

Poly[tetraquadi- μ_4 -malonato-
barium(II)zinc(II)]

Ming-Lin Guo* and Chen-Hu Guo

College of Materials and Chemical Engineering, Tianjin Polytechnic University,
Tianjin 300160, People's Republic of China

Correspondence e-mail: guomlin@yahoo.com

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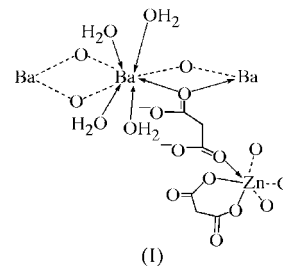
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The title complex, $[\text{BaZn}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_4]_n$, is polymeric, due to the connectivity brought about by each malonate dianion bonding to two different Zn^{II} cations and two different Ba^{II} cations. The Ba^{II} cations, on crystallographic twofold axes, have slightly distorted square-antiprismatic coordination, with $\text{Ba}-\text{O}$ distances ranging from 2.795 (2) to 2.848 (2) Å. The Zn^{II} cations, which lie on crystallographic centres of symmetry, have distorted octahedral coordination, with $\text{Zn}-\text{O}$ bonds in the range 2.0364 (19)–2.3248 (18) Å. The water molecules participate in extensive $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding. The structure comprises alternating layers along [100], with one type containing Zn^{II} cations and malonate dianions, while the other is primarily composed of Ba^{II} cations and water molecules.

Comment

In recent years, the rational design and synthesis of coordination polymers has been one of the most active research fields in coordination chemistry and materials science (Selby *et al.*, 2003). There has been considerable interest in the design and synthesis of complexes with carboxylate ligands because carboxylates can give rise to different coordination modes with metal ions and increase recognition of the role of metals in biological systems (Wang *et al.*, 2004; Maji *et al.*, 2003). One special class of such compounds concerns coordination polymers based on assemblies of transition metal ions and α,ω -dicarboxylic acids. As one of the lower members in the α,ω -dicarboxylate family, malonate anions are of particular interest in the construction of coordination polymers with specific architectures (Rodriguez-Martin *et al.*, 2002). The malonate ligand, with two neighbouring carboxylate groups, is a very flexible ligand. Its basic coordination mode is as a chelate *via* two distal carboxylate O atoms to form a six-membered ring, and the coordinating ability of the non-chelating O atoms makes the formation of polymeric networks possible (Djeghri *et al.*, 2005). In addition, the malonate anion, with its versatile coordinating ability as a monodentate, chelated bidentate or bridging ligand, can create various patterns (Delgado *et al.*,

2004). However, only a very limited amount of detailed structural data for heterobimetallic complexes, especially those involving alkaline earth metals, is currently available (Gil de Muro *et al.*, 2004). We report here the structure of the title heterobimetallic malonate complex, (I).



The asymmetric unit in the structure of (I) comprises half a Ba^{II} cation, half a Zn^{II} cation, a complete malonate dianion (defined by atoms C1–C3/O1–O4) and two independent water molecules, O5 and O6, and is shown in Fig. 1 in a symmetry-expanded view which displays the full coordination of the Ba^{II} and Zn^{II} cations. The unique $M-\text{O}$ distances and $\text{O}-M-\text{O}$ angles are given in Table 1.

The Ba^{II} cation, lying on a crystallographic twofold axis, is eight-coordinate, bonded to O atoms from four different malonate groups (O4) and four water molecules (O5 and O6). The $\text{Ba}-\text{O}(\text{water})$ distances are in the range 2.825 (2)–2.848 (2) Å, while the $\text{Ba}-\text{O}(\text{malonate})$ distances are shorter and cover the slightly narrower range 2.795 (2)–2.807 (2) Å. These $\text{Ba}-\text{O}$ distances are comparable with the values reported for barium malonate (Hodgson & Asplund, 1991). The Ba polyhedra may be described as slightly distorted square antiprisms. They share edges to form chains propagating in the c direction. The $\text{Ba}\cdots\text{Ba}$ separation within the chains [4.7101 (7) Å] is too long to imply any metal–metal bonding.

The Zn^{II} cations, coincident with crystallographic centres of symmetry, have octahedral coordination, with atoms O2 and O3 of two bidentate malonate anions at the equatorial sites [$\text{Zn}-\text{O} = 2.0364$ (19) and 2.0391 (18) Å, respectively], and

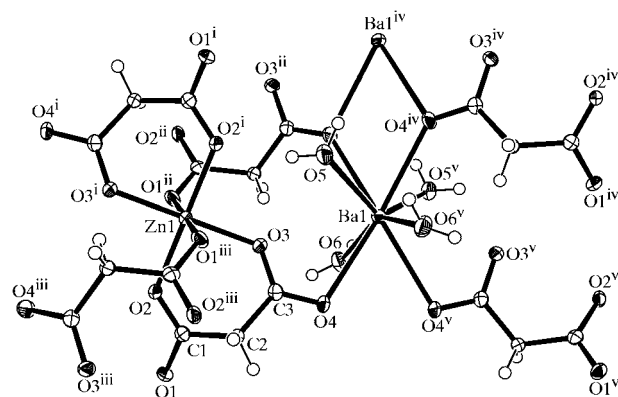


Figure 1

The coordination of the metal ions in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$.]

two O1 atoms from two other malonate anions at the apical sites [Zn—O = 2.3248 (18) Å]. All of the *cis* O—Zn—O bond angles are close to 90° [range 85.47 (7)–94.53 (7)°] and, because of the site symmetry of Zn, all of the *trans* angles are exactly 180°. Thus, the coordination octahedra around the Zn^{II} ions can be visualized as being distorted due to axial elongation.

Also evident in Fig. 1 is the variability of the coordination modes of the malonate dianion, with monodentate (O1), bidentate chelating (O2 and O3) and bridging (O4) modes all present. The chelate rings around the Zn^{II} cations have an envelope conformation, with the methylene groups (C2) displaced by 0.561 (3) Å from the plane defined by the other atoms in the ring.

The structure as a whole consists of two distinct types of layer, both parallel to (100) and stacked alternately in the *a* direction. The first of these, type 1 (Fig. 2), is composed entirely of Zn^{II} cations and malonate dianions and occurs at *x* = 0 and $\frac{1}{2}$. In this case, complete two-dimensional connectivity is achieved by means of O1—C1—O2 bridges between neighbouring Zn coordination octahedra. The O4 atoms, which bridge between Ba^{II} cations in neighbouring layers of the other type, project from the layer surfaces. Within the type 1 layers, the Zn···Zn separations are 5.822 (1) Å, while between the layers they are 6.843 (1) Å. It is within these layers that the weak C2—H2A···O2 and C2—H2B···O3 hydrogen bonds (Table 2) appear (dashed lines in Fig. 2).

The other type of layer, type 2, alternating with the first and centred on *x* = $\frac{1}{4}$ and $\frac{3}{4}$, primarily contains the Ba^{II} cations and the water molecules (Fig. 2). Two forms of connectivity occur within the type 2 layers. Atoms O4 on the surfaces of the type 1 layers create chains of edge-sharing Ba polyhedra propa-

gating in the *c* direction and, at the same time, link the two types of layer and complete the three-dimensional connectivity of the structure. The interlayer connectivity is further enhanced by O5—H5A···O2 and O6—H6A···O1 hydrogen bonds (Table 2). The remaining hydrogen bonds given in Table 2 occur entirely within the type 2 layers. Those of the form O5—H5B···O6 reinforce the connectivity of the chains of edge-sharing polyhedra, while those of the form O6—H6B···O5 interconnect neighbouring chains and complete the connectivity within the type 2 layers.

Experimental

The title complex was prepared under continuous stirring with successive addition of malonic acid (0.43 g, 4 mmol), zinc chloride (0.28 g, 2 mmol) and Ba(OH)₂·8H₂O (0.63 g, 2 mmol) to distilled water (40 ml) at room temperature. After filtration, slow evaporation over a period of a week at room temperature provided colourless plate-like crystals of (I).

Crystal data

[BaZn(C₃H₂O₄)₂(H₂O)₄]
M_r = 478.87
 Orthorhombic, *Pccn*
a = 19.014 (3) Å
b = 6.8434 (10) Å
c = 9.4203 (14) Å
V = 1225.8 (3) Å³
Z = 4
D_x = 2.595 Mg m⁻³

Mo Kα radiation
 Cell parameters from 3082 reflections
 θ = 3.2–26.3°
 μ = 5.21 mm⁻¹
T = 294 (2) K
 Plate, colourless
 0.20 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.370, *T_{max}* = 0.662
 6308 measured reflections

1262 independent reflections
 1042 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{max} = 26.4°
h = -23 → 19
k = -8 → 8
l = -7 → 11

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.019
wR (*F*²) = 0.046
S = 1.08
 1262 reflections
 93 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.24P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.56 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ba1—O4	2.807 (2)	Zn1—O1 ⁱⁱ	2.3248 (18)
Ba1—O4 ⁱ	2.795 (2)	Zn1—O2	2.0364 (19)
Ba1—O5	2.825 (2)	Zn1—O3	2.0391 (18)
Ba1—O6	2.848 (2)		
O1 ⁱⁱ —Zn1—O2	88.44 (7)	O4—Ba1—O5 ^{iv}	136.32 (7)
O2—Zn1—O3	90.88 (8)	O4—Ba1—O6	75.52 (6)
O1 ⁱⁱ —Zn1—O3	85.47 (7)	O4 ⁱ —Ba1—O6	78.36 (6)
O4 ⁱ —Ba1—O4 ⁱⁱⁱ	65.72 (8)	O4—Ba1—O6 ^{iv}	78.77 (6)
O4 ^{iv} —Ba1—O4	65.38 (8)	O4 ⁱⁱⁱ —Ba1—O6	130.22 (6)
O4 ⁱ —Ba1—O4	121.51 (7)	O5—Ba1—O6 ^{iv}	65.91 (6)
O4 ⁱⁱⁱ —Ba1—O4	153.04 (10)	O5—Ba1—O6	128.26 (6)
O4 ⁱ —Ba1—O5	70.19 (6)	O5—Ba1—O5 ^{iv}	132.94 (8)
O4 ⁱⁱⁱ —Ba1—O5	70.62 (6)	O6 ^{iv} —Ba1—O6	149.35 (9)
O4—Ba1—O5	87.07 (6)		

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

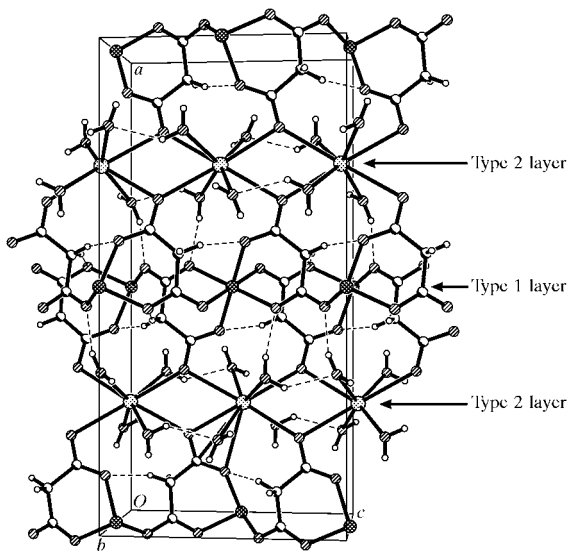


Figure 2

A view, approximately along the *b* axis, showing the alternation of type 1 and type 2 layers along the *a* axis. Ba atoms are represented as dotted spheres, Zn atoms as cross-hatched spheres, O atoms as fully shaded spheres, C atoms as part-shaded spheres and H atoms as open circles. Dashed lines indicate hydrogen bonds.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots O2 ^v	0.85	1.98	2.812 (3)	165
O5—H5B \cdots O6 ⁱ	0.85	2.14	2.836 (3)	140
O6—H6A \cdots O1 ^{vi}	0.85	1.99	2.810 (3)	161
O6—H6B \cdots O5 ^{vii}	0.85	2.02	2.825 (3)	157
C2—H2A \cdots O2 ⁱⁱ	0.97	2.59	3.506 (3)	157
C2—H2B \cdots O3 ^{viii}	0.97	2.29	3.217 (3)	159

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

The water H atoms were found in difference Fourier maps and were fixed during refinement at an O—H distance of 0.85 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The H atoms of C—H groups were positioned geometrically and were treated using a riding model, with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1619). Services for accessing these data are described at the back of the journal.

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