Poly\{diaqua(\mu_4-3-fluorophthalato-\kappa^4O:O:O':O")cadmium(II)\}

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Poly[\text{diaqua}(\mu_4\text{-3-fluorophthalato-} \kappa^4 \text{O}^2\text{O} \cdot \text{O}^2\text{O})\text{cadmium(II)}]

Diana Rishmawi, Katie Lewis, Mark D. Smith, LeRoy Peterson Jr and Hans-Conrad zur Loye
Poly[diaqua($\mu_4$-3-fluorophthalato-$\kappa^4O:O':O''$)-cadmium(II)]

The crystal structure of the title compound, [Cd(C$_6$H$_7$FO$_4$)$_2$-(H$_2$O)$_2$], 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 $\pi$-$\pi$ 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 (Rowsell 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.
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

\[
\begin{align*}
(Cd(C₆H₄FO₂)₁(H₂O)₂) & \quad V = 471.86 (6) \text{ Å}^3 \\
M_r & = 330.54 \\
\text{Triclinic, } P\overline{1} & \quad Z = 2 \\
a & = 6.9460 (5) \text{ Å} & \quad D_c = 2.326 \text{ Mg m}^{-3} \\
b & = 7.2330 (5) \text{ Å} & \quad \mu = 2.34 \text{ mm}^{-1} \\
c & = 10.8199 (8) \text{ Å} & \quad T = 294 (2) \text{ K} \\
\alpha & = 103.217 (1) & \quad \text{Irregular cleavage fragment, colorless} \\
\beta & = 93.351 (1)^{\circ} & \\
\gamma & = 115.066 (1)^{\circ} & 0.36 \times 0.22 \times 0.16 \text{ mm}
\end{align*}
\]

Table 1

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>Cdl—O2⁺</th>
<th>2.3226 (15)</th>
<th>Cdl—O4⁻</th>
<th>2.2312 (16)</th>
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<tbody>
<tr>
<td>Cdl—O3</td>
<td>2.2591 (16)</td>
<td>Cdl—O5</td>
<td>2.2866 (17)</td>
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<tr>
<td>O₂⁻—Cdl—O₂⁺</td>
<td>75.64 (6)</td>
<td>O₄⁻—Cdl—O3</td>
<td>115.46 (6)</td>
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<tr>
<td>O₂⁻—Cdl—O6</td>
<td>167.55 (6)</td>
<td>O₄⁻—Cdl—O5</td>
<td>157.03 (6)</td>
<td></td>
</tr>
<tr>
<td>O₃—Cdl—O2⁺</td>
<td>109.30 (6)</td>
<td>O₅—Cdl—O2⁺</td>
<td>98.11 (7)</td>
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<tr>
<td>O₃—Cdl—O5</td>
<td>85.61 (6)</td>
<td>O₅—Cdl—O4⁻</td>
<td>82.76 (5)</td>
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<tr>
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<td>82.16 (7)</td>
<td>O₅—Cdl—O6</td>
<td>93.58 (7)</td>
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<tr>
<td>O₄⁻—Cdl—O2⁺</td>
<td>81.61 (6)</td>
<td>O₆—Cdl—O2⁺</td>
<td>91.96 (6)</td>
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<tr>
<td>O₄⁻—Cdl—O4⁻</td>
<td>82.27 (6)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Symmetry codes: (i) x, –y, z; (ii) x, y, z; (iii) x, y, z.

Table 2

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>D—H—A</th>
<th>D—H</th>
<th>H—A</th>
<th>D···A</th>
<th>D···D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₅—H₅A—O₄⁻</td>
<td>0.765 (18)</td>
<td>2.076 (19)</td>
<td>2.840 (2)</td>
<td>175 (3)</td>
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<tr>
<td>O₅—H₅B—O₁</td>
<td>0.758 (19)</td>
<td>1.994 (22)</td>
<td>2.749 (2)</td>
<td>175 (4)</td>
<td></td>
</tr>
<tr>
<td>O₆—H₆B—O₁</td>
<td>0.764 (19)</td>
<td>2.040 (19)</td>
<td>2.804 (2)</td>
<td>179 (5)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (v) x, y, z; (w) x, y, z.

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

The 3-fpt⁻²⁻ ligand acts in a μ₄-bridging fashion that links four symmetrically related CdII 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 CdII 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-fpt⁻²⁻ ligands projecting outward from each side (Fig. 2). Adjacent sheets are connected through π–π interactions involving the protruding aromatic rings of 3-fpt⁻²⁻ from successive layers, with a centroid–centroid distance of 3.67 (2) Å between rings.
H atoms bonded to C atoms were placed in geometrically idealized positions and included as riding atoms \([\text{C—H} = 0.95 \text{ Å} \text{ and } U_{eq}(\text{H}) = 1.2U_{eq}(\text{C})]\). 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 Å.

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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References