

[Cd{C₂(COO)₂}(H₂O)₃].H₂O, the first cadmium salt of acetylenedicarboxylic acid

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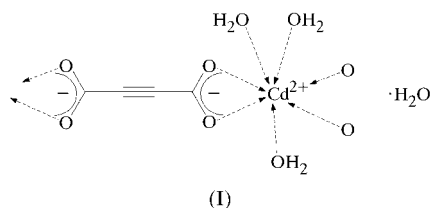
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In *catena*-poly[[[triacuacadmium(II)]- μ -acetylenedicarboxylato- $\kappa^4 O, O': O'', O'''$] hydrate], {[Cd(C₄O₄)(H₂O)₃].H₂O}_n, the Cd^{II} atom is coordinated by two bidentate carboxylate groups and three water molecules, thus forming a sevenfold coordination polyhedron with all atoms located on general sites. These polyhedra are connected by the bifunctional acetylenedicarboxylate ligands, forming zigzag chains running parallel to [120]. Hydrogen bonds, which involve the non-coordinated water molecule, connect these chains to form a three-dimensional framework.

Comment

During our studies of coordination polymers of the acetylenedicarboxylate dianion, C₂(COO)₂²⁻ (Pantenburg & Ruschewitz, 2002; Hohn *et al.*, 2002), colourless crystals of the title compound, (I), were obtained, and its crystal structure is presented here.



The structure of (I) is composed of sevenfold coordination polyhedra at the Cd^{II} ions, which are linked by the bifunctional acetylenedicarboxylate ligands to form zigzag chains. The coordination polyhedron around the Cd^{II} ion is formed by two chelating bidentate carboxylate groups and three water molecules (Fig. 1). The Cd—O distances range between 2.259 (2) and 2.664 (2) Å (Table 1). As the latter Cd—O distance (Cd1—O221) is longer than the next longest [Cd1—O122 = 2.487 (2) Å] by about 0.2 Å, the description of the Cd coordination as a 6+1 polyhedron may be an appropriate alternative. The Cd—O distances are similar to those found in

other cadmium(II) carboxylates, *e.g.* rhombohedral cadmium malonate dihydrate [2.280 (3)–2.543 (3) Å, coordination number 7; Naumov *et al.*, 2001].

The weakly coordinating nature of atom O221 is associated with the shortest carboxylate C—O distance [C22—O221 = 1.237 (3) Å], indicative of more double-bond character for this C—O bond and consistent with its slightly higher U_{eq} value. The other C—O distances range from 1.247 (3) to 1.269 (3) Å.

The C—C distances in the two crystallographically distinct acetylenedicarboxylate dianions are as expected; C11—C11ⁱ = 1.197 (5) Å and C21—C21ⁱⁱ = 1.189 (5) Å for a C≡C triple bond, and C11—C12 = 1.461 (3) Å and C21—C22 = 1.468 (4) Å for a C—C single bond [symmetry codes: (i) 2 - x, 1 - y, 1 - z; (ii) 1 - x, -1 - y, 1 - z]. The dianions are almost linear [C11ⁱ—C11—C12 = 177.7 (3)° and C21ⁱⁱ—C21—C22 = 177.6 (3)°] and the carboxylate groups of one anion are almost coplanar. The torsion angles in the two anions are in the ranges 0.0 (2)–1.6 (3) and 0.0 (2)–1.1 (3)°.

The Cd polyhedra are linked by the bifunctional carboxylates to form zigzag chains running parallel to [120] (Fig. 2).

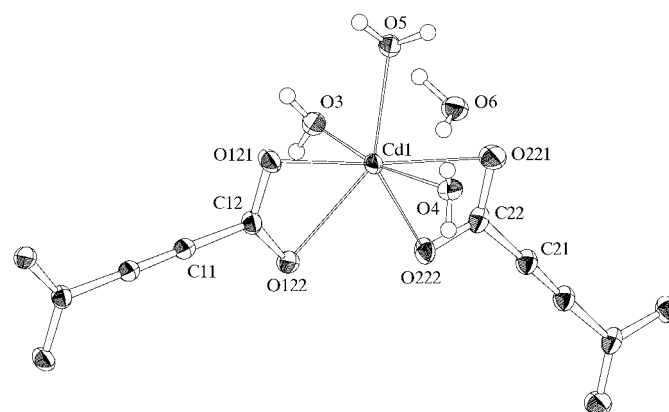


Figure 1

A view of (I), showing the atomic numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

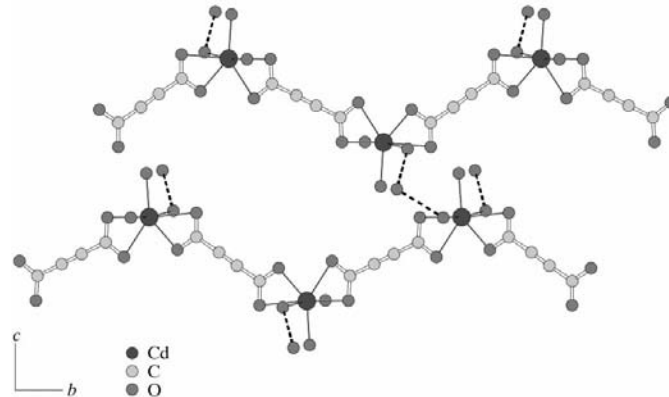


Figure 2

The crystal structure of (I), viewed along the *a* axis. Two polymeric zigzag chains connected by hydrogen bonds, which involve the non-coordinated O6 water molecule, are shown. H atoms have been omitted for clarity.

The deviation from linearity is defined by the C12—Cd1—C22 angle, which is 131.09 (7)°. In [Co{C₂(COO)₂}(H₂O)₄].2H₂O (Pantenburg & Ruschewitz, 2002), the only other known example of a coordination polymer of acetylenedicarboxylate crystallizing in a chain structure, the Co^{II} ion is coordinated octahedrally by two monodentate carboxylate groups in *trans* positions and four water molecules. Thus, a linear polymeric chain structure is formed.

In both [Co{C₂(COO)₂}(H₂O)₄].2H₂O and (I), these chains are connected by hydrogen bonds, which involve additional water molecules [atom O6 in (I)]. In (I), the O—H...O hydrogen bonds vary between 2.671 (4) Å (O121...O5) and 2.770 (4) Å (O3...O6), connecting the zigzag chains to form a three-dimensional network.

Experimental

[Cd(CH₃COO)₂].2H₂O (1.33 g, 5 mmol) was dissolved in deionized water (10 ml). A solution of acetylenedicarboxylic acid (0.57 g, 5 mmol) in deionized water (10 ml) was added; the resulting solution had a pH of 2. Immediately, a colourless precipitate formed, which was filtered off after 2 h at 278 K. The resulting colourless crystals of (I) decomposed slowly in air, forming a brown solid, but in a sealed capillary during the X-ray analysis no decomposition of the single crystal was observed. In a vacuum, a yellow solid was obtained, which was amorphous to X-rays.

Crystal data

[Cd(C ₄ O ₄)(H ₂ O) ₃].H ₂ O	$D_x = 2.249 \text{ Mg m}^{-3}$
$M_r = 296.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 19 461 reflections
$a = 6.8195 (7) \text{ \AA}$	$\theta = 1.5\text{--}32.4^\circ$
$b = 7.953 (1) \text{ \AA}$	$\mu = 2.51 \text{ mm}^{-1}$
$c = 16.387 (2) \text{ \AA}$	$T = 170 (2) \text{ K}$
$\beta = 99.811 (8)^\circ$	Column, colourless
$V = 875.74 (17) \text{ \AA}^3$	$0.54 \times 0.14 \times 0.13 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS II diffractometer	1545 reflections with $I > 2\sigma(I)$
Oscillation scans	$R_{\text{int}} = 0.046$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 2001)	$\theta_{\text{max}} = 27^\circ$
$T_{\text{min}} = 0.242$, $T_{\text{max}} = 0.785$	$h = -8 \rightarrow 8$
16 485 measured reflections	$k = -10 \rightarrow 10$
1912 independent reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 0.4864P]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.048$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
1912 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
151 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
All H-atom parameters refined	Extinction coefficient: 0.0049 (4)

The absorption correction was performed after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999). The H atoms were identified in difference Fourier syntheses and refined freely.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve

Table 1

Selected geometric parameters (Å, °).

Cd1—O222	2.259 (2)	C11—C12	1.461 (3)
Cd1—O3	2.272 (2)	C12—O122	1.247 (3)
Cd1—O5	2.276 (2)	C12—O121	1.262 (3)
Cd1—O4	2.298 (2)	C21—C21 ⁱⁱ	1.189 (5)
Cd1—O121	2.352 (2)	C21—C22	1.468 (4)
Cd1—O122	2.487 (2)	C22—O221	1.237 (3)
Cd1—O221	2.664 (2)	C22—O222	1.269 (3)
C11—C11 ⁱ	1.197 (5)		
O121—Cd1—O122	54.07 (6)	O3—Cd1—O4	169.15 (7)
O221—Cd1—O222	52.42 (6)	O3—Cd1—O121	90.57 (8)
O221—Cd1—O4	82.28 (7)	O3—Cd1—O122	90.73 (7)
O221—Cd1—O122	130.17 (6)	O4—Cd1—O121	97.43 (7)
O221—Cd1—O121	175.75 (6)	O4—Cd1—O122	99.89 (7)
O221—Cd1—O3	89.19 (7)	O5—Cd1—O4	91.19 (8)
O221—Cd1—O5	84.92 (7)	O5—Cd1—O121	90.85 (7)
O222—Cd1—O3	92.29 (8)	O5—Cd1—O122	144.11 (7)
O222—Cd1—O5	137.07 (7)	C11 ⁱ —C11—C12	177.7 (4)
O222—Cd1—O4	87.83 (8)	O122—C12—O121	122.7 (2)
O222—Cd1—O121	131.83 (6)	C21 ⁱⁱ —C21—C22	177.6 (4)
O222—Cd1—O122	77.81 (6)	O221—C22—O222	123.1 (2)
O3—Cd1—O5	81.34 (8)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H31...O6 ⁱ	0.75 (4)	2.03 (4)	2.770 (3)	175 (4)
O3—H32...O222 ⁱⁱ	0.72 (4)	1.99 (4)	2.711 (3)	173 (4)
O4—H41...O122 ⁱⁱⁱ	0.78 (4)	1.96 (4)	2.722 (3)	165 (3)
O4—H42...O6	0.77 (5)	1.95 (5)	2.713 (3)	167 (5)
O5—H51...O4 ⁱ	0.78 (4)	2.12 (5)	2.892 (3)	169 (4)
O5—H52...O121 ^{iv}	0.86 (4)	1.82 (4)	2.670 (3)	169 (3)
O6—H61...O221 ⁱ	0.91 (4)	1.83 (4)	2.732 (3)	175 (4)
O6—H62...O5 ^v	0.73 (5)	2.33 (5)	3.009 (3)	156 (5)
O6—H62...O3 ^v	0.73 (5)	2.62 (5)	3.129 (3)	129 (4)

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

structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1517). Services for accessing these data are described at the back of the journal.

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