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Crystal Structure
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Poly[[diaqua(μ_3-2,2-dimethylmalonato)cadmium(II)] tetrahydrate]

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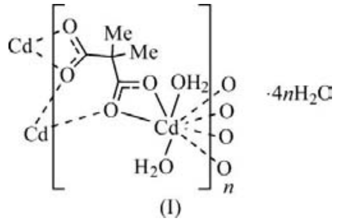
In the title complex, $\{[Cd(C_5H_6O_4)(H_2O)_2]\cdot 4H_2O\}_n$, the dimethylmalonate–cadmium metal–organic framework co-exists with an extended structure of water molecules, which resembles a sodalite-type framework. In the asymmetric unit, there are five independent solvent water molecules, two of which are in special positions. The Cd atoms are eight-coordinated in a distorted square-antiprismatic geometry by six O atoms of three different dimethylmalonate groups and by two water molecules, and form a two-dimensional honeycomb layer parallel to the *bc* plane. Two such layers sandwich the hydrogen-bonded water layer, which has a sodalite-type structure with truncated sodalite units composed of coordinated and solvent water molecules. This work is the first example of a dimethylmalonate cadmium complex containing truncated sodalite-type water clusters.

Comment

Malonate and substituted malonate derivatives are often ligands of choice for the design of metal–organic frameworks or molecular assemblies because of their manifold coordination modes and the variety of the resulting architectures (Rodriguez-Martin *et al.*, 2002). Some complexes with Cd^{II} have been reported and they contain mainly dianionic malonate, which can be found coordinating to the metal both through two distal carboxylate O atoms to form a six-membered ring, and through the nonchelating O atoms to build up bridged compounds, as in poly[tetraaquabis(μ_3-malonato)dicadmium(II)] (Fu *et al.*, 2006; Zhao *et al.*, 2007), or by two bidentate ligands to form polymeric poly[aqua(μ_3-malonato)cadmium(II)] (Post & Trotter, 1974) and rhombohedral poly[[aqua(μ_3-malonato)cadmium(II)] monohydrate] complexes (Naumov *et al.*, 2001). However, only a few complexes with dimethylmalonate as ligand are known. Recently, we reported a five-coordinated dimethylmalonate zinc complex (Guo & Zhao, 2006) and a novel cocrystallization complex of neutral molecules of dimethylmalonic acid with a dianionic dimethylmalonate–barium metal–organic framework (Guo & Guo, 2008). Using dimethylmalonic acid as ligand, in an unsuccessful attempt to obtain a structure similar to or isotypic with that of poly[tetraaqua-di-μ_4-malonato-barium(II)zinc(II)] (Guo & Guo, 2006), we obtained the title eight-coordinate dimethylmalonate–cadmium complex, (I), which exhibits the unexpected co-existence of an extended sodalite-type water structure and a metal–organic framework.



(I)

The asymmetric unit of (I) comprises one Cd^{II} cation, one complete dimethylmalonate dianion, two coordinated water molecules and five noncoordinated water molecules, of which molecules O10 and O11 are in special positions. Fig. 1 shows the structure of (I) in a symmetry-expanded view displaying the full coordination of the Cd^{II} centre. Selected geometric parameters are given in Table 1.

In the dianionic dimethylmalonate ligand, the O—C—O angles for the two carboxylate groups are almost the same and the four C—O bond distances of the two carboxylate groups are in the range 1.251 (4)–1.266 (4) Å. This indicates that both carboxylate groups are delocalized. As observed in other dimethylmalonate structures, the two carboxylate groups are non-coplanar (Guo & Guo, 2008). The O1/C1/O2 carboxylate group is rotated by 40.2 (4)° out of the central atom plane (C1/C2/C3), while the other carboxylate group, O3/C3/O4, forms an angle with the same plane of 87.9 (4)°; the dihedral angle between the two carboxylate groups is 82.6 (5)°.

The Cd atoms have distorted square-antiprism geometry, coordinated by two chelating O atoms (O2^{ii} and O3^{ii}; see Fig. 1 for symmetry code) of one dimethylmalonate dianion, four O atoms (O1 and O2, and O3^{i} and O4^{i}) from the other two dimethylmalonates and two mutually *trans* O atoms from

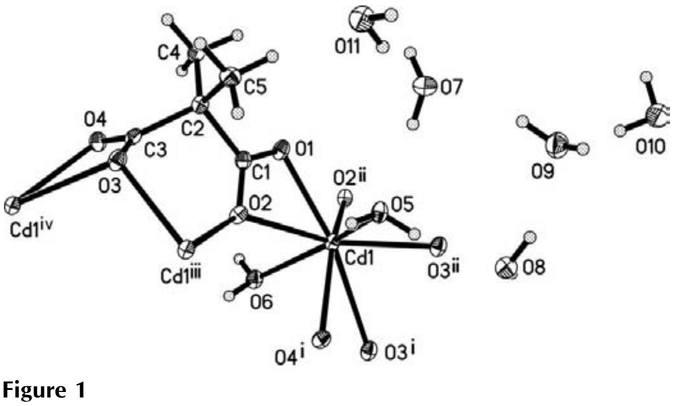


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination polyhedra for the Cd^{II} centres. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $x, -y + 1, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]

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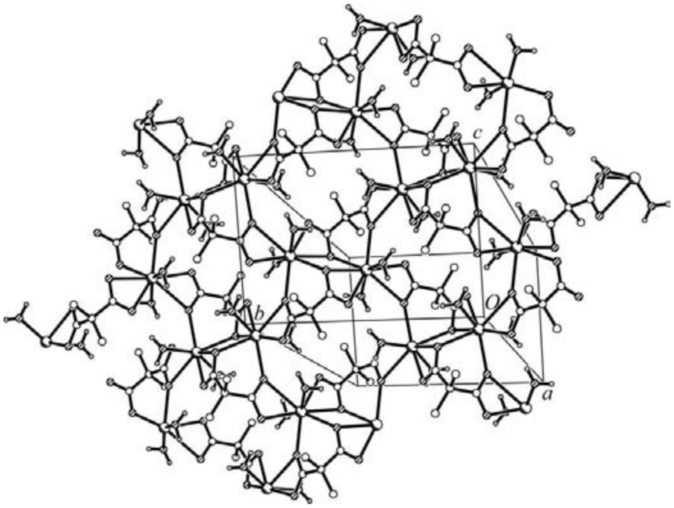

Figure 2
A packing diagram for (I), showing the two-dimensional polymeric layer in the *bc* plane, viewed approximately down the *a* axis. The H atoms of the methyl groups have been omitted for clarity.

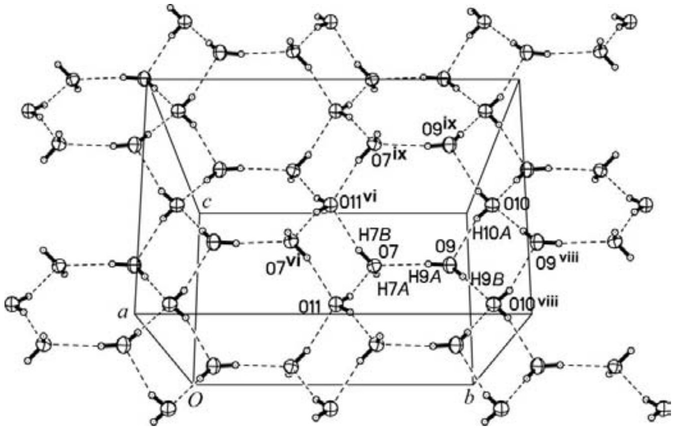

Figure 3
A packing diagram for (I), showing the layered water cluster. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (vi) $-x+1, -y+1, -z+1$; (viii) $-x+1, -y+2, -z+1$; (ix) $-x+1, y, -z+\frac{3}{2}$.]

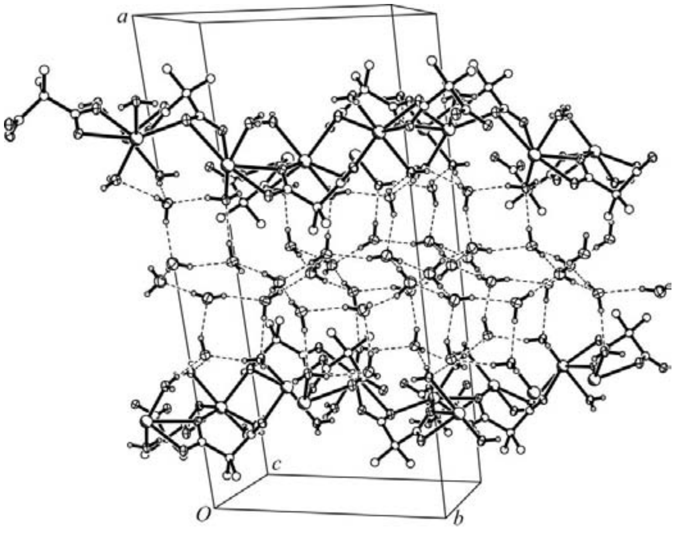

Figure 4
The packing of (I), showing the two-dimensional polymeric layers in the *bc* plane and the hydrogen-bonding interactions (dashed lines) that link them in the *a*-axis direction. Displacement ellipsoids are drawn at the 50% probability level.

water molecules (O5 and O6). The whole dimethylmalonate dianion chelates Cd1^{iii} to form a six-membered ring (see Fig. 1 for symmetry code). The bond angle at atom C2 [C3—C2—C1 = 103.8 (2)°] is smaller than the normal value, suggesting that there is greater strain in the six-membered ring of (I) than in the poly[tetraaquabis(μ_3-malonato)dicadmium(II)] complex (Fu *et al.*, 2006). Atoms O1 and O2 of the O1/C1/O2 carboxylate group coordinate to atom Cd1, and similarly, atoms O3 and O4 coordinate to atom Cd1^{iv} (see Fig. 1 for symmetry code). In this way, one complete dimethylmalonate dianion links three Cd atoms. This results in a $\text{Cd1}\cdots\text{Cd1}^{\text{iii}}$ distance of 4.7753 (10) Å and a $\text{Cd1}^{\text{iii}}\cdots\text{Cd1}^{\text{iv}}$ distance of 4.1711 (9) Å. In the *bc* plane, two adjacent Cd atoms are bridged by two O3 atoms or one O2 atom, respectively. This results in two Cd distorted square antiprisms sharing an edge or a corner. In this way, each Cd is connected to three other Cd^{II} centres, and each group of six Cd^{II} centres is associated into a 12-membered ring in the *bc* plane. These are further joined into a two-dimensional honeycomb layer structure (Fig. 2).

The detailed structure of an extended water layer in the *bc* plane is shown in Fig. 3. The $(H_2O)_4$ subunit comprises water molecules O7, O9, O10 and O11. Along the *b*-axis direction, adjacent tetramers are connected to each other by hydrogen bonds. In this way, the tetramers produce a one-dimensional water tape T4(0) (Infantes & Motherwell, 2002), which contains $\text{O7}\cdots\text{O11}^{\text{vi}}\cdots\text{O7}^{\text{vi}}\cdots\text{O11}$ and $\text{O9}\cdots\text{O10}\cdots\text{O9}^{\text{viii}}\cdots\text{O10}^{\text{viii}}$ tetramers (see Fig. 3 for symmetry codes). In the *c* direction, these tetramers form two different T4(1) water tapes and connect further with each other into an $\text{O7}\cdots\text{O9}\cdots\text{O10}\cdots\text{O9}^{\text{ix}}\cdots\text{O7}^{\text{ix}}\cdots\text{O11}^{\text{vi}}$ hexamer. Adjacent tetramers and hexamers share an edge or a corner, giving rise to an extended water layer L4(6)6(8). The hydrogen-bonding parameters of the water molecules are summarized in Table 2. As can be seen from Table 2 and Fig. 3, within the water layer, water molecules O10 and O11 display tetrahedral geometries with double hydrogen-bond donors and acceptors. The $\text{O}\cdots\text{O}$ distances are in the range 2.750 (3)–2.897 (4) Å, with an average of 2.860 (4) Å, which is comparable with the range observed in ice II (2.77–2.84 Å; Gregory *et al.*, 1997). The $\text{O}\cdots\text{O}\cdots\text{O}$ angles vary from 83.5 (1) to 123.8 (1)°.

One of the most important features of the present structure is the fact that the two-dimensional metal–organic framework formed by Cd^{II} cations and dimethylmalonate ligands integrates with the two-dimensional hydrogen-bonded water framework, which has a sodalite-type structure with truncated sodalite units. Each truncated sodalite unit comprises 16 solvent water molecules and three coordinated water molecules. To the best of our knowledge, such an extended sodalite-type water structure has not been reported previously. As can be seen in Fig. 4, the structure as a whole consists of two distinct layers that stack alternately in the [100] direction. In addition to the two-dimensional dimethylmalonate–cadmium metal–organic layer, there is the extended two-dimensional hydrogen-bonded water layer, which is based on water molecules O8, O5 and O6 and the above-mentioned L4(6)6(8) water cluster, and has a sodalite-type structure with truncated sodalite units. The connectivity between neighbouring layers is completed by intra- and interlayer hydrogen-bond interactions.

Experimental

The title complex was prepared by successive addition of dimethylmalonic acid (0.53 g, 4 mmol), $Ba(OH)_2·8H_2O$ (0.63 g, 2 mmol) and $3CdSO_4·8H_2O$ (0.77 g, 1 mmol) to distilled water (20 ml) at room temperature with continuous stirring. After filtration, slow evaporation over a period of two weeks at room temperature provided colourless needle-shaped crystals of (I).

Crystal data

$[Cd(C_5H_6O_4)(H_2O)_2]·4H_2O$
$M_r = 350.59$
Monoclinic, $C2/c$
$a = 26.015$ (5) Å
$b = 12.094$ (2) Å
$c = 8.4579$ (17) Å
$\beta = 108.91$ (3)°
$V = 2517.5$ (9) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.77$ mm^{-1}
$T = 133$ K
0.18 × 0.10 × 0.08 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.804$, $T_{max} = 0.876$
7015 measured reflections
2206 independent reflections
1994 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.070$
$S = 1.11$
2206 reflections
148 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}

One H atom of each water molecule in a special position and the H atoms of other water molecules were found in difference Fourier maps. However, during refinement, they were restrained at O—H = 0.85 (1) Å, with $U_{iso}(H) = 1.2U_{eq}(O)$. The H atoms of the C—H groups were treated as riding, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.303 (2)	O2—Cd1^{iii}	2.379 (2)
Cd1—O2	2.678 (2)	O4—Cd1^{iv}	2.305 (2)
Cd1—O5	2.407 (2)	C1—O1	1.256 (4)
Cd1—O6	2.315 (2)	C1—O2	1.266 (4)
Cd1—O3^{i}	2.690 (2)	C3—O3	1.251 (4)
Cd1—O3^{ii}	2.338 (2)	C3—O4	1.258 (4)
O6—Cd1—O5	150.79 (7)	C3—C2—C1	103.8 (2)
O1—C1—O2	122.6 (3)	O3—C3—O4	122.4 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O1^{iii}	0.84	1.97	2.788 (3)	162
O5—H5B···O8	0.84	2.00	2.819 (3)	164
O6—H6A···O8^{iv}	0.86	1.90	2.745 (3)	168
O6—H6B···O4^{v}	0.85	1.85	2.701 (3)	172
O7—H7A···O5	0.84	1.96	2.797 (3)	170
O7—H7B···O11^{vi}	0.85	2.05	2.879 (3)	165
O8—H8A···O9	0.85	1.95	2.750 (3)	156
O8—H8B···O6^{vii}	0.85	2.09	2.849 (3)	148
O8—H8B···O3^{ii}	0.85	2.35	2.910 (3)	124
O9—H9A···O7	0.84	2.08	2.897 (4)	165
O9—H9B···O10^{viii}	0.85	1.99	2.837 (3)	180
O10—H10A···O9	0.85	2.14	2.833 (3)	139
O11—H11A···O7	0.86	2.02	2.856 (3)	164

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3007). Services for accessing these data are described at the back of the journal.

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