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Poly[[aqua(μ-2,2-dimethylmalonato)barium(II)] 2,2-dimethylmalonic acid solvate]

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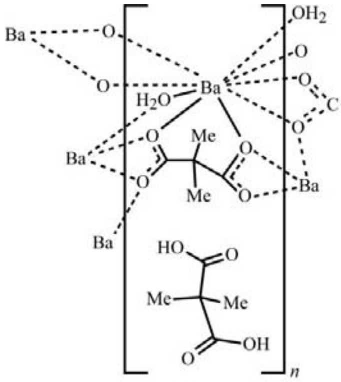
In the title complex, $\{[Ba(C_5H_6O_4)(H_2O)]\cdot C_5H_8O_4\}_n$, the neutral dimethylmalonic acid molecules and the dianionic (dimethylmalonato)barium metal–organic framework are linked by cocrystallization. The Ba atom, in a distorted monocapped square-antiprismatic geometry, is nine-coordinated by seven O atoms of four different dimethylmalonate groups and by two water molecules. This arrangement generates a two-dimensional layer parallel to the *bc* plane. Two such layers sandwich another layer composed of neutral dimethylmalonic acid molecules that are involved in intermolecular hydrogen bonds within this layer and to neighboring layers. This complex is different from the dimethylmalonate–Ba complex reported previously. The title compound displays a novel structure type and represents a new member of the substituted malonate series of alkaline earth complexes.

Comment

The characterization of alkaline earth carboxylates is an area of continuous interest owing to the relevance of these compounds in a wide range of applications in materials science, including their use as processible oxide precursors by soft chemistry routes (Baggio *et al.*, 2004; Bae *et al.*, 2002) and in studies of heterobimetallic complexes (Guo & Guo, 2006; Guo & Cao, 2006; Guo & Zhang, 2008). Malonate and substituted malonate derivatives are often ligands of choice for the design of such metal–organic frameworks or molecular assemblies because of their manifold coordination modes and the variety of the resulting architectures. Two complexes with barium have been reported, one containing both a malonate dianion and a malonic acid molecule (Hodgson & Asplaund, 1991) and the other involving ligands such as monodeprotonated benzylmalonic acid, *viz.* benzylmalonate, the dimethylmalonate dianion and the hydrogen ethylmalonate anion (Yokomori *et al.*, 1998). In heterobimetallic malonate complexes involving transition and alkaline earth metals, Ba atoms have also been used to construct coordination polymers by acting as building blocks (Guo & Guo, 2006; Guo & Cao, 2006; Guo & Zhang, 2008). In the course of our studies of heterobimetallic malonate complexes involving Zn and Ba atoms, we used dimethylmalonic acid as a ligand, expecting to obtain a structure similar or isotypic to that of $[BaZn(C_3H_2O_4)_2(H_2O)_4]_n$ (Guo & Guo, 2006). When we used only barium hydroxide and dimethylmalonic acid, a stoichiometric mixture proved unsuccessful, but interestingly, use of a slight excess of dimethylmalonic acid did allow the formation of a novel nine-coordinated dimethylmalonate–barium complex (I), which exhibits the unexpected result of cocrystallization of neutral



(I)

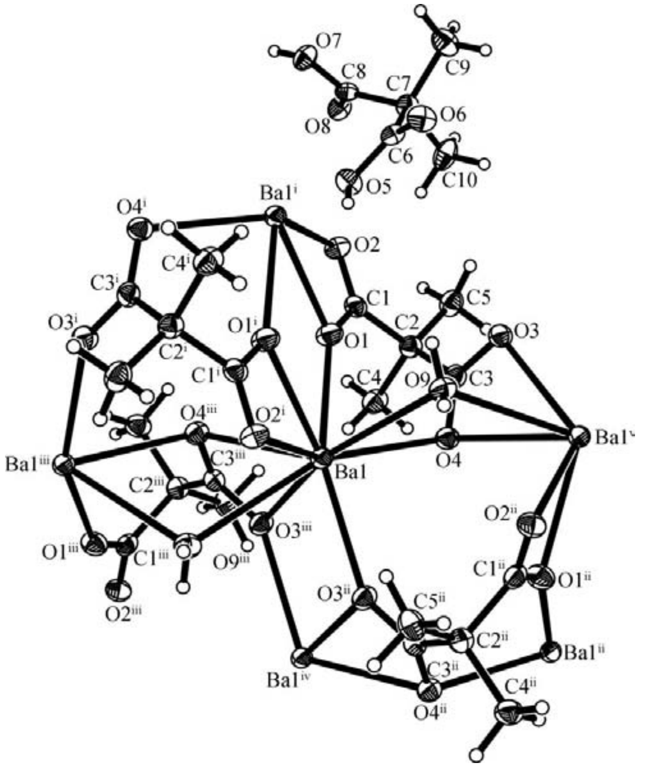


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination polyhedron for the Ba atom; displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $-x, -y + 1, -z$; (v) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.]

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molecules of dimethylmalonic acid with a dianionic dimethylmalonate–barium metal–organic framework. We report here the crystal structure of (I).

The asymmetric unit in the structure of (I) comprises one Ba atom, one complete dimethylmalonate dianion, one coordinated water molecule and one neutral dimethylmalonic acid molecule, and is shown in Fig. 1 in a symmetry-expanded view which displays the full coordination of the Ba atom. Selected geometric parameters are given in Table 1.

As can be seen in Fig. 1, the coordination polyhedron around barium is nine-coordinate. The Ba atom has a distorted monocapped square-antiprismatic environment. The four coordination sites of the basal plane are occupied by atoms O1, O4, $O3^{iii}$ and $O4^{iii}$ (see Fig. 1 for symmetry codes). The adjacent plane contains atoms $O1^{i}$ and $O3^{ii}$ and two coordinated water molecules (O9 and $O9^{iii}$). Finally, the capping site is occupied by atom $O2^{i}$. The Ba—O(dimethylmalonate) distances are in the range 2.7072 (18)–2.916 (2) Å, which is not inconsistent with the distances in *catena*-poly-[pentaaqua(μ_5-dimethylmalonato)(μ_3-dimethylmalonato)dibarium], which has two crystallographically independent Ba atoms; the distances in (I) are a little longer than those for the eight-coordinate Ba atom but are somewhat shorter than those reported for the nine-coordinate Ba atom (Yokomori *et al.*, 1998).

In the present structure, the variability of the substituted malonate ligand can be clearly seen (Fig. 1). Monodentate, bidentate–chelating, chelated six-membered and bridging bonding modes are all present. Atoms O1 and O2 of the O1/C1/O2 carboxylate group use a bidentate 1,2-chelating mode to connect with atom $Ba1^{i}$; atoms O3 and O4 are coordinated to atom $Ba1^{v}$ in a similar manner (see Fig. 1 for symmetry codes). Atom $O3^{ii}$ adopts both a monodentate mode, to connect with atom Ba1, and a bridging bonding mode, to link atoms $Ba1^{iv}$ and Ba1. Furthermore, the whole dianionic dimethylmalonate ligand chelates atom Ba1 to form a six-membered ring. The bond angle at C2 [C3—C2—C1 = 102.7 (2)°] is smaller than the normal value, suggesting that there is greater strain in the six-membered ring than in the ten-coordinate *catena*-poly[μ_2-aqua-bis(μ_2-benzylhydrogenmalonato-O,O,O',O'')barium] complex (Yokomori *et al.*, 1998). At the same time, atoms O1 and O4 also adopt a bridging bonding mode to connect with two different Ba atoms. In the dianionic dimethylmalonate ligand, the O—C—O angles for the two carboxylate groups are both 122.1 (2)°, and the four C—O bond distances are in the range 1.259 (3)–1.270 (3) Å. This indicates that both carboxylate groups have an evident mesomeric effect. As is observed in other alkylmalonate structures, the two carboxylate groups are noncoplanar (Yokomori *et al.*, 1998). The O1/C1/O2 carboxylate group is rotated by 42.7 (4)° out of the C1/C2/C3 plane, while the O3/C3/O4 group forms an angle with the same plane of 80.9 (4)°; the dihedral angle between the two carboxylate groups is 89.3 (4)°.

As can be seen in Fig. 2, the structure as a whole consists of two distinct layers that stack alternatingly in the *a* direction. The first is composed entirely of Ba atoms, dimethylmalonate dianions and water molecules and occurs near $x = 0$ and $x = 1$. In this case, each dianionic dimethylmalonate ligand binds to four different Ba atoms, and each Ba atom binds to four different dimethylmalonate dianions. In the crystallographic *c* direction, neighboring Ba atoms are bridged *via* atom O4 and water molecule O9; in the crystallographic *b* direction, the connection between Ba atoms is achieved *via* bridging involving two O3 and two O1 atoms, which occur alternately. In this way, each group of four Ba atoms builds up a grid. These grids are further joined into a two-dimensional layer structure with a (4,4)-grid topology in the direction of the *bc* plane (Fig. 2).

The other layer, alternating with the first and centered on $x = \frac{1}{2}$, only contains neutral molecules of dimethylmalonic acid. Within this layer (Fig. 2), intermolecular $O7—H7\cdots O8^{vii}$ hydrogen-bond interactions form dimers of graph set $R_2^2(8)$ (Bernstein *et al.*, 1995) comprising two molecules of dimethylmalonic acid (see Table 2 for geometric details and symmetry codes). The connection between the neighboring layers is mainly completed *via* a hydrogen-bond interaction between atom H9*A* of water molecule O9 and atom $O6^{ii}$ and a strong intramolecular $O5—H5\cdots O2$ hydrogen-bond interaction (Brown, 1976). In addition, atom H9*B* of water molecule O9 and atom $O4^{vi}$ engage in another distinct hydrogen-bonding interaction (see Table 2). These together make the structure a three-dimensional network.

In the dimethylmalonic acid molecule, the O—C—O angles for the two carboxylate groups are almost the same [O6—

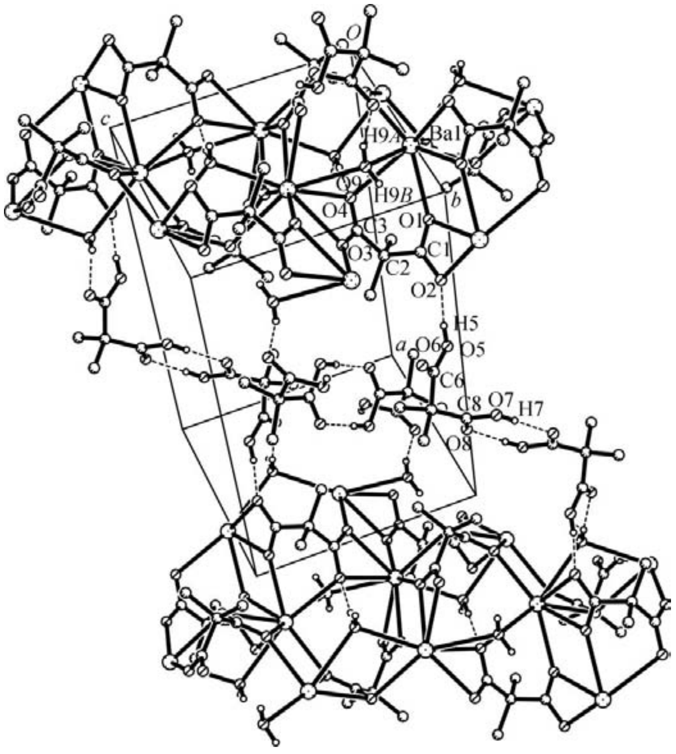

Figure 2
The packing of (I), showing the two-dimensional polymeric layers in the *bc* plane and the hydrogen-bonding interactions (dashed lines) that link them in the *a*-axis direction.

C6—O5 = 123.8 (3)° and O8—C8—O7 = 124.0 (2)°]. Each carboxylate group has one single and one double bond. The two C—O single-bond distances (O5—C6 and O7—C8) are 1.324 (3) and 1.322 (3) Å, respectively, while the two C—O double-bond distances (O6—C6 and O8—C8) are 1.213 (3) and 1.218 (3) Å, respectively; they are longer than the values of 1.308 (3) and 1.206 (2) Å reported for the free acid (Sheng-zhi & Mak, 1986). As is observed in the above dimethylmalonate structure, the two carboxylate groups are noncoplanar; the dihedral angle between the O5/C6/O6 and O7/C8/O8 planes is 79.6 (4)°, with the group at C6 lying 45.6 (4)° out of the C6/C7/C8 plane, while the other group forms an angle of 50.1 (4)° with this plane.

A comparison with other reported malonate and substituted malonate–barium compounds (Hodgson & Asplaund, 1991; Yokomori *et al.*, 1998) reveals that the title compound has a novel structure type and represents a new member of the substituted malonate series of alkaline earth complexes. The previously reported complex *catena*-poly[pentaaqua(μ_5-dimethylmalonato)(μ_3-dimethylmalonato)dibarium] (Yokomori *et al.*, 1998) is quite different as two crystallographically independent Ba atoms are present. One is coordinated to five dimethylmalonate O atoms and three water molecules, while the other is bonded to six dimethylmalonate O atoms and three water molecules. Moreover, the two independent dimethylmalonate dianions exhibit different coordination modes.

Experimental

For the preparation of the title complex, dimethylmalonic acid (0.53 g, 4 mmol) and $Ba(OH)_2·8H_2O$ (0.63 g, 2 mmol) were added successively to distilled water (15 ml) under continuous stirring at room temperature. After filtration, slow evaporation over a period of two weeks at room temperature provided colorless needle-shaped crystals of (I).

Crystal data

$[Ba(C_5H_6O_4)(H_2O)]·C_5H_8O_4$
M_r = 417.57
Monoclinic, $P2_1/c$
a = 17.300 (3) Å
b = 8.6107 (17) Å
c = 9.6027 (19) Å
β = 92.41 (3)°

V = 1429.2 (5) $Å^3$
Z = 4
Mo *Kα* radiation
μ = 2.82 mm^{-1}
T = 133 (2) K
0.14 × 0.08 × 0.06 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.738, T_{max} = 0.852

7812 measured reflections
2488 independent reflections
2224 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.068
S = 1.04
2488 reflections

187 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.23 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.88 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Ba1—O1^{i}	2.7072 (18)	O4—Ba1^{v}	2.910 (2)
Ba1—O3^{ii}	2.7108 (17)	O1—C1	1.259 (3)
Ba1—O1	2.7243 (18)	O2—C1	1.267 (3)
Ba1—O3^{iii}	2.7835 (18)	O3—C3	1.270 (3)
Ba1—O2^{i}	2.875 (2)	O4—C3	1.270 (3)
Ba1—O9	2.8861 (18)	O5—C6	1.324 (3)
Ba1—O4	2.916 (2)	O6—C6	1.213 (3)
Ba1—O9^{iii}	3.0215 (19)	O7—C8	1.322 (3)
Ba1—Ba1^{i}	4.6138 (9)	O8—C8	1.218 (3)
Ba1—Ba1^{iv}	4.3338 (8)		
O1—C1—O2	122.1 (2)	O6—C6—O5	123.8 (3)
C3—C2—C1	102.7 (2)	C8—C7—C6	111.1 (2)
O3—C3—O4	122.1 (2)	O8—C8—O7	124.0 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9*A*···O6^{ii}	0.86	1.94	2.778 (3)	163
O9—H9*B*···O4^{vi}	0.86	2.02	2.883 (2)	177
O5—H5···O2	0.82	1.78	2.601 (3)	174
O7—H7···O8^{vii}	0.82	1.84	2.656 (3)	178

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

The H atoms of the water molecule were found in difference Fourier maps. However, during refinement, they were fixed at O—H distances of 0.86 Å and their U_{iso}(H) values were set at 1.2U_{eq}(O). The H atoms of CH_3 and OH groups were treated as riding [C—H = 0.96 Å, O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(C,O)].

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3267). Services for accessing these data are described at the back of the journal.

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