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Key indicators

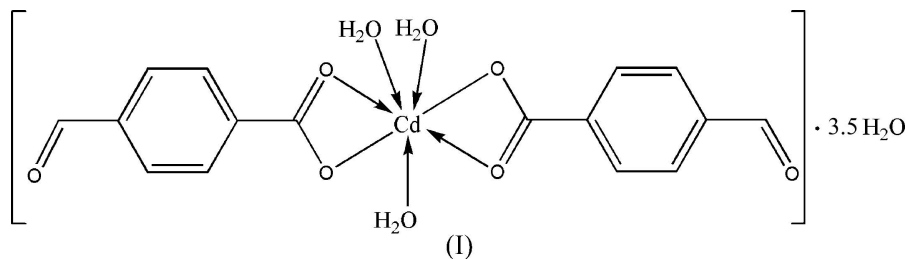
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.023
 wR factor = 0.053
Data-to-parameter ratio = 16.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Triaquabis(4-formylbenzoato- $\kappa^2\text{O},\text{O}'$)-
cadmium(II) 3.5-hydrate

The title complex, $[\text{Cd}(\text{4-FBA})_2(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$ (4-FBA[−] is the 4-formylbenzoate monoanion, $\text{C}_8\text{H}_5\text{O}_3$), is a neutral mononuclear molecule consisting of a Cd^{II} atom, two 4-FBA[−] ligands and three coordinated water molecules, together with three and a half uncoordinated water molecules. One uncoordinated water O atom lies on a twofold rotation axis. The Cd^{II} atom displays a distorted pentagonal-bipyramidal geometry, defined by four carboxylate O atoms of two different 4-FBA[−] groups and three water molecules. A three-dimensional supramolecular network is formed by intermolecular hydrogen bonds.

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Comment

Molecular self-assembly of supramolecular complexes with extended architectures utilizing non-covalent linkages, such as hydrogen-bond interactions, has been a rapidly developing research area during recent decades (Iglesias *et al.*, 2003; Burrows *et al.*, 1997). Hydrogen-bonding interactions between ligands are specific and directional, and they play a critical role in the structures and functions of the products. In this sense, 4-formylbenzoic acid is an excellent candidate for the construction of supramolecular complexes, since it can form regular hydrogen bonds by functioning as both a hydrogen-bond donor and a hydrogen-bond acceptor (Haisa *et al.*, 1976). However, the coordination chemistry of 4-formylbenzoic acid has received little attention to date. Recently, we have reported two supramolecular complexes of 4-formylbenzoic acid, $[\text{Mn}(\text{4-FBA})_2(\text{Im})_2(\text{H}_2\text{O})_2]$ (Deng *et al.*, 2006a) and $[\text{Ni}(\text{4-FBA})_2(\text{Im})_2(\text{H}_2\text{O})_2]$ (Deng *et al.*, 2006b) (4-FBA[−] is the 4-formylbenzoate monoanion, $\text{C}_8\text{H}_5\text{O}_3$, Im = imidazole, $\text{C}_3\text{H}_4\text{N}_2$), in which the 4-FBA ligands are both in monodentate mode and the two formyl groups occupy *trans* positions. In a continuation of our research on the synthesis of supramolecular transition metal complexes with the 4-FBA[−] ligand, we have synthesized the title new Cd^{II} complex, $[\text{Cd}(\text{4-FBA})_2(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$ (I), and report its structure here.



The molecular structure of the title complex (I) is shown in Fig. 1, and selected bond distances and angles are given in

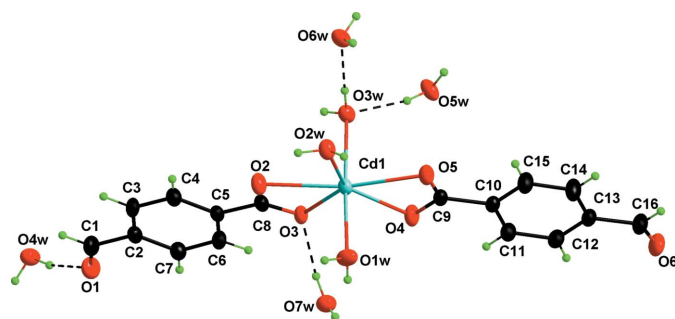


Figure 1

The molecular structure of the title complex, with displacement ellipsoids drawn at the 30% probability level. The hydrogen bonds are denoted by dashed lines.

Table 1. The asymmetric unit of (I) consists of a neutral mononuclear Cd^{II} complex [Cd(4-FBA)₂(H₂O)₃] and three and a half uncoordinated water molecules, of which O5W occupies a special position having crystallographic twofold rotation symmetry. The uncoordinated water molecules form hydrogen bonds with the O atoms of the 4-FBA[−] ligand and the coordinated water molecules (Table 2). The Cd^{II} atom has a distorted pentagonal-bipyramidal geometry involving four carboxylate O atoms of two different 4-FBA[−] ligands and three water molecules. The Cd—O(carboxylate) bond distances are slightly longer than the Cd—O(water) bond distances (Table 1), but still within the normal range for reported carboxylate cadmium(II) complexes (Clegg *et al.*, 1995; Gao *et al.*, 2004; Yuan *et al.*, 2001). In contrast to the reported manganese(II) and nickel(II) complexes (Deng *et al.*, 2006a; Deng *et al.*, 2006b), the Cd^{II} atom of (I) is coordinated by the 4-FBA[−] ligands in bidentate mode and the two formyl groups occupy *cis*-positions.

The carboxylate and the formyl groups of the 4-FBA[−] ligand, together with the coordinated and uncoordinated water molecules, connect with each other to furnish a tightly bound three-dimensional supramolecular network (Table 2, Fig. 2).

Experimental

Cadmium diacetate dihydrate (0.133 g, 0.5 mmol) was added to an aqueous solution (10 ml) of 4-formylbenzoic acid (0.15 g, 1 mmol). The pH value of the mixture was adjusted to 5 with 0.1 M sodium hydroxide. The solution was allowed to evaporate at room temperature, and colorless prismatic crystals of (I) were separated from the filtered solution after several days. Analysis calculated for C₃₂H₄₆O₂₅Cd₂: C 36.41, H 4.39%. Found: C 36.39, H 4.33%.

Crystal data

[Cd(C₈H₅O₃)₂(H₂O)₃].3.5H₂O
M_r = 527.75
 Monoclinic, C2/c
a = 32.746 (7) Å
b = 5.9269 (12) Å
c = 22.238 (4) Å
 β = 95.10 (3)°
V = 4298.9 (15) Å³

Z = 8
D_x = 1.631 Mg m^{−3}
 Mo K α radiation
 μ = 1.08 mm^{−1}
T = 295 (2) K
 Prism, colorless
 0.36 × 0.25 × 0.18 mm

Data collection

Rigaku RAXIS-RAPID
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.698, *T_{max}* = 0.830

19472 measured reflections
 4937 independent reflections
 4119 reflections with *I* > 2 σ (*I*)
R_{int} = 0.023
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.023
wR(*F*²) = 0.053
S = 1.07
 4937 reflections
 306 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0303P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cd1—O2W	2.2821 (13)	Cd1—O5	2.3823 (15)
Cd1—O1W	2.2882 (16)	Cd1—O4	2.3906 (14)
Cd1—O3W	2.3183 (14)	Cd1—O2	2.4458 (15)
Cd1—O3	2.3488 (13)		
O2W—Cd1—O1W	89.18 (6)	O1W—Cd1—O4	86.51 (6)
O2W—Cd1—O3W	90.03 (5)	O3W—Cd1—O4	92.55 (5)
O1W—Cd1—O3W	177.40 (6)	O3—Cd1—O4	84.18 (5)
O2W—Cd1—O3	134.71 (5)	O5—Cd1—O4	54.55 (4)
O1W—Cd1—O3	95.49 (6)	O2W—Cd1—O2	80.31 (5)
O3W—Cd1—O3	86.82 (5)	O1W—Cd1—O2	95.06 (6)
O2W—Cd1—O5	86.77 (5)	O3W—Cd1—O2	87.25 (5)
O1W—Cd1—O5	88.94 (6)	O3—Cd1—O2	54.43 (5)
O3W—Cd1—O5	88.54 (5)	O5—Cd1—O2	166.39 (5)
O3—Cd1—O5	138.19 (4)	O4—Cd1—O2	138.57 (5)
O2W—Cd1—O4	141.11 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...O7W ⁱ	0.84 (2)	1.905 (10)	2.740 (2)	174 (3)
O1W—H1W2...O4W ⁱⁱ	0.84 (2)	1.985 (14)	2.794 (2)	162 (3)
O2W—H2W1...O4 ⁱ	0.841 (9)	1.916 (12)	2.7265 (19)	161 (2)
O2W—H2W2...O3 ⁱ	0.841 (9)	2.213 (16)	2.9086 (19)	140.1 (18)
O3W—H3W1...O6W	0.856 (19)	1.812 (10)	2.665 (2)	176 (2)
O3W—H3W2...O6 ⁱⁱⁱ	0.846 (9)	1.954 (9)	2.797 (2)	174 (2)
O4W—H4W1...O1	0.85 (2)	1.937 (10)	2.764 (2)	166 (2)
O4W—H4W2...O7W ^{iv}	0.843 (19)	1.897 (10)	2.715 (2)	163 (2)
O5W—H5W1...O3W	0.834 (10)	2.02 (3)	2.837 (2)	169 (3)
O6W—H6W1...O5W ⁱ	0.85 (2)	1.990 (10)	2.834 (2)	176 (3)
O6W—H6W2...O5 ^v	0.847 (9)	1.891 (10)	2.736 (2)	175 (3)
O7W—H7W1...O3	0.84 (2)	1.904 (11)	2.7250 (19)	167 (2)
O7W—H7W2...O4W ⁱⁱ	0.84 (2)	1.917 (10)	2.754 (2)	177 (2)

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x*, −*y* + 2, *z* + $\frac{1}{2}$; (iii) *x*, −*y* + 2, *z* − $\frac{1}{2}$; (iv) −*x* + $\frac{1}{2}$, −*y* + $\frac{1}{2}$, −*z*; (v) −*x*, *y*, −*z* + $\frac{1}{2}$.

Carbon-bound H atoms were placed in calculated positions, with C—H = 0.93 and *U*_{iso}(H) = 1.2*U*_{eq}(C), and were refined in the riding-model approximation. The H atoms of the water molecules were located in a difference Fourier map and refined with O—H and H...H distance restraints of 0.85 (1) Å and 1.39 (1) Å, respectively, and with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure*

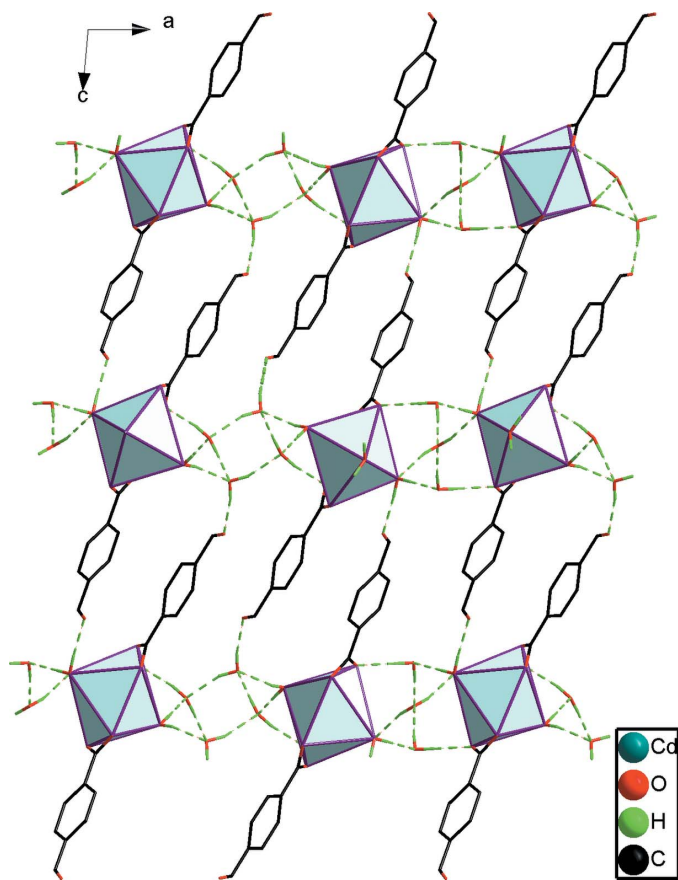


Figure 2
Packing diagram of the title complex, viewed along the *b* axis, with the O—H...O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

(Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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