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A rhombohedral polymorph of aqua(malonato)-cadmium(II) hydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.030
wR factor = 0.088
Data-to-parameter ratio = 13.4

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

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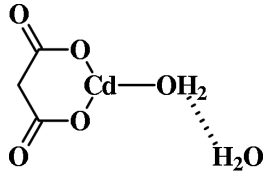
The Cd atom in the rhombohedral modification of aqua-(malonato)cadmium(II) hydrate, $[Cd(C_3H_2O_4)(H_2O)].H_2O$, shows pentagonal bipyramidal coordination. The malonate group chelates to the water-coordinated Cd atom; its two carboxyl groups also chelate adjacent Cd atoms.

Comment

The malonate derivatives of divalent metals provide the framework for supramolecular crystal engineering (Li *et al.*, 1997; Ruiz-Pérez *et al.*, 2000; Shen *et al.*, 2000; Zhang *et al.*, 2000) when ligands such as 2,2′-bipyridine and 4,4′-bipyridine are used as spacers. The structural diversity of divalent metal malonates arises from the low point-group symmetry of the compounds, which leads to the formation of polymorphs. The cadmium malonates are suitable models for examining the coordination of metalloproteins in saccharide-specific lectin concanavalin A (Bailey *et al.*, 1978) and parvalbumin (Drakenberg *et al.*, 1978; Cave *et al.*, 1979). The mode of coordination of the carboxyl entity in the models can be established by ^{113}Cd NMR spectroscopy (Chung *et al.*, 1995). The starting material, cadium malonate, exists as a monohydrate (Post & Trotter, 1974) whose Cd atom is seven-coordinate, and as a dihydrate (Chung *et al.*, 1995), in which six- and eight-coordinated atoms are present. In the title dihydrate, (I), the Cd atom is seven-coordinate; the atom is chelated by the O atoms of two carboxyl entities, as well as by one malonate dianion through its two carboxyl ends. The seventh coordination site is occupied by a water molecule.



(I)

As shown in Fig. 2, the malonate dianion links the water-coordinated cadmium ions into a three-dimensional network structure. The coordinated water molecule is hydrogen bonded to the uncoordinated water molecule [O···O = 2.669 (5) Å] and also to an adjacent carboxyl O2 atom [O···O = 2.754 (4) Å]. The uncoordinated water molecule consolidates the crystal structure by forming hydrogen bonds to another coordinated water molecule [O···O = 2.289 (5) Å] and also to an adjacent carboxyl O4 atom [O···O = 2.867 (6) Å]. The hydrogen-bonding scheme renders all four carboxyl O atoms three-coordinate.

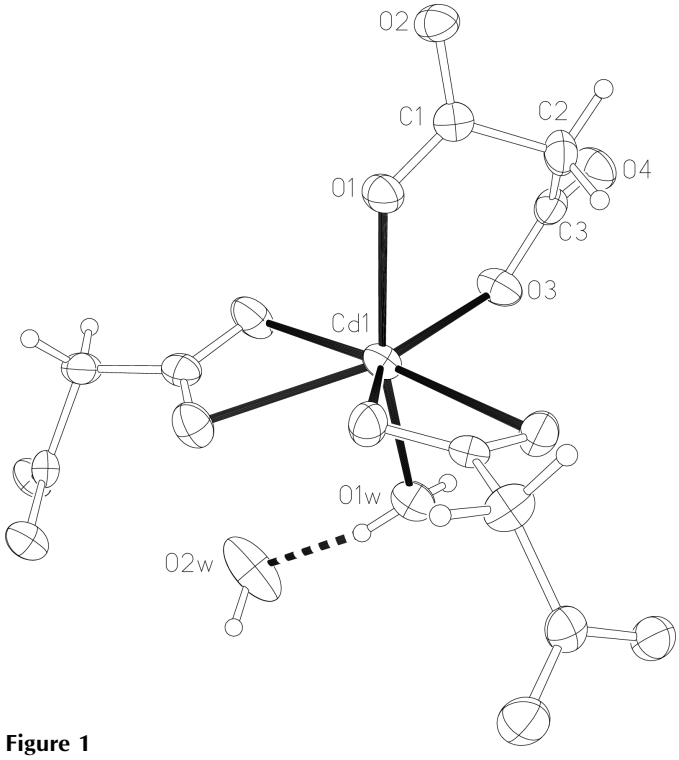


Figure 1
Part of the structure showing the complete coordination and displacement ellipsoids at the 50% probability level.

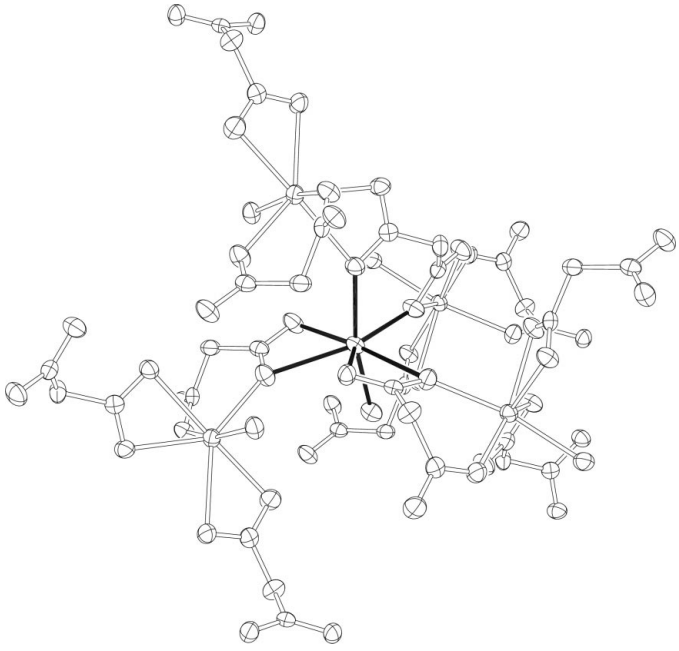


Figure 2
The polymeric network, omitting the uncoordinated water molecules.

Experimental

The title compound separated as crystals from a cooled filtered aqueous solution of cadmium carbonate and malonic acid (1:2 molar ratio) after one month.

Crystal data

$[Cd(C_3H_2O_4)(H_2O)]\cdot H_2O$
$M_r = 250.48$
Tetragonal, $R\overline{3}$
$a = 17.0355$ (9) Å
$c = 12.3934$ (5) Å
$V = 3114.8$ (3) Å^3
$Z = 18$
$D_x = 2.404$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–14.5°
$\mu = 3.13$ mm^{-1}
$T = 298$ (2) K
Block, colorless
0.3 × 0.3 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968) in the *WinGX* suite (Farrugia, 1999)
$T_{min} = 0.458$, $T_{max} = 0.535$
2010 measured reflections
1223 independent reflections
1123 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25^\circ$
$h = -6 \rightarrow 20$
$k = -20 \rightarrow 0$
$l = -13 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.088$
$S = 1.15$
1223 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 11.6164P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.280 (3)	Cd1—O3^{ii}	2.527 (3)
Cd1—O1^{i}	2.543 (3)	Cd1—O4^{ii}	2.323 (4)
Cd1—O2^{i}	2.302 (3)	Cd1—O1*w*	2.283 (3)
Cd1—O3	2.290 (3)		
O1—Cd1—O1^{i}	93.7 (2)	O2^{i}—Cd1—O3	138.6 (1)
O1—Cd1—O2^{i}	83.8 (1)	O2^{i}—Cd1—O3^{ii}	77.8 (1)
O1—Cd1—O3	81.9 (1)	O2^{i}—Cd1—O4^{ii}	127.9 (1)
O1—Cd1—O3^{ii}	105.9 (1)	O2^{i}—Cd1—O1*w*	106.8 (1)
O1—Cd1—O4^{ii}	92.2 (1)	O3—Cd1—O3^{ii}	143.6 (1)
O1—Cd1—O1*w*	165.4 (1)	O3—Cd1—O4^{ii}	91.3 (1)
O1^{i}—Cd1—O2^{i}	53.2 (1)	O3—Cd1—O1*w*	83.5 (1)
O1^{i}—Cd1—O3	89.2 (1)	O3^{ii}—Cd1—O4^{ii}	53.5 (1)
O1^{i}—Cd1—O3^{ii}	124.7 (1)	O3^{ii}—Cd1—O1*w*	86.4 (1)
O1^{i}—Cd1—O4^{ii}	174.1 (1)	O4^{ii}—Cd1—O1*w*	89.0 (1)
O1^{i}—Cd1—O1*w*	85.2 (1)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*W*2···O2^{i}	0.86	1.91	2.753 (4)	169
O1*W*—H1*W*1···O2*w*	0.86	1.84	2.669 (5)	165
O2*W*—H2*W*1···O4^{i}	0.86	2.02	2.867 (6)	170
O2*W*—H2*W*2···O1*w*^{ii}	0.86	2.22	2.895 (5)	136

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

The water H atoms were placed in calculated positions (Nardelli, 1999).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CELDIM* in *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine struc-

ture: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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