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Poly[disodium bis(μ-malonato)zincate(II) dihydrate]

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Key indicators

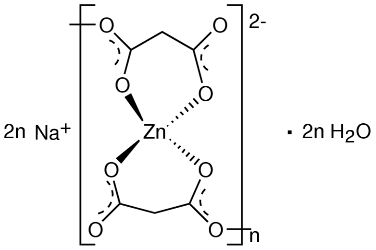
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.023
wR factor = 0.056
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $\{Na_2[Zn(C_3H_2O_4)_2]\cdot 2H_2O\}_n$, is a three-dimensional polymeric complex bridged by malonate dianions. The malonate ligand exhibits versatile coordination modes and links two Zn^{II} and four Na^{I} atoms. The Zn atom occupies a special position in an inversion centre and is chelated by two malonate ligands [Zn—O = 2.0230 (10) and 2.0875 (11) Å]; two other malonates are involved in monodentate coordination of the Zn atom [Zn—O = 2.2789 (12) Å], thus completing its octahedral coordination environment. The Na atom also has a distorted octahedral coordination, formed by four carboxylate O atoms of four malonate ligands [2.4328 (15)–2.5493 (13) Å] and two water molecules [2.3749 (15) and 2.4144 (14) Å].

Comment

The versatile coordination modes of dicarboxylates have been revealed in metal complexes. This work presents the coordination modes of malonate in the title polymeric Zn^{II} and Na^{I} complex, (I).



(I)

The coordination environments of the Zn^{II} and Na^{I} atoms are illustrated in Fig. 1. The Zn^{II} atom is located at an inversion centre and assumes a distorted octahedral coordination geometry. Two malonate dianions chelate the Zn^{II} atom, with normal Zn—O bond distances of 2.0230 (10) and 2.0875 (11) Å, while two other malonate ligands are involved in the monodentate coordination of the Zn^{II} atom, with a longer Zn—O bond distance of 2.2789 (12) Å. A similar elongated octahedral coordination geometry was observed in the Cu^{II} analogue (Barnes & Weakley, 1997). The Na^{I} atom also has a distorted octahedral coordination, formed by four carboxylate O atoms of four malonate ligands [Na—O = 2.4328 (15)–2.5493 (13) Å] and two water molecules [2.3749 (15) and 2.4144 (14) Å].

Thus, the malonate dianion in the structure of the title compound exhibits versatile coordination modes and bridges two Zn^{II} and four Na^{I} atoms, as shown in Fig. 2. While the

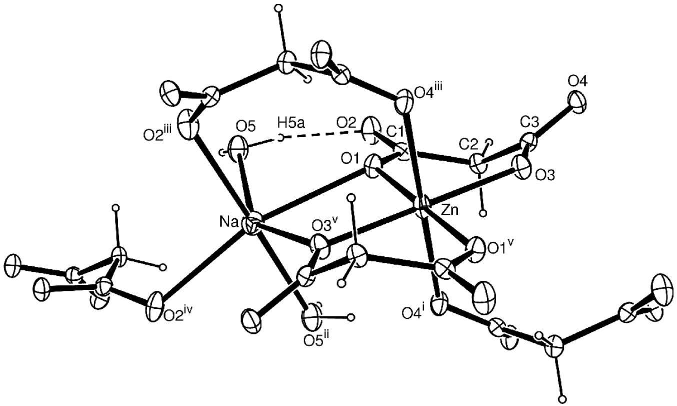


Figure 1

The coordination environments of the Zn^{II} and Na^{I} atoms, showing 40% probability displacement ellipsoids. The dashed line denotes the hydrogen bond. [Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (ii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $1-x, -y, -z$.]

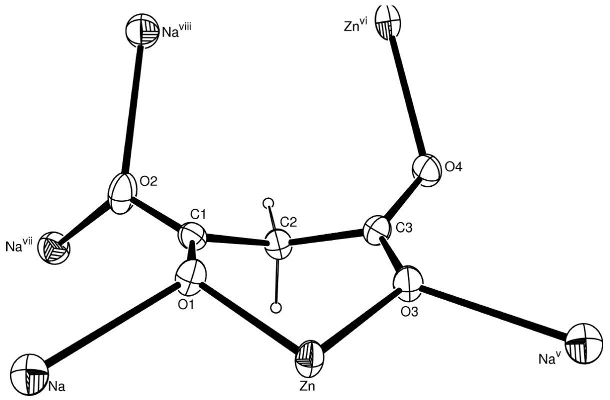


Figure 2

A diagram showing the versatile coordination modes of a malonate dianion. [Symmetry codes: (v) $1-x, -y, -z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (vii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{3}{2}-x, \frac{1}{2}+y, z$.]

malonate ligand chelates the Zn^{II} atom by both terminal carboxyl groups (through atoms O1 and O3), it also bridges the Zn^{II} and Na^{I} atoms through atoms O2 and O4 of both carboxyl groups. The C3-carboxyl group of the malonate bridges a Zn^{II} and an Na^{I} atom, and the C1-carboxyl group bridges three neighbouring Na^{I} atoms. Atom O4 coordinates only one Zn^{II} atom, whereas atoms O1, O2 and O3 of the malonate bind two metal atoms each and bring about forced contacts between metal atoms, with a Zn···Na separation of 3.5634 (7) Å and an $Na^{vii}\cdots Na^{viii}$ separation of 3.7751 (11) Å (Fig. 2).

Two water molecules (O5 and $O5^{ii}$) coordinate to each Na atom (Fig. 1). The Na—O5—H5*A* and Na—O5—H5*B* angles are significantly different (94.1 and 137.6°, respectively), whereas the $Na—O5^{ii}—H5A^{ii}$ and $Na—O5^{ii}—H5B^{ii}$ angles are essentially identical (107.2 and 101.5°). The smaller Na—O5—H5*A* angle of 94.1°, related to the shorter Na···H5*A* separation of 2.63 Å, is due to the involvement of O5—H5*A*···O2 hydrogen bonding in the six-membered pseudo-ring, the O5···O2 distance and O5—H5*A*···O2 angle being 2.7129 (17) Å and 169°, respectively.

Experimental

An aqueous solution (10 ml) containing zinc(II) chloride (1 mmol) and benzimidazole (2 mmol) was mixed with an aqueous solution (10 ml) of malonic acid (1 mmol) and Na_2CO_3 (1 mmol). The mixture was refluxed for 2 h. After 5 d, prismatic crystals of the title compound were obtained along with crystals of a different type, *viz*. thin plates. The latter, however, were not suitable for X-ray analysis.

Crystal data

$Na_2[Zn(C_3H_2O_4)_2]\cdot 2H_2O$
$M_r = 351.49$
Orthorhombic, *Pbca*
$a = 6.8359$ (10) Å
$b = 9.3875$ (13) Å
$c = 16.5518$ (14) Å
$V = 1062.2$ (2) $Å^3$
$Z = 4$
$D_x = 2.198$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 8742 reflections
$\theta = 2.5–24.5°$
$\mu = 2.44$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.26 × 0.20 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.530$, $T_{max} = 0.626$
8878 measured reflections

1206 independent reflections
1089 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.4°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.056$
$S = 1.17$
1206 reflections
88 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.6078P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e $Å^{-3}$
$\Delta\rho_{min} = -0.37$ e $Å^{-3}$

Table 1

Selected geometric parameters (Å).

Zn—O1	2.0230 (10)	$Na—O2^{iii}$	2.4328 (15)
Zn—O3	2.0875 (11)	$Na—O3^{v}$	2.5419 (13)
$Zn—O4^{i}$	2.2789 (12)	Na—O5	2.4144 (14)
Na—O1	2.5493 (13)	$Na—O5^{ii}$	2.3749 (15)
$Na—O2^{iv}$	2.5338 (15)		

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

The H atoms of the water molecule were located in a difference Fourier map and included in structure-factor calculations with fixed positional parameters and displacement parameters set equal to 0.05 $Å^2$. The C-bound H atoms were placed in calculated positions, with C—H = 0.97 Å, and were included in the final cycles of refinement in the riding mode, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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