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Poly[aqua-μ_3-2,2-dimethylmalonato-zinc(II)]

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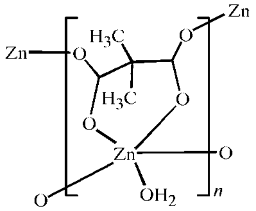
The title complex, $[Zn(C_5H_6O_4)(H_2O)]_n$, has a two-dimensional layer structure. The Zn atoms, in a geometry that is closer to trigonal bipyramidal than square pyramidal, are coordinated by two O atoms of a bidentate dimethylmalonate ligand, two O atoms of monodentate dimethylmalonate ligands and one O atom from the aqua ligand. The crystal structure is characterized by the intralayer motif of a hydrogen-bonded network. Neighboring layers are linked together to build up a three-dimensional network *via* van der Waals forces.

Comment

From a coordination standpoint, malonate is a versatile ligand, displaying a variety of bonding modes. For example, monodeprotonation of malonic acid can lead to complexes containing the coordinated $HOOCCH_2CO_2^-$ ($malH^-$) anion. This anion is known to bond to metals simultaneously *via* chelating bidentate and monodentate carboxylate groups, *e.g.* in $[Cu(malH)_2]$ (Delgado, Sanchiz *et al.*, 2004). Deprotonation of the parent acid generates the $[CH_2(CO_2)_2]^{2-}$ (mal^{2-}) dianion, which can be found coordinating to metals both through two distal carboxylate O atoms to form a six-membered ring and through non-chelating O atoms to build up bridged compounds, as in $\{[Co(H_2O)_2][Co(mal)_2(H_2O)_2]\}_n$ (Delgado, Hernandez-Molina *et al.*, 2004). In heterobimetallic malonate complexes involving transition and alkaline-earth metals, malonate dianions have also been used to construct coordination polymers by acting as chelating bidentate ligands or as simple bridges between metal centers. Consequently, many heteronuclear malonate complexes have been synthesized and structurally characterized (Djeghri *et al.*, 2005, 2006; Gil de Muro *et al.*, 1998, 2000, 2004; Guo & Cao, 2006; Guo & Guo, 2006; Fu *et al.*, 2006).

Although many complexes that use malonate as a ligand have been synthesized, only a few complexes that use dimethylmalonate as a ligand are known (Zhang *et al.*, 2002). Five-coordinate complexes of metal ions are not common, and those that are known are mainly complexes involving copper, malonate and other ligands (Sieroń, 2004; Xiong *et al.*, 2001). Among the complexes of Zn and the malonate ligand, five-coordinate complexes are rarely reported. In the course of our studies of heterobimetallic malonate complexes involving zinc and alkaline-earth metals, we used dimethylmalonic acid as a ligand, expecting to obtain a structure similar or isotypic to that of $[BaZn\{CH_2(CO_2)_2\}(H_2O)_4]_n$ (Guo & Guo, 2006); interestingly, a completely different crystal structure was obtained, the title novel five-coordinated dimethylmalonate–zinc complex, (I), and we report its crystal structure here.



(I)

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

The Zn atoms are five-coordinated by two chelating O atoms (atoms O1 and O3) of the dimethylmalonate dianion, one O atom from the water molecule (O5) and two O atoms ($O2^i$ and $O4^{ii}$; see Table 1 for symmetry code) from two symmetry-related dimethylmalonate anions acting in a monodentate fashion. The Zn atom deviates by 0.0120 (3) Å from the least-squares plane defined by atoms O5, $O2^i$ and O3, all of the *cis* O—Zn—O bond angles are close to 90° [in the

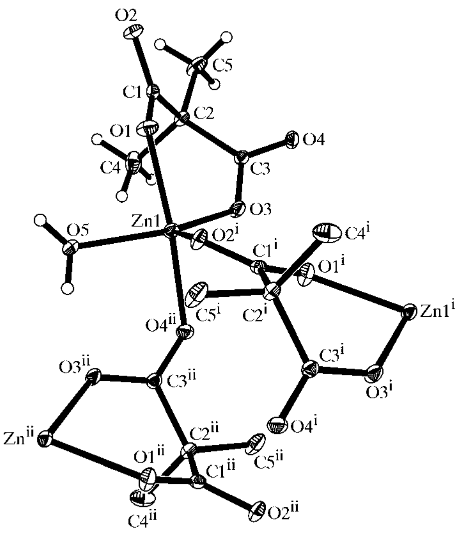


Figure 1
A view of part of the structure of (I), showing the atom-numbering scheme and the coordination of the Zn1 atom; displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{5}{2}, z - \frac{1}{2}$.]

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range 86.23 (7)–97.86 (7)°; Table 1], and the *trans* O4^{ii}—Zn1—O1 angle is 168.74 (7)°. The structure index τ, indicating the relative amount of trigonality ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid; Addison *et al.*, 1984), is 0.58; thus, the coordination geometry of Zn is closer to distorted trigonal bipyramidal than to square pyramidal.

In the present structure, the variability of the malonate ligand can be clearly seen (Fig. 1). A single dimethylmalonate molecule chelates the Zn atom to form a six-membered ring. The resulting six-membered chelate ring (Zn1/O1/C1–C3/O3) has a boat conformation, with atoms Zn1 and C2 lying 0.4166 (4) and 0.6295 (8) Å, respectively, out of the O1/C1/C3/O3 mean plane. Atom O2^{i} of the O1^{i}/C1^{i}/O2^{i} carboxylate group adopts a monodentate mode to connect to Zn (see Fig. 1 for symmetry codes); thus, the two Zn atoms are linked together *via* atoms O1^{i}, C1^{i} and O2^{i}, with a Zn1···Zn1^{i} distance of 5.098 (8) Å. Similarly, atom O4^{ii} of the O3^{ii}/C3^{ii}/O4^{ii} carboxylate group coordinates to Zn, leading to a Zn1···Zn1^{ii} distance of 5.001 (1) Å. Two Zn atoms are linked together *via* these carboxylate groups acting in monodentate mode, forming a 12-membered ring. Four Zn atoms are associated into a 16-membered ring *via* carboxylate groups acting in chelating and monodentate fashions. Each Zn atom is connected to four other Zn atoms through carboxylate bridges in the *bc* plane, resulting in the formation of a two-dimensional polymeric layer perpendicular to the [100] direction (Fig. 2).

The Zn—O(water) bond and the Zn—O(dimethylmalonate) bonds (Table 1) are somewhat shorter than those in the six-coordinate complex $[CaZn(mal)_2(H_2O)_4]_n$ (Fu *et al.*, 2006), and are comparable to the values reported for a five-coordinate zinc complex involving carboxylate and other ligands (Erxleben, 2001). The O—C—O angles for the two carboxylate groups are almost the same (Table 1). The values of the C—O bond distances in the carboxylate groups (Table 1) indicate that the mesomeric effect for the O1/C1/O2 carboxylate group is larger than that of the O3/C3/O4 group.

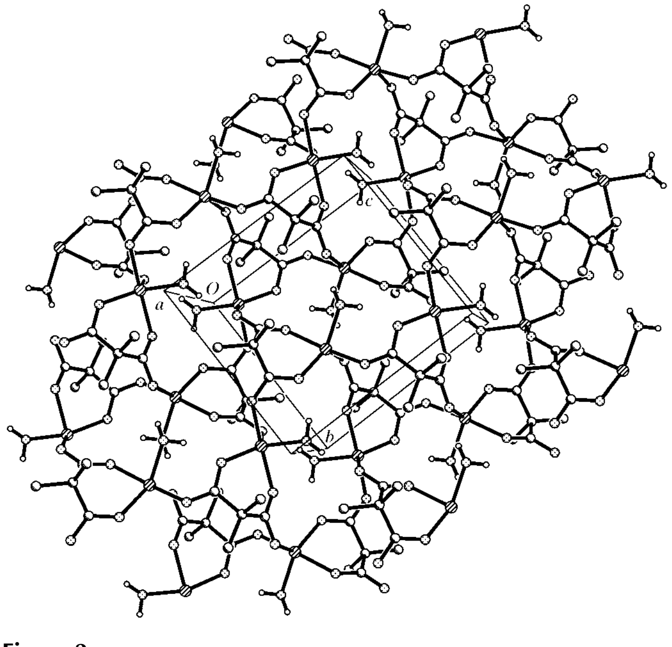

Figure 2
The packing of (I), showing the two-dimensional polymeric layer in the direction of the *bc* plane, viewed down the *a* axis.

The crystal structure owes its formation to a strong intermolecular hydrogen bond (Brown, 1976) between atom O3^{ii} and atom H5*E* of the water molecule (Table 2). Hydrogen bonding plays an important role in the stabilization of the extended two-dimensional network structure. The structure consists of alternating layers in the [100] direction, with neighboring layers linked mainly by van der Waals forces to build up a three-dimensional network.

Experimental

The title complex was prepared under continuous stirring with successive addition of dimethylmalonic acid (0.53 g, 4 mmol), Na_2CO_3 (0.22 g, 2 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.49 g, 2 mmol) and barium nitrate (0.52 g 2 mmol) to distilled water (30 ml) at room temperature. After filtration, slow evaporation over a period of three weeks at room temperature provided colorless plate-shaped crystals of (I).

Crystal data

$[Zn(C_5H_6O_4)(H_2O)]$
$M_r = 213.48$
Monoclinic, $P2_1/c$
$a = 8.7030\ (15)$ Å
$b = 8.5986\ (15)$ Å
$c = 9.4773\ (16)$ Å
$\beta = 102.532\ (3)°$
$V = 692.3\ (2)$ Å^3
$Z = 4$
$D_x = 2.048$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 3.52$ mm^{-1}
$T = 294\ (2)$ K
Plate, colorless
0.16 × 0.14 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.585$, $T_{max} = 0.762$
3431 measured reflections
1226 independent reflections
1095 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.059$
$S = 1.06$
1226 reflections
102 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.2489P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O3	1.9776 (16)	O1—C1	1.246 (3)
Zn1—O2^{i}	1.9967 (17)	O2—C1	1.266 (3)
Zn1—O5	2.0276 (16)	O3—C3	1.271 (3)
Zn1—O4^{ii}	2.0761 (16)	O4—C3	1.244 (3)
Zn1—O1	2.0815 (16)		
O3—Zn1—O2^{i}	120.48 (7)	O3—Zn1—O4^{ii}	90.52 (7)
O3—Zn1—O5	134.07 (8)	O5—Zn1—O4^{ii}	87.95 (7)
O2^{i}—Zn1—O5	105.44 (7)	O5—Zn1—O1	86.23 (7)
O3—Zn1—O1	86.63 (7)	O4^{ii}—Zn1—O1	168.74 (7)
O2^{i}—Zn1—O1	97.86 (7)	O1—C1—O2	122.3 (2)
O2^{i}—Zn1—O4^{ii}	92.98 (7)	O4—C3—O3	122.8 (2)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{5}{2}, z-\frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5E···O3^{ii}	0.85	1.83	2.645 (2)	159
O5—H5D···O2^{iii}	0.85	1.92	2.765 (2)	170

Symmetry codes: (ii) $x, -y + \frac{5}{2}, z - \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

The H atoms of the water molecule were found in difference Fourier maps. However, during refinement, they were fixed at O—H distances of 0.85 Å and their $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(O). The H atoms of methyl groups were treated as riding, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(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*; 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: SK3044). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Delgado, F. S., Hernandez-Molina, M., Sanchiz, J., Ruiz-Perez, C., Rodriguez-Martin, Y., Lopez, T., Lloret, F. & Julve, M. (2004). *CrystEngComm*, **6**, 106–111.

Delgado, F. S., Sanchiz, J., Ruis-Perez, C., Lloret, F. & Julve, M. (2004). *CrystEngComm*, **6**, 443–450.

Djeghri, A., Balegroune, F., Guehria Laidoudi, A. & Toupet, L. (2005). *J. Chem. Crystallogr.* **35**, 603–607.

Djeghri, A., Balegroune, F., Guehria Laidoudi, A. & Toupet, L. (2006). *Acta Cryst.* C**62**, m126–m128.

Erxleben, A. (2001). *Inorg. Chem.* **40**, 208–213.

Fu, X.-C., Li, M.-T., Wang, X.-Y., Wang, C.-G. & Deng, X.-T. (2006). *Acta Cryst.* C**62**, m258–m260.

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. & Cao, H.-X. (2006). *Acta Cryst.* C**62**, m431–m433.

Guo, M.-L. & Guo, C.-H. (2006). *Acta Cryst.* C**62**, m7–m9.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sieroń, L. (2004). *Acta Cryst.* E**60**, m297–m299.

Xiong, Y., Tong, M.-L., An, T.-C. & Karlsson, H. T. (2001). *Acta Cryst.* C**57**, 1385–1387.

Zhang, Y.-J., Livens, F. R., Collison, D., Helliwell, M., Heatley, F., Powell, A. K., Wocadlo, S. & Eccles, H. (2002). *Polyhedron*, **21**, 69–79.