metal-organic compounds

Poly[[diaqua-μ_3-malonato-iron(II)] monohydrate]

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The title coordination polymer, $[[Fe(C_4H_4O_5)(H_2O)_2]\cdot H_2O]_n$, was obtained by the hydrothermal reaction of $FeSO_4$ with malic acid in alkaline aqueous solution. Each Fe^{II} atom is coordinated by four O atoms from three malate ligands and two water molecules, and displays a distorted octahedral geometry. The polychelated malate ligands bridge Fe ions to form corrugated layers; these layers are further assembled by intermolecular O—H···O hydrogen-bonding interactions to form a three-dimensional supramolecular network, with channels running along the b axis in which the uncoordinated water molecules are located. The solvent water molecule is disordered over two positions, with occupancy ratios of 0.78/0.22.

Related literature

For related literature, see: Iglesias *et al.* (2003); Karipides & Reed (1976); Moulton & Zaworotko (2001).
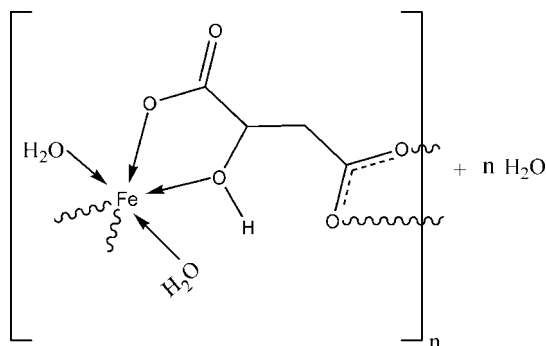
Experimental

Crystal data

$[Fe(C_4H_4O_5)(H_2O)_2]\cdot H_2O$
$M_r = 241.97$
Orthorhombic, $Pbca$
$a = 14.2225$ (8) Å
$b = 8.2788$ (5) Å
$c = 14.7043$ (8) Å
$V = 1731.36$ (17) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.76$ mm^{-1}
$T = 293$ (2) K
$0.32 \times 0.26 \times 0.23$ mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.587$, $T_{max} = 0.670$
8229 measured reflections
1603 independent reflections
1420 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.083$
$S = 1.10$
1603 reflections
142 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1W^i	0.81 (3)	1.95 (3)	2.749 (2)	174 (3)
O1W—H11···O2^{ii}	0.820 (10)	1.882 (14)	2.660 (3)	158 (3)
O1W—H12···O5^{iii}	0.809 (10)	2.18 (2)	2.856 (3)	141 (3)
O1W—H12···O4^i	0.809 (10)	2.47 (3)	3.067 (3)	131 (3)
O2W—H21···O30A	0.811 (10)	1.866 (14)	2.662 (4)	167 (4)
O2W—H21···O30B	0.811 (10)	1.785 (18)	2.575 (13)	164 (4)
O2W—H22···O2^{iv}	0.81 (3)	1.915 (11)	2.720 (3)	172 (4)
O30A—H31B···O1^v	0.84	2.17	2.984 (5)	165
O30A—H32B···O1^{vi}	0.83	2.18	2.887 (5)	142

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

References

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supplementary materials

Poly[[diaqua-μ_3-malonato-iron(II)] monohydrate]

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Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Iglesias *et al.*, 2003; Moulton & Zaworotko, 2001; Karipides & Reed, 1976). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metals ions and bridging building blocks as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π-π stacking interactions.

In the structure of (I), each Fe^{II} atom is coordinated by four O atoms from three malate ligands and two water molecules, and displayed a distorted octahedral geometry (Fig. 1). Pairs of Fe···Fe ions are bridged by the malate ligands at a distance of 6.789 (3) Å to form corrugated layers which are further assembled into a three-dimensional supramolecular network through intermolecular hydrogen bonding interactions (Table 1) with channels running along the *b* axis hosting the uncoordinated water molecules (Fig 2).

Experimental

A mixture of $FeSO_4$ (0.5 mmol), malic acid (0.5 mmol), NaOH(1 mmol) and H_2O (10 ml) was placed in a 23 ml Teflon reactor, which was heated at 433 K for three days and then cooled to room temperature at a rate of 5 K h^{-1}. Single crystals were obtained after washing with water and drying in air.

Refinement

The solvate water molecule is disordered over two positions with occupancy ratios of 0.78/0.22. Water and hydroxyl H atoms were located in difference density Fourier maps and were refined using restraints (O—H= 0.82 (1) Å and H···H= 1.33 (2) Å) with $U_{iso}(H) = 1.5\ U_{eq}(O)$. The hydrogen atoms of the disordered water molecule were set to have each the same coordinates for both disordered H_2O molecules. H atoms attached to carbon were placed at calculated positions and were treated as riding on their parent C atoms with C—H = 0.97 Å (methylene) or 0.98 Å (methine), and with $U_{iso}(H) = 1.2\ U_{eq}(C)$.
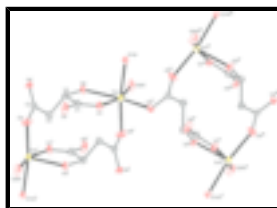
Figures

Fig. 1. The structure of (I), showing the atom-numbering scheme and the formation of the polymetric structure. displacement ellipsoids are drawn at the 30% probability level. The solvate water molecule and H atoms have been omitted for clarity. [Symmetry codes: (i) −*x*, −*y* + 2, −*z*; (ii) *x*, −*y* + 3/2, *z* + 1/2; (iii) −*x*, *y* − 1/2, −*z* + 1/2]
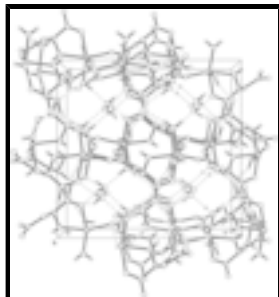
Fig. 2. View of the supramolecular network along the *b* axis. The minor moiety of the disordered water molecules were omitted for clarity.

catena-[Diaqua-(μ₄-malato-*O*,*O*',*O*'',*O*''')-\ iron(II) monohydrate]

Crystal data

[Fe(C₄H₄O₅)(H₂O)₂]·H₂O	$F_{000} = 992$
$M_r = 241.97$	$D_x = 1.857$ Mg m⁻³
Orthorhombic, *Pbca*	Mo *K*α radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 1506 reflections
$a = 14.2225$ (8) Å	$\theta = 1.4–28.0°$
$b = 8.2788$ (5) Å	$\mu = 1.76$ mm⁻¹
$c = 14.7043$ (8) Å	$T = 293$ (2) K
$V = 1731.36$ (17) Å³	Blocky, red
$Z = 8$	$0.32 \times 0.26 \times 0.23$ mm

Data collection

Bruker APEXII area-detector diffractometer	1603 independent reflections
Radiation source: fine-focus sealed tube	1420 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.026$
$T = 293(2)$ K	$\theta_{max} = 25.5°$
φ and ω scan	$\theta_{min} = 2.8°$
Absorption correction: multi-scan SADABS (Sheldrick, 1996)	$h = -17 \rightarrow 14$
$T_{min} = 0.587$, $T_{max} = 0.670$	$k = -10 \rightarrow 7$
8229 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 1.9411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.003$

1603 reflections

$\Delta\rho_{max} = 0.38$ e Å^{-3}

142 parameters

$\Delta\rho_{min} = -0.38$ e Å^{-3}

7 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
C1	0.20311 (17)	0.8001 (3)	0.04422 (16)	0.0237 (5)	
C2	0.13407 (16)	0.7905 (3)	−0.03528 (15)	0.0219 (5)	
H2	0.1599	0.7192	−0.0822	0.026*	
C3	0.11770 (18)	0.9566 (3)	−0.07561 (16)	0.0252 (5)	
H3A	0.1781	1.0064	−0.0880	0.030*	
H3B	0.0855	1.0230	−0.0311	0.030*	
C4	0.06047 (18)	0.9543 (3)	−0.16261 (16)	0.0240 (5)	
Fe1	0.02997 (3)	0.68818 (4)	0.14709 (2)	0.02428 (15)	
O1	0.17406 (12)	0.7638 (2)	0.12267 (11)	0.0272 (4)	
O2	0.28461 (13)	0.8461 (3)	0.02750 (12)	0.0414 (5)	
O3	0.04782 (12)	0.7240 (2)	−0.00225 (12)	0.0281 (4)	
H3	0.018 (2)	0.677 (3)	−0.0408 (17)	0.042*	
O4	0.06326 (15)	0.8301 (2)	−0.21102 (12)	0.0317 (4)	
O5	0.01587 (17)	1.0778 (3)	−0.18482 (14)	0.0469 (6)	
O1W	0.06641 (13)	0.4258 (2)	0.12724 (12)	0.0263 (4)	
H11	0.1195 (11)	0.402 (4)	0.1098 (18)	0.039*	
H12	0.0556 (19)	0.378 (4)	0.1741 (13)	0.039*	
O2W	−0.11083 (13)	0.6067 (3)	0.12508 (14)	0.0416 (5)	
H21	−0.144 (2)	0.595 (5)	0.1692 (14)	0.062*	
H22	−0.143 (2)	0.630 (5)	0.0812 (14)	0.062*	
O30A	−0.2284 (3)	0.5249 (6)	0.2582 (3)	0.0559 (11)	0.77
H31A	−0.2472	0.6044	0.2892	0.084*	0.77
H32A	−0.2001	0.4884	0.3040	0.084*	0.77
O30B	−0.1891 (9)	0.5849 (17)	0.2825 (10)	0.055 (4)	0.23
H31B	−0.2473	0.6043	0.2888	0.083*	0.23
H32B	−0.2002	0.4883	0.3036	0.083*	0.23

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0222 (13)	0.0283 (13)	0.0207 (12)	0.0000 (10)	−0.0009 (10)	0.0008 (9)
C2	0.0206 (12)	0.0278 (13)	0.0173 (11)	−0.0018 (10)	−0.0014 (9)	−0.0005 (9)
C3	0.0288 (13)	0.0256 (13)	0.0211 (12)	−0.0023 (10)	−0.0020 (10)	−0.0018 (9)
C4	0.0286 (13)	0.0251 (13)	0.0183 (11)	0.0003 (10)	0.0005 (10)	0.0010 (10)
Fe1	0.0240 (2)	0.0278 (2)	0.0211 (2)	−0.00038 (14)	−0.00096 (13)	−0.00105 (13)
O1	0.0233 (9)	0.0404 (10)	0.0180 (8)	−0.0054 (8)	−0.0034 (7)	0.0032 (7)
O2	0.0217 (10)	0.0778 (15)	0.0247 (9)	−0.0132 (10)	−0.0012 (7)	0.0072 (10)
O3	0.0265 (9)	0.0387 (11)	0.0190 (9)	−0.0141 (8)	−0.0037 (7)	0.0006 (7)
O4	0.0504 (12)	0.0260 (9)	0.0187 (9)	0.0045 (8)	−0.0066 (8)	−0.0028 (7)
O5	0.0678 (15)	0.0368 (11)	0.0362 (11)	0.0268 (11)	−0.0182 (10)	−0.0093 (9)
O1W	0.0281 (9)	0.0277 (9)	0.0232 (9)	−0.0001 (8)	0.0050 (7)	0.0010 (7)
O2W	0.0231 (10)	0.0722 (15)	0.0293 (10)	−0.0078 (10)	−0.0031 (8)	0.0100 (10)
O30A	0.048 (3)	0.076 (3)	0.043 (2)	0.0182 (19)	0.0119 (17)	0.024 (2)
O30B	0.050 (9)	0.061 (9)	0.054 (9)	0.035 (7)	0.029 (7)	0.025 (7)

Geometric parameters (Å, °)

C1—O2	1.245 (3)	Fe1—O1W	2.2522 (18)
C1—O1	1.262 (3)	O3—H3	0.81 (3)
C1—C2	1.529 (3)	O1W—H11	0.820 (10)
C2—O3	1.430 (3)	O1W—H12	0.809 (10)
C2—C3	1.515 (3)	O2W—H21	0.811 (10)
C2—H2	0.9800	O2W—H22	0.81 (3)
C3—C4	1.516 (3)	O30A—O30B	0.828 (14)
C3—H3A	0.9700	O30A—H31A	0.8441
C3—H3B	0.9700	O30A—H32A	0.8407
C4—O5	1.247 (3)	O30A—H31B	0.8404
C4—O4	1.251 (3)	O30A—H32B	0.8348
Fe1—O5^i	2.118 (2)	O30B—H31A	0.8472
Fe1—O2W	2.1376 (19)	O30B—H32A	0.8736
Fe1—O4^{ii}	2.1448 (17)	O30B—H31B	0.8482
Fe1—O1	2.1728 (18)	O30B—H32B	0.8724
Fe1—O3	2.2304 (18)		
O2—C1—O1	123.9 (2)	C1—O1—Fe1	121.91 (15)
O2—C1—C2	117.6 (2)	C2—O3—Fe1	118.91 (13)
O1—C1—C2	118.5 (2)	C2—O3—H3	114 (2)
O3—C2—C3	110.5 (2)	Fe1—O3—H3	124 (2)
O3—C2—C1	108.14 (18)	C4—O4—Fe1^{iii}	127.20 (16)
C3—C2—C1	110.55 (19)	C4—O5—Fe1^i	146.95 (17)
O3—C2—H2	109.2	Fe1—O1W—H11	119 (2)
C3—C2—H2	109.2	Fe1—O1W—H12	109 (2)
C1—C2—H2	109.2	H11—O1W—H12	109 (2)
C2—C3—C4	113.64 (19)	Fe1—O2W—H21	118 (3)
C2—C3—H3A	108.8	Fe1—O2W—H22	124 (3)

C4—C3—H3A	108.8	H21—O2W—H22	110 (2)
C2—C3—H3B	108.8	O30B—O30A—H31A	60.9
C4—C3—H3B	108.8	O30B—O30A—H32A	63.1
H3A—C3—H3B	107.7	H31A—O30A—H32A	90.0
O5—C4—O4	122.8 (2)	O30B—O30A—H31B	61.1
O5—C4—C3	118.9 (2)	H31A—O30A—H31B	0.4
O4—C4—C3	118.3 (2)	H32A—O30A—H31B	90.4
O5^{i}—Fe1—O2W	92.28 (10)	O30B—O30A—H32B	63.3
O5^{i}—Fe1—O4^{ii}	82.98 (7)	H31A—O30A—H32B	90.2
O2W—Fe1—O4^{ii}	109.38 (8)	H32A—O30A—H32B	0.3
O5^{i}—Fe1—O1	94.01 (9)	H31B—O30A—H32B	90.6
O2W—Fe1—O1	161.71 (7)	O30A—O30B—H31A	60.5
O4^{ii}—Fe1—O1	88.44 (7)	O30A—O30B—H32A	59.1
O5^{i}—Fe1—O3	99.86 (8)	H31A—O30B—H32A	87.6
O2W—Fe1—O3	89.97 (7)	O30A—O30B—H31B	60.2
O4^{ii}—Fe1—O3	160.39 (8)	H31A—O30B—H31B	0.5
O1—Fe1—O3	72.04 (6)	H32A—O30B—H31B	87.7
O5^{i}—Fe1—O1W	170.75 (8)	O30A—O30B—H32B	58.7
O2W—Fe1—O1W	83.78 (8)	H31A—O30B—H32B	87.5
O4^{ii}—Fe1—O1W	90.41 (7)	H32A—O30B—H32B	0.5
O1—Fe1—O1W	92.26 (7)	H31B—O30B—H32B	87.6
O3—Fe1—O1W	88.54 (7)		

Symmetry codes: (i) −x, −y+2, −z; (ii) x, −y+3/2, z+1/2; (iii) x, −y+3/2, z−1/2.

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
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O1W—H12$\cdots$O4^{iv}	0.809 (10)	2.47 (3)	3.067 (3)	131 (3)
O2W—H21$\cdots$O30A	0.811 (10)	1.866 (14)	2.662 (4)	167 (4)
O2W—H21$\cdots$O30B	0.811 (10)	1.785 (18)	2.575 (13)	164 (4)
O2W—H22$\cdots$O2^{vi}	0.81 (3)	1.915 (11)	2.720 (3)	172 (4)
O30A—H31B$\cdots$O1^{vii}	0.84	2.17	2.984 (5)	165
O30A—H32B$\cdots$O1^{viii}	0.83	2.18	2.887 (5)	142

Symmetry codes: (iv) −x, −y+1, −z; (v) −x+1/2, y−1/2, z; (ii) x, −y+3/2, z+1/2; (vi) x−1/2, −y+3/2, −z; (vii) x−1/2, y, −z+1/2; (viii) −x, y−1/2, −z+1/2.

Fig. 1

Fig. 2