gamma = 115.066(1)^\circ$

$V = 471.86(6)$ Å³
 $Z = 2$
 $D_x = 2.326$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.34$ mm⁻¹
 $T = 294(2)$ K
 Irregular cleavage fragment,
 colorless
 $0.36 \times 0.22 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2003)
 $T_{\min} = 0.882$, $T_{\max} = 1.000$
 (expected range = 0.607–0.688)

4370 measured reflections
 1927 independent reflections
 1893 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.042$
 $S = 1.11$
 1927 reflections
 161 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 0.4118P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.51$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1—O2 ⁱ	2.3226 (15)	Cd1—O4 ⁱⁱⁱ	2.2312 (16)
Cd1—O2 ⁱⁱ	2.3951 (15)	Cd1—O5	2.2866 (17)
Cd1—O3	2.2518 (16)	Cd1—O6	2.3308 (19)
O2 ⁱ —Cd1—O2 ⁱⁱ	75.64 (6)	O4 ⁱⁱⁱ —Cd1—O3	115.46 (6)
O2 ⁱ —Cd1—O6	167.55 (6)	O4 ⁱⁱⁱ —Cd1—O5	157.03 (6)
O3—Cd1—O2 ⁱ	109.30 (6)	O4 ⁱⁱⁱ —Cd1—O6	98.11 (7)
O3—Cd1—O2 ⁱⁱ	161.87 (6)	O5—Cd1—O2 ⁱ	82.75 (6)
O3—Cd1—O5	85.61 (6)	O5—Cd1—O2 ⁱⁱ	77.62 (6)
O3—Cd1—O6	82.16 (7)	O5—Cd1—O6	93.58 (7)
O4 ⁱⁱⁱ —Cd1—O2 ⁱ	81.61 (6)	O6—Cd1—O2 ⁱⁱ	91.96 (6)
O4 ⁱⁱⁱ —Cd1—O2 ⁱⁱ	82.27 (6)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A ^{iv} ...O4 ^{iv}	0.765 (18)	2.076 (19)	2.840 (2)	175 (3)
O5—H5B ^v ...O1	0.758 (19)	1.994 (19)	2.749 (2)	175 (4)
O6—H6B ^v ...O1 ^v	0.764 (19)	2.040 (19)	2.804 (2)	179 (5)

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

H atoms bonded to C atoms were placed in geometrically idealized positions and included as riding atoms [$C-H = 0.95 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$]. The water H atoms were located in difference maps and refined with the six O—H distances restrained to be equal with an effective s.u. of 0.015 \AA .

Data collection: *SMART-NT* (Bruker, 2003); cell refinement: *SAINT-Plus-NT* (Bruker, 2003); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

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