

Poly[diacquabis(μ_3 -2,2-dimethylpropanedioato)calcium(II)copper(II)]

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Received 8 April 2010

Accepted 28 May 2010

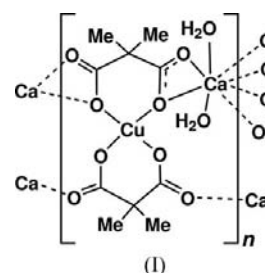
Online 10 June 2010

The title complex, $[\text{CaCu}(\text{C}_5\text{H}_6\text{O}_4)_2(\text{H}_2\text{O})_2]_n$, is the first heterobimetallic complex based on a substituted malonate dianion. The Cu^{II} cation and two independent 2,2-dimethylmalonate (or 2,2-dimethylpropanedioate) dianions build up a robust dianionic $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$ complex, which acts as a building block to coordinate to four Ca^{2+} cations. Each Cu^{II} centre is in a four-coordinate square plane of dimethylmalonate O atoms, while each Ca^{II} atom is in an eight-coordinate distorted bicapped trigonal-prismatic environment of six O atoms from four different dimethylmalonate groups and two water molecules. This arrangement creates a two-dimensional layer connectivity of the structure. The dianionic $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$ units are involved in different intermolecular hydrogen-bonding interactions with water molecules *via* the formation of hydrogen-bonded rings of graph sets $R_1^2(8)$ and $R(6)$ within this layer. The crystal was nonmerohedrally twinned by rotation about $[011]$ with a major twin volume fraction of 0.513 (3).

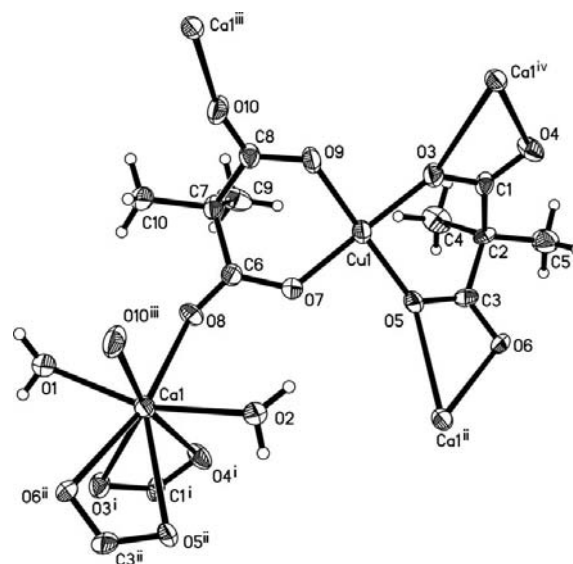
Comment

An important objective in crystal engineering is the control of the assembly of donor and acceptor building blocks in order to tune the properties of metal-organic frameworks (Burrows *et al.*, 2000; Guo, 2009). Recent developments have demonstrated that suitable chelating ligands can facilitate the generation of particularly robust coordination complexes with free hydrogen-bonding positions, which can provide effective building blocks for the construction of hydrogen-bonded networks (Zhao *et al.*, 2007). Malonate is often a ligand of choice for the design of metal-organic frameworks or molecular assemblies because of its manifold coordination modes and the variety of the resulting architectures. Of these, many heterobimetallic malonate complexes involving transition and alkaline earth metals have been reported (Gil de Muro *et al.*, 1998, 2000, 2004; Djeghri *et al.*, 2005, 2006; Guo & Cao, 2006; Guo & Guo, 2006; Guo & Zhang, 2008; Fu *et al.*, 2006, 2007). For dimethylmalonate, however, in spite of this wealth of

possibilities, no complexes of heterobimetallic systems have been reported to date. Using dimethylmalonic acid in an attempt to obtain structures with heterobimetallic complexes involving transition and alkaline earth metals, we have previously found an unusual five-coordinated dimethylmalonate zinc complex (Guo & Zhao, 2006) and an eight-coordinated dimethylmalonate cadmium complex with an extended sodalite-type water structure (Guo & Guo, 2009). Now, we have obtained the title heterobimetallic compound, (I), with a robust dianionic $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$ complex that provides an effective building block for the construction of a heterobimetallic metal-organic framework, and we report its crystal structure here.



The asymmetric unit of (I) comprises one Cu^{II} cation, two complete dimethylmalonate dianions, one Ca^{II} cation and two coordinated water molecules (Fig. 1). The Cu^{II} centre has a slightly distorted square-planar coordination, with atoms O3, O5, O7 and O9 of two non-equivalent dimethylmalonate dianions in a planar arrangement. Atom Cu1 deviates by 0.0703 (10) Å from the least-squares plane defined by the four O atoms. The bite angles subtended by the two ligands at the


Figure 1

A view of the structure of (I), showing the atom-numbering scheme and the coordination environments of the metal atoms. Additional metal atoms are included to show the connectivity modes of the dimethylmalonate anions. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x, y, z + 1$.]

Cu1 atom are both slightly larger than 90° (Table 1). The Cu—O bond lengths are somewhat shorter than those reported for the octahedral Cu atom in poly[tetraaquabis(μ_3 -malonato)calcium(II)copper(II)] (Fu *et al.*, 2007) and comparable with those reported for 1,3-propanediammonium bis(malonato)copper(II) complexes (Delgado *et al.*, 2006). There are no additional Cu—O contacts in (I) out to 3 Å.

The coordination polyhedron around the Ca^{II} ion is an eight-coordinate distorted bicapped trigonal prism defined by six O atoms from four carboxylate groups and two O atoms from coordinated water molecules. Two of the four carboxylate groups coordinate with the Ca^{II} ion in a chelate fashion, whereas the other two are in a monodentate mode and serve as bridges between the Cu and Ca atoms. Atoms O3ⁱ, O4ⁱ, O2 and O6ⁱⁱ (see Fig. 1 for symmetry codes) are nearly coplanar within deviations of less than 0.088 (6) Å and form one rectangular face with O5ⁱⁱ as the capping atom. Atoms O3ⁱ, O4ⁱ, O8 and O1 are almost coplanar, with no deviations of more than 0.022 (7) Å, and form the second, uncapped, rectangular face. Atoms O6ⁱⁱ, O2, O8 and O1 are in the same plane with displacements of less than 0.026 (6) Å, forming the third rectangular face capped by atom O10ⁱⁱⁱ. The angle between the planes defined by the triangles O4ⁱ/O8/O2 and O3ⁱ/O1/O6ⁱⁱ is $31.5(3)^\circ$. The Ca—dimethylmalonate Ca—O distances (Table 1) are similar to those observed in another eight-coordinate calcium carboxylate complex, poly[aqua(μ_5 -hydrogen 1,2,4-benzenetricarboxylato-*O,O,O',O'',O''',O''''*)-calcium] (Volkringer *et al.*, 2007), as well as in the heterobimetallic malonate complexes $[\text{CaM}(\text{mal})_2(\text{H}_2\text{O})_4]_n$ ($M = \text{Mn, Ni, Co, Zn and Cu}$; Gil de Muro *et al.*, 2000; Djeghri *et al.*, 2006; Fu *et al.*, 2006, 2007).

The coordination behaviour of the dimethylmalonate ligands in (I) is diverse, with monodentate, bidentate-chelating, chelated six-membered and bridging bonding modes all present. In the case of the C1—C5/O3—O6 dimethylmalonate dianion, atoms O5 and O6 of one carboxylate group have a bidentate chelating mode to atom Ca1ⁱⁱ. Atoms O3 and O4 are similarly coordinated to atom Ca1^{iv}. At the same time, atoms O3 and O5 also adopt a bridging bonding mode to connect atom Cu1 to two different Ca atoms, respectively. For the C6—C10/O7—O10 dimethylmalonate dianion, atoms O8 and O10 both adopt a monodentate mode to coordinate to atoms Ca1 and Ca1ⁱⁱⁱ, respectively. The O7/C6/O8 and O9/C8/O10 carboxylate groups act as bridging groups to link atom Cu1 and two Ca1 atoms together. Furthermore, both of the dianionic dimethylmalonate anions coordinate to atom Cu1 to form a new dianionic complex, $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$, via six-membered chelating modes. This robust dianion has a boat conformation, with atoms C2 and C7 lying 1.102 (7) and 0.989 (8) Å, respectively, out of the O3/O5/O7/O9 mean plane. The carboxylate groups show some evidence of localization in the C—O distances (Table 1), with the O atom that bonds to both Cu and Ca (O3 and O5) showing the longer C—O distance in each case.

Each dimethylmalonate dianion of (I) binds to one Cu atom and two different Ca atoms, while each Ca atom binds to four

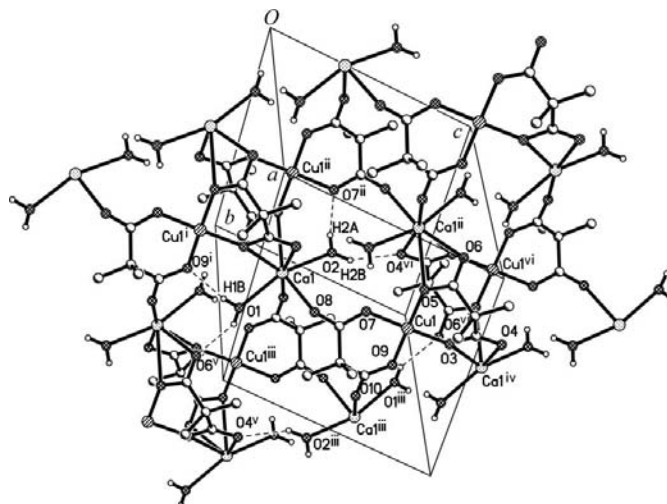


Figure 2

A packing diagram for (I), showing a single two-dimensional polymeric layer. Hydrogen-bonding interactions are shown as dashed lines. [Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x, y, z + 1$; (v) $x, y + 1, z - 1$; (vi) $-x + 1, -y + 1, -z + 2$.]

different dimethylmalonate dianions. In this way, each group of two Ca and two Cu atoms participates in four different 12-membered rings. The most compact of these rings has four bidentate chelating carboxylate groups as ligands. The metal–metal separations in this ring are 4.3335 (19), 4.277 (2) and 4.8708 (16) Å, which correspond to $\text{Cu1} \cdots \text{Ca1}^{\text{iv}}$, $\text{Cu1} \cdots \text{Ca1}^{\text{ii}}$ and $\text{Cu1} \cdots \text{Cu1}^{\text{vi}}$, respectively (Fig. 2; symmetry codes as in the figure caption). The smallest angle between three metal atoms in this unit, $\text{Cu1} \cdots \text{Ca1}^{\text{iv}} \cdots \text{Cu1}^{\text{vi}}$, is $68.90(4)^\circ$. The other 12-membered rings have four monodentate carboxylate group modes and two different carboxylate group modes, respectively. As a result, a two-dimensional puckered layer is generated and lies parallel to (100) (Fig. 2). An alternative description, perhaps more revealing from the viewpoint of crystal engineering, is that the dianionic $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$ unit acts as a building block to coordinate to four Ca atoms. The result is that each group of two Ca and two Cu atoms connects to different grids. These grids are further joined into a two-dimensional layer structure with a (4,4) topology.

Within the two-dimensional layer, atoms O4^{vi}, O6^v, O7ⁱⁱ and O9ⁱ of the $[\text{Cu}(\text{C}_5\text{H}_6\text{O}_4)_2]^{2-}$ complex dianion, acting as hydrogen-bond acceptors, are involved in intermolecular hydrogen-bonding interactions with the H atoms of the two coordinated water molecules (Fig. 2 and Table 2). They are responsible for the formation of two mainly hydrogen-bonded graph sets (Bernstein *et al.*, 1995), one $R_1^2(8)$ ring containing a Ca atom, and one $R(6)$ ring containing both a Cu atom and a Ca atom. One $R_4^4(20)$ ring involving two Ca atoms is also observed via $\text{O1} - \text{H1A} \cdots \text{O6}^{\text{v}}$ and $\text{O2} - \text{H2B} \cdots \text{O4}^{\text{vi}}$ hydrogen bonds (Fig. 2). These further enhance the connectivity of the extended two-dimensional layer.

A comparison with the previously reported calcium–transition metal–malonate complexes (Fu *et al.*, 2007, 2006) reveals that (I) is a novel structure type and is the first example of the substituted malonate series of heterobimetallic

complexes. The chemically similar complex poly[tetraaquabis(μ_3 -malonato)calcium(II)copper(II)] (Fu *et al.*, 2007) is quite different as it is not a layered structure. Moreover, the two carboxylate groups of the crystallographically unique malonate dianion have monodentate and bidentate chelating modes, respectively, and the extended structure features a 16-membered ring with three Cu and three Ca atoms. The previously reported complex poly[tetraaquadimulato-calcium(II)zinc(II)] (Fu *et al.* 2006) has some similarities in that it contains bis(malonato)zinc units joined by eight-coordinate Ca atoms into two-dimensional layers with a grid (4,4) topology, but it has the connectivities of only two different 12-membered rings containing two Zn and two Ca atoms, instead of the four such rings observed in (I).

Experimental

The title complex was prepared under continuous stirring, with successive addition of dimethylmalonic acid (0.53 g, 4 mmol), CaCO₃ (0.20 g, 2 mmol), Cu(NO₃)₂·6H₂O (0.48 g, 2 mmol) and an aqueous solution (5 ml) of piperazine (0.17 g, 2 mmol) to distilled water (15 ml) at room temperature. After filtration, slow evaporation over a period of 2 d at room temperature provided blue plate-shaped crystals of (I). The role of piperazine is to adjust the pH value of the mixture to be approximately neutral. Experiment shows that this is necessary, otherwise high-quality crystals cannot be obtained. The resulting complex was further separated by filtration (yield 0.42 g, 52.5%).

Crystal data

[CaCu(C ₅ H ₆ O ₄) ₂ (H ₂ O) ₂]	$\gamma = 71.40 (3)^\circ$
$M_r = 399.85$	$V = 748.8 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.0113 (18) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.6052 (19) \text{ \AA}$	$\mu = 1.85 \text{ mm}^{-1}$
$c = 9.6248 (19) \text{ \AA}$	$T = 294 \text{ K}$
$\alpha = 79.95 (3)^\circ$	$0.14 \times 0.12 \times 0.06 \text{ mm}$
$\beta = 72.14 (3)^\circ$	

Data collection

Rigaku Saturn CCD area-detector diffractometer	2608 measured reflections
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MS, 2005)	2608 independent reflections
$T_{\min} = 0.783$, $T_{\max} = 0.887$	1622 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.000$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	204 parameters
$wR(F^2) = 0.152$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
2608 reflections	$\Delta\rho_{\text{min}} = -0.95 \text{ e \AA}^{-3}$

Initially, the structure refined poorly, with $R_1 = 0.153$ ($F > 4\sigma F$ reflections) and 0.170 (all data), $wR_2 = 0.369$, a highest peak of residual electron density of 8.58 e \AA^{-3} and a deepest hole of -0.87 e \AA^{-3} . *PLATON* (Spek, 2009) indicated the presence of nonmerohedral twinning in the data with a twin law of $(-0.999 \ 0.501 \ 0.499 \ 0.001 \ 0.002 \ 0.997 \ 0.001 \ 1.002 \ -0.003)$, which corresponds with a twofold rotation about [011]. From the existing reflection file, a twinned reflection file in the HKLF5 format (Sheldrick, 2008) was created, in which all the overlapped reflections (3779), plus the non-

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ca1—O4 ⁱ	2.546 (6)	Cu1—O3	1.917 (5)
Ca1—O6 ⁱⁱ	2.446 (6)	Cu1—O5	1.936 (5)
Ca1—O5 ⁱⁱ	2.647 (5)	O3—C1	1.291 (9)
Ca1—O8	2.315 (6)	O4—C1	1.222 (9)
Ca1—O10 ⁱⁱⁱ	2.366 (7)	O5—C3	1.265 (9)
Ca1—O2	2.402 (5)	O6—C3	1.246 (9)
Ca1—O1	2.405 (5)	O7—C6	1.301 (10)
Ca1—O3 ⁱ	2.681 (5)	O8—C6	1.204 (10)
Cu1—O7	1.893 (5)	O9—C8	1.286 (10)
Cu1—O9	1.909 (5)	O10—C8	1.221 (9)
O7—Cu1—O9	92.55 (18)	O7—Cu1—O5	88.4 (2)
O9—Cu1—O3	86.9 (2)	O3—Cu1—O5	91.84 (17)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O6 ^v	0.85	2.24	2.996 (8)	149
O1—H1B \cdots O9 ⁱ	0.85	2.00	2.806 (8)	159
O2—H2A \cdots O7 ⁱⁱ	0.84	2.02	2.851 (7)	168
O2—H2B \cdots O4 ^{vi}	0.85	2.24	3.012 (8)	150

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

overlapping reflections (6627) from one twin domain only were included. This procedure led to a successful refinement of the model with a major twin volume fraction of 0.513 (3).

The H atoms of the water molecules were found in difference Fourier maps. However, during refinement, they were fixed at $O-H = 0.85 \text{ \AA}$, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(O)$. The H atoms of the C—H groups were treated as riding, with $C-H = 0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$.

Data collection: *CrystalClear* (Version 1.3.6; Rigaku/MS, 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3244). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Burrows, A. D., Harrington, R. W., Mahon, M. F. & Price, C. E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3845–3854.
- Delgado, F. S., Ruiz-Perez, C., Sanchiz, J., Lloret, F. & Julve, M. (2006). *CrystEngComm*, **8**, 530–544.
- Djehri, A., Balegrone, F., Guehria-Laidoudi, A. & Toupet, L. (2005). *J. Chem. Crystallogr.* **35**, 603–607.
- Djehri, A., Balegrone, F., Guehria Laidoudi, A. & Toupet, L. (2006). *Acta Cryst.* **C62**, m126–m128.
- Fu, X.-C., Li, M.-T., Wang, X.-Y., Wang, C.-G. & Deng, X.-T. (2006). *Acta Cryst.* **C62**, m258–m260.
- Fu, X.-C., Wang, C.-G., Li, M.-T. & Wang, X.-Y. (2007). *Chin. J. Inorg. Chem.* **23**, 1784–1788.

- Gil de Muro, I., Insausti, M., Lezama, L., Urtiaga, M. K., Arriortua, M. I. & Rojo, T. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3360–3364.
- Gil de Muro, I., Lezama, L., Insausti, M. & Rojo, T. (2004). *Polyhedron*, **23**, 929–936.
- Gil de Muro, I., Mautner, F. A., Insausti, M., Lezama, L. & Rojo, T. (1998). *Inorg. Chem.* **37**, 3243–3251.
- Guo, M.-L. (2009). *Acta Cryst.* **C65**, m395–m397.
- Guo, M.-L. & Cao, H.-X. (2006). *Acta Cryst.* **C62**, m431–m433.
- Guo, M.-L. & Guo, C.-H. (2006). *Acta Cryst.* **C62**, m7–m9.
- Guo, M.-L. & Guo, C.-H. (2009). *Acta Cryst.* **C65**, m266–m268.
- Guo, M.-L. & Zhang, H.-Y. (2008). *Acta Cryst.* **C64**, m30–m32.
- Guo, M.-L. & Zhao, Y.-N. (2006). *Acta Cryst.* **C62**, m563–m565.
- Rigaku/MSD (2005). *CrystalClear*. Rigaku/MSD, The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Volkringer, C., Loiseau, T., Ferey, G., Warren, J. E., Wragg, D. S. & Morris, R. E. (2007). *Solid State Sci.* **9**, 455–458.
- Zhao, X.-J., Zhang, Z.-H., Wang, Y. & Du, M. (2007). *Inorg. Chim. Acta*, **360**, 1921–1928.