

Poly[[diaqua(μ_4 -squarato-*O,O',O'',O'''*)-manganese(II)] 0.93-hydrate]

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

H-atom completeness 69%

Disorder in solvent or counterion

R factor = 0.037

wR factor = 0.112

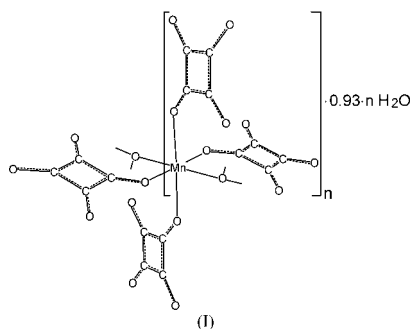
Data-to-parameter ratio = 15.7

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

In the title compound, $\{[\text{Mn}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_2] \cdot 0.93\text{H}_2\text{O}\}_n$, the Mn atoms are each coordinated by four O atoms of two pairs of symmetry-related squarate dianions and two O atoms of two symmetry-related water molecules within slightly distorted octahedra. The water molecules occupy general positions and the two crystallographically independent squarate dianions, as well as the Mn atom, are located in special positions. The squarate dianions and the water molecules are connected *via* O–H...O hydrogen bonding. In the crystal structure, voids are found that are filled with additional, disordered, clathrate water molecules.

Comment

Recently, we have prepared new coordination polymers based of transition metal squarates and aromatic amine ligands, such as 4,4'-bipyridine (Näther *et al.*, 2002a; Greve, 2000) and pyrazine (Greve, 2000; Näther & Jeß, 2001; Näther *et al.*, 2002b). The preparation of these compounds, usually performed under solvothermal conditions, leads sometimes to mixtures of different compounds that must all be identified. During the preparation of poly[[diaqua(μ_2 -squarato-*O,O'*)(μ_2 -4,4'-bipyridine)manganese(II)] hydrate] (Näther *et al.*, 2002a; Greve, 2000), we obtained colourless crystals of a second phase, which was identified as poly[diaqua(μ_4 -squarato-*O,O',O'',O'''*)]manganese(II) hydrate, (I). Until now, only the tetrahydrate *catena*-[tetraqua(μ_2 -squarato-*O,O'*)-manganese(II)] (Weiss, Riegler, Alt *et al.*, 1986) and the dihydrate *catena*-[[tris(μ_4 -squarato)diaquamanganese] acetic acid hydrate] (Weiss, Riegler & Robl, 1986) are known.

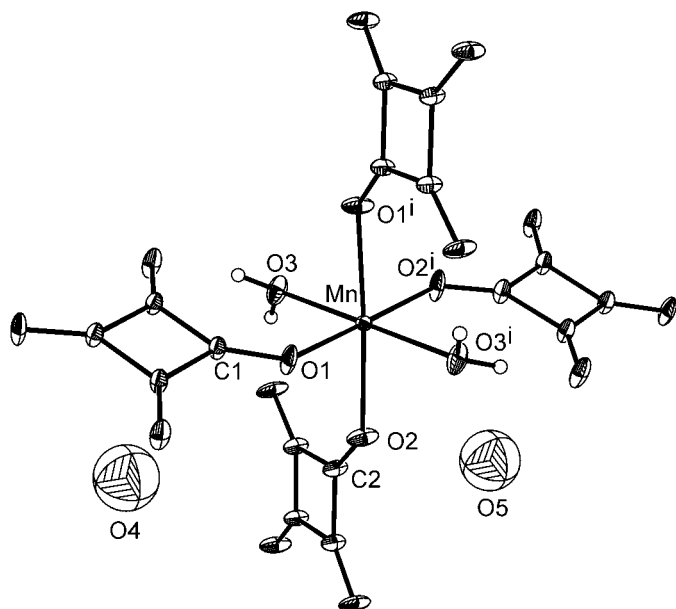


The structure of (I) is isotypic with the previously reported Fe, namely poly[diaqua(μ_4 -squarato-*O,O',O'',O'''*)iron(II)] (Näther *et al.*, 2002c), and Co compounds (Lee *et al.*, 1996). In the crystal structure, the Mn atoms are surrounded by four squarate O atoms and two O atoms of two symmetry-related water molecules within a slightly distorted octahedron. The Mn–O bond lengths are comparable to those retrieved from the Cambridge Structural Database (Cambridge Structural

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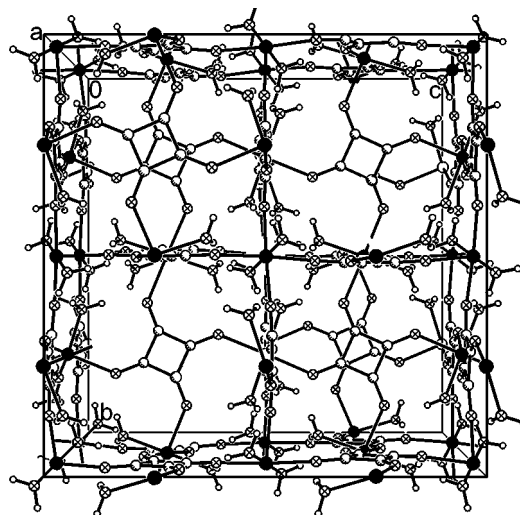

Figure 1

The crystal structure of the title compound, showing the Mn coordination with labelling and with displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $y, x, -z + \frac{1}{2}$].

Database, 2002; Allen & Kennard, 1993). The Mn atom is located on a twofold axis and the water molecules occupy general positions. There are two crystallographically independent squarate dianions in the asymmetric unit. One is located around a fourfold axis and the second around a fourfold rotoinversion axis. The bond lengths and angles of both dianions are similar. The squarate dianions are coordinated by only one O atom to each metal centre and the Mn atoms are positioned in the direction of one of the lone pairs of the squarate O atoms. Each squarate dianion is connected to four Mn atoms, forming a three-dimensional coordination network, which contains cubic voids surrounded by six squarate dianions. The squarate O atoms and the coordinated water molecules are connected *via* O—H...O hydrogen bonds, with bond lengths and angles indicating strong interactions. Within these voids are located some extremely disordered water molecules (see Experimental). This is also found in the isotypic Co compound (Lee *et al.*, 1996) and an indication of clathrate water molecules is also observed in the isotypic Fe compound (Näther *et al.*, 2002c).

Experimental

The title compound was prepared by the reaction of 0.5 mmol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.5 mmol squaric acid and 0.5 mmol 4,4'-bipyridine in 5 ml of water in a teflon-lined steel autoclave at 423 K under hydrothermal conditions. After 5 d, the reaction mixture was cooled to room temperature, filtered, and the resulting product washed with water. The precipitate consisted of a mixture of colourless crystals of the 4,4'-bipyridine compound poly[[diaqua(μ_2 -squarato-*O, O'*)(μ_2 -4,4'-bipyridine)manganese(II)] trihydrate] (Greve, 2000; Näther *et al.*, 2002a) and colourless crystals of the the title compound, (I). The composition of the precipitate was determined by X-ray powder diffraction analysis.


Figure 2

The crystal structure of the title compound, viewed along the crystallographic *a* axis. The disordered water molecules have been omitted for clarity.

Crystal data

$[\text{Mn}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_2] \cdot 0.93\text{H}_2\text{O}$
 $M_r = 219.77$
 Cubic, $Pn\bar{3}n$
 $a = 16.5527(8) \text{ \AA}$
 $V = 4535.3(4) \text{ \AA}^3$
 $Z = 24$
 $D_x = 1.931 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation

Cell parameters from 8000 reflections
 $\theta = 2.5\text{--}28^\circ$
 $\mu = 1.74 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colourless
 $0.15 \times 0.05 \times 0.05 \text{ mm}$

Data collection

Stoe IPDS diffractometer
 φ scans
 28 798 measured reflections
 908 independent reflections
 821 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -21 \rightarrow 21$
 $k = -21 \rightarrow 18$
 $l = -21 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.113$
 $S = 1.18$
 908 reflections
 58 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 5.7874P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn—O3	2.1409 (14)	C1—C1 ⁱ	1.466 (2)
Mn—O1	2.1727 (13)	C2—O2	1.250 (2)
Mn—O2	2.1898 (13)	C2—C2 ⁱⁱ	1.465 (3)
C1—O1	1.248 (2)		
O3—Mn—O3 ⁱⁱⁱ	179.21 (8)	O1—C1—C1 ⁱ	135.93 (19)
O3 ⁱⁱⁱ —Mn—O1	84.40 (5)	O1—C1—C1 ^{iv}	133.91 (19)
O3 ⁱⁱⁱ —Mn—O1 ⁱⁱⁱ	96.17 (5)	C1 ⁱ —C1—C1 ^{iv}	90.0
O1—Mn—O1 ⁱⁱⁱ	89.34 (8)	C1—O1—Mn	134.60 (12)
O3—Mn—O2 ⁱⁱⁱ	86.09 (5)	O2—C2—C2 ^v	136.0 (2)
O3 ⁱⁱⁱ —Mn—O2 ⁱⁱⁱ	93.37 (5)	O2—C2—C2 ^v	134.0 (2)
O1—Mn—O2 ⁱⁱⁱ	176.62 (6)	C2 ⁱⁱ —C2—C2 ^v	89.990 (4)
O1—Mn—O2	88.37 (6)	C2—O2—Mn	136.83 (13)
O2 ⁱⁱⁱ —Mn—O2	94.03 (8)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3–H1 \cdots O1 ⁱ	0.86	1.92	2.7602 (19)	165
O3–H2 \cdots O2 ⁱⁱ	0.86	1.93	2.7742 (19)	166

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

The H atoms of the coordinated water molecules were located in a difference Fourier map and these molecules were refined as rigid groups with idealized O–H bond lengths of 0.86 Å and fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. In the final refinement, significant residual electron-density peaks (maximum 1.59 e Å⁻³) were found in voids in the structure, which should correspond to incorporated clathrate water molecules. Several peaks were found with extremely short intermolecular distances, indicating strong disorder. The distance between the highest peak in the difference map and the next adjacent atom was 3.278 Å. Thermogravimetric experiments show a mass loss which is slightly larger than that expected if only two molecules of water are removed. Therefore, two of these maxima were assigned to water O atoms, which were refined isotropically with variable site-occupation factors and a common displacement parameter. The site-occupation factors refined to 0.48 (2) for O4 and 0.345 (15) for O5. The H atoms of these water molecules could not be located.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program*

Package; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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