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Poly[tetraaquadi-μ_3-malonato-calcium(II)zinc(II)]

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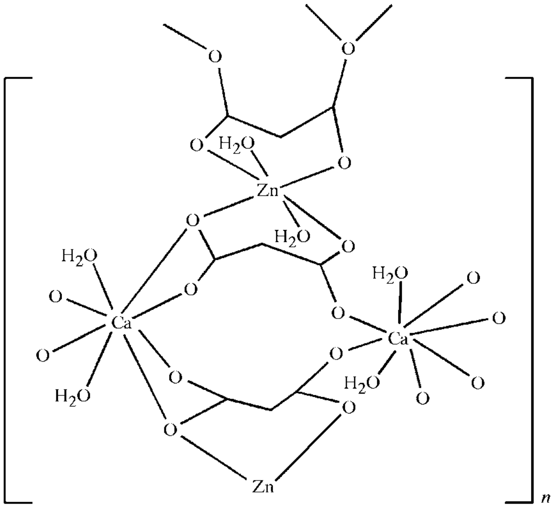
The title complex, $[CaZn(C_3H_2O_4)_2(H_2O)_4]_n$, is a two-dimensional polymer and consists of CaO_8 and ZnO_6 polyhedra linked together by malonate ligands. The Ca^{II} cation, lying on a twofold axis, is coordinated by two water molecules and six malonate O atoms. The Zn^{II} cation, which lies on an inversion center in an octahedral environment, is coordinated by four malonate O atoms in an equatorial arrangement and two water molecules in axial positions. The Zn—O and Ca—O bond lengths are in the ranges 2.0445 (12)–2.1346 (16) and 2.3831 (13)–2.6630 (13) Å, respectively. The structure comprises alternating layers along the [101] plane, the shortest Zn$\cdots$Zn distance being 6.8172 (8) Å. The whole three-dimensional structure is maintained and stabilized by the presence of hydrogen bonds.

Comment

There has been considerable interest in the design and synthesis of transition metal complexes with carboxylate ligands in coordination chemistry, owing to the fact that such complexes have potential applications in molecular-based magnets, catalysis, supramolecular chemistry and biological systems (Li *et al.*, 2002; Shi *et al.*, 2000; Devereux *et al.*, 2000). Because of the significant flexibility of dicarboxylate ligands, the malonate (mal) dianion may act as a monodentate, a chelated bidentate or a tridentate bridging ligand to form various one-, two- and three-dimensional structures (Ray & Hathaway, 1982; Saadeh *et al.*, 1993; Xue *et al.*, 2003; Delgado *et al.*, 2004). Zinc(II) complexes with the malonate ligand have potential applications in modified metalloenzymes and in precursor systems for Zn-containing ceramic materials, and several structures of Zn^{II} complexes with malonate ligands have been reported (Zhang *et al.*, 2003; Lin *et al.*, 2003; Burrows *et al.*, 2000; Delgado *et al.*, 2003; Fu *et al.*, 2006). However, to the best of our knowledge, there are few structural reports on hetero-bimetallic Zn^{II}–malonate complexes, especially those involving alkaline-earth metals (Guo & Guo, 2006). We report here the synthesis and crystal structure of the title complex, $[CaZn(mal)_2(H_2O)_4]$, (I), one such hetero-bimetallic Zn^{II}–malonate complex.



(I)

The molecular structure of (I), shown in Fig. 1, can be described as a two-dimensional network of metal ions, which are linked by the malonate ligands (Fig. 2). Two of the coordinated water molecules are linked to the Ca^{II} ion and the other two to the transition metal ion. The Zn^{II} ion lies on an inversion center and is octahedrally coordinated by six O atoms from two malonate groups (atoms O1 and O3) and two water molecules (atoms O2). The Zn—O bond lengths are slightly different (Table 1), and the Zn—O_{mal} bonds are somewhat longer than those in $[BaZn(mal)_2(H_2O)_4]$ (Guo &

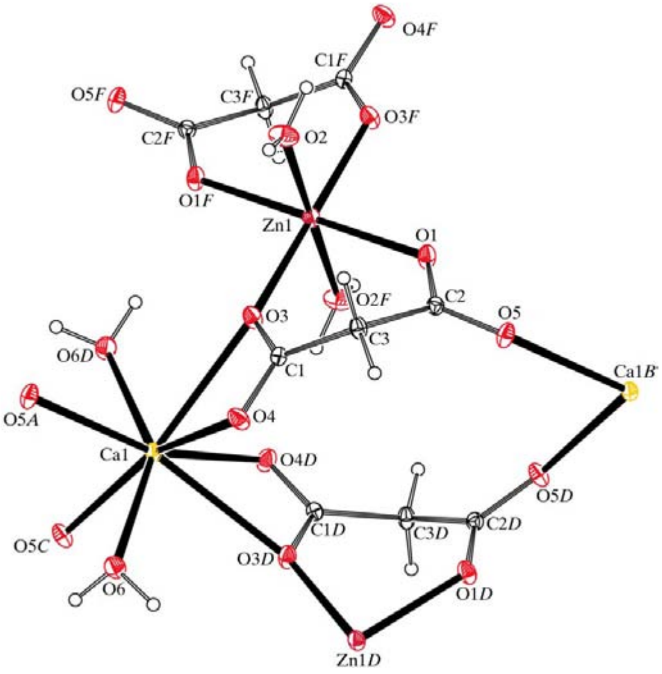


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (*A*) $x, -1 + y, z$; (*B*) $x, 1 + y, z$; (*C*) $-x, y, \frac{1}{2} - z$; (*D*) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$; (*F*) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.]

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Guo, 2006). The Ca^{II} ion, which lies on a twofold axis, is six-coordinated by two O atoms (O6) from two water molecules and six O atoms (O3, O4 and O5) from four malonate ligands, forming an irregular polyhedron. The Ca—O bonds lengths are significantly different (Table 1), and the Ca—O$_{mal}$ bond lengths are comparable to the corresponding values found in the [CaMn(mal)$_2$(H$_2$O)$_4$] and [CaNi(mal)$_2$(H$_2$O)$_4$]·2H$_2$O complexes (Gil de Muro *et al.*, 2000). Each malonate ligand adopts three coordination modes to connect with metal cations. As shown in Fig. 1, one carboxyl group adopts both a bidentate 1,2-chelating and a monodentate bridging mode (through atoms O3 and O4), and the other carboxyl group adopts a monodentate bridging mode (through atoms O1 and O5). Furthermore, the two carboxyl groups adopt a bidentate 1,3-chelating mode (through atoms O1 and O3); the resulting chelate ring exhibits an envelope conformation in which only the methylene group is significantly shifted from the ring plane [by 0.369 (2) Å]. The O—C—O angle for the monodentate carboxylate group is 123.19 (15)°, slightly larger than the value of 120.54 (15)° for the chelating group. Atoms O3 link the Zn and Ca ions [Zn1—O3—Ca1 = 141.43 (6)°], forming planes perpendicular to the [101] direction, the shortest Zn···Zn distance being 6.8172 (8) Å and the shortest Ca···Ca distance 7.0582 (9) Å. The coordinated water molecules are linked to carboxylate atoms O1, O4 and O5 through hydrogen bonds (Table 2), and the whole three-dimensional structure is maintained and stabilized by the presence of these hydrogen bonds (Fig. 3).

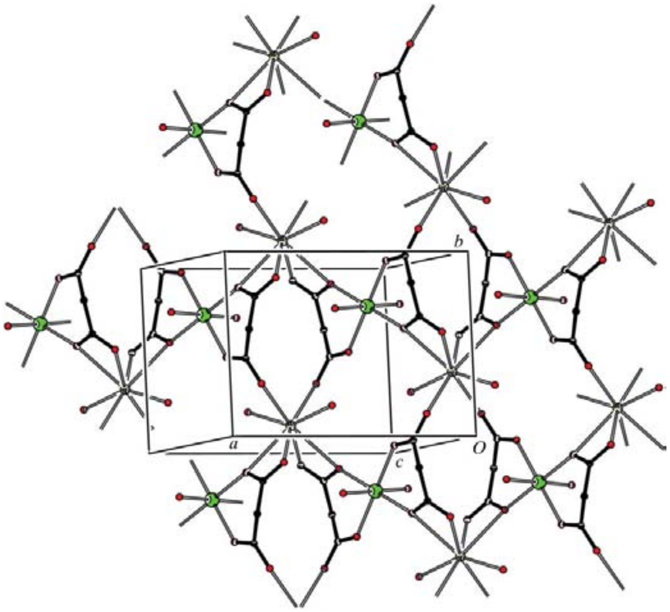

Figure 2
The polymeric chains of (I), viewed along the *b* axis.

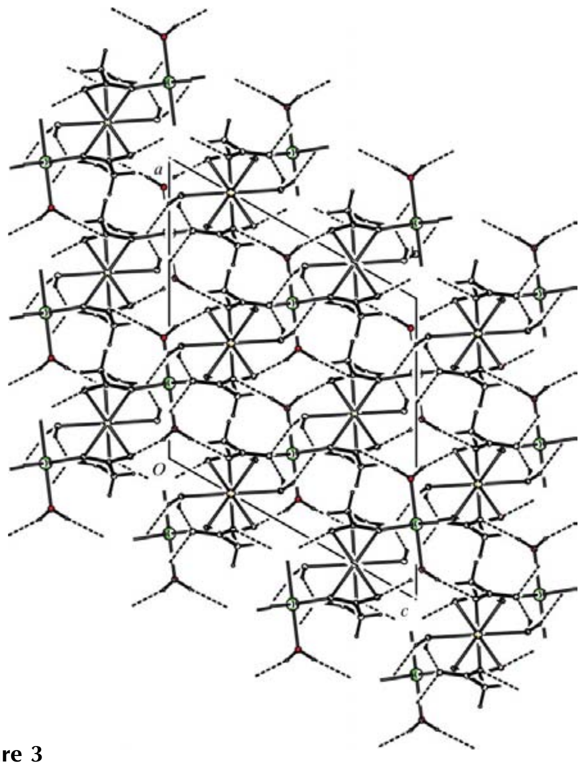

Figure 3
The hydrogen-bond interactions (dashed lines) in (I), viewed along the *b* axis.

Experimental

ZnO (0.81 g, 1 mmol) and Ca(OH)$_2$ (0.0714 g, 1 mmol) were added slowly to an aqueous solution (20 ml) of malonic acid (0.312 g, 3 mmol), and the reaction mixture was stirred continuously at 328 K. After 2 h, the reaction mixture was cooled to room temperature and filtered. Colorless single crystals were obtained from the filtrate after several months.

Crystal data

[CaZn(C$_3$H$_2$O$_4$)$_2$(H$_2$O)$_4$]
M_r = 381.61
Monoclinic, $C2/c$
a = 13.9736 (17) Å
b = 7.5445 (9) Å
c = 13.1729 (15) Å
β = 119.788 (2)°
V = 1205.2 (2) Å^3
Z = 4
D_x = 2.103 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.53 mm^{-1}
T = 292 (2) K
Prism, colorless
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.518, T_{max} = 0.632
3428 measured reflections
1368 independent reflections
1302 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 27.5°

Table 1
Selected geometric parameters (Å, °).

C1—O4	1.243 (2)	O3—Zn1	2.0445 (12)
C1—O3	1.267 (2)	O3—Ca1	2.6630 (13)
C2—O5	1.246 (2)	O4—Ca1	2.4368 (13)
C2—O1	1.269 (2)	O5—Ca1^{i}	2.3831 (13)
O1—Zn1	2.0989 (12)	O6—Ca1	2.4024 (14)
O2—Zn1	2.1346 (16)		
O3—C1—O4	120.54 (15)	O6—Ca1—O6^{iii}	147.07 (7)
O5—C2—O1	123.19 (15)	O4—Ca1—O3	50.37 (4)
Zn1—O3—Ca1	141.43 (6)	O2—Zn1—O2^{iv}	180
O5^{ii}—Ca1—O6^{iii}	78.28 (5)		

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.060$
$S = 1.06$
1368 reflections
105 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.8399P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6A···O1^{v}	0.868 (12)	1.996 (15)	2.7973 (19)	153.0 (17)
O6—H6B···O1^{vi}	0.857 (13)	2.191 (15)	3.019 (2)	163 (2)
O2—H2A···O4^{viii}	0.834 (13)	1.976 (14)	2.791 (2)	166 (3)
O2—H2B···O5^{vii}	0.844 (13)	2.089 (13)	2.931 (2)	175 (3)

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

All the water H atoms were located in a difference Fourier map and their positional parameters were refined with O—H distances restrained to 0.95 (2) Å. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H bond lengths of 0.97 Å [$U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C)].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: AV3015). Services for accessing these data are described at the back of the journal.

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