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Δ-Aqua-*S*-citrato(2−)manganese(II)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.048
wR factor = 0.094
Data-to-parameter ratio = 12.1

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

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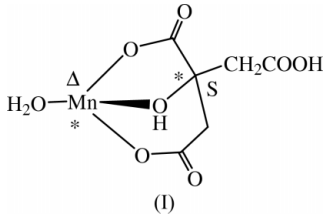
The citrato(2−) ligand in aquacitrato(2−)manganese(II), $[Mn(C_6H_6O_7)(H_2O)]$, chelates the Mn atom through the α-hydroxyl, the α-carboxyl and one β-carboxyl O atom, while the other β-carboxylic acid group remains uncoordinated. Each O atom of the α-carboxyl groups is bonded to an adjacent Mn atom, leading to octahedral Mn and a helical chain. Neighboring chains are consolidated into a tightly held crystal structure by hydrogen bonds.

Comment

The chemistry of metal derivatives of citric acid is of interest owing to the importance of this acid in physiological processes (Glusker, 1980; Mayers *et al.*, 2002). An early structural study of a 3:2 Mn derivative of citric acid had documented a compound having the formulation $[Mn(OH_2)_6][Mn(C_6H_5O_7)(H_2O)]_2\cdot 2H_2O$ (Carrell & Glusker, 1973; Glusker & Carrell, 1973). A more recent study reported $[NH_4]_4[Mn(C_6H_5O_7)_2]$ (Matzapetakis *et al.*, 2000), which is obtained from a neutral solution containing a 1:2 molar ratio of Mn^{2+} and citric acid. Moreover, a solid 1:1 complex formulated as $[Mn(C_6H_6O_7)(H_2O)]$ has been characterized with IR spectra and elemental anaylses (Fujita, 1982; Kemmett *et al.*, 2001). In our work, acidic conditions yielded a 1:1 Mn-citrate complex as a monohydrate, with a free β-carboxylic acid group (Fig. 1 and Table 1). The citrate dianion chelates, in tridentate mode, to the water-coordinated Mn atom through two carboxyl and one α-hydroxyl O atoms. The bonded O atom of the α-carboxyl group is further coordinated to an adjacent Mn atom [Mn—O^{i} 2.290 (3) Å; symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$], and the other O atom of this carboxyl group is also bonded strongly to another Mn atom [Mn—O^{ii} 2.142 (3) Å; symmetry code: (ii) $1+x, y, z$]. The Mn atom thereby exists in an octahedral coordination geometry. Adjacent molecules are linked by a screw axis, to form a helical chain running along the *a* axis of the crystal (Fig. 2). Neighboring chains are consolidated into a tightly held chain structure by hydrogen bonds (Table 2).



(I)

Experimental

Manganese dichloride (0.99 g, 5 mol) and citric acid monohydrate (2.10 g, 10 mmol) were dissolved in water (10 ml). The pH of the

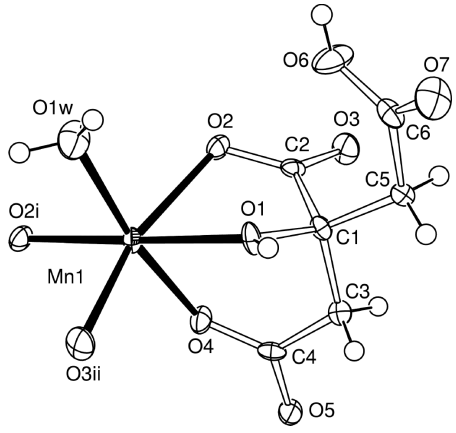


Figure 1
*ORTEP*II (Johnson, 1976) plot of aquacitrato(2−)manganese, with ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ (ii) $1+x, y, z$;.]

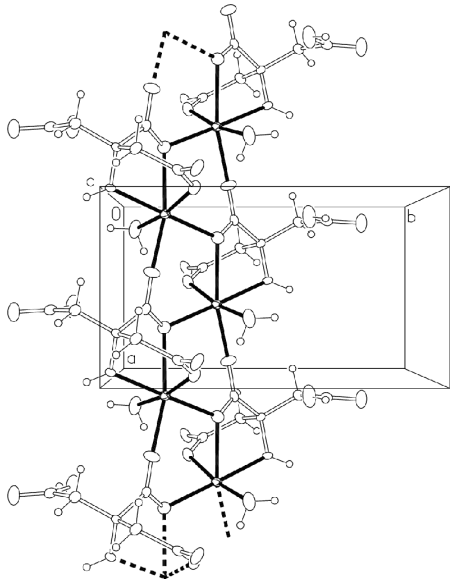


Figure 2
*ORTEP*II (Johnson, 1976) plot, depicting the helical chain propagating along the *a* axis.

solution was adjusted to 1.5–3.0 by the addition of aqueous ammonia. The mixture was warmed and then filtered. The solution was left in a refrigerator for several days. Colorless crystals of the compound were obtained in 90% yield. Elemental analysis. Found (calculated) for $C_6H_8O_8Mn$ (%): C 27.1 (27.4), H 2.8 (3.1). IR (KBr): 3481, 3397, 2974, 2292, 2618, 2531, 1732, 1594, 1546, 1475, 1417, 1395, 1323, 1284, 1260, 1153, 1072, 890. 581, 540 cm^{-1}.

Crystal data

$[Mn(C_6H_6O_7)(H_2O)]$
M_r = 263.06
Orthorhombic, $P2_12_12_1$
a = 6.030 (1) Å
b = 10.467 (1) Å
c = 13.568 (1) Å
V = 856.4 (2) Å^3
Z = 4
D_x = 2.040 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2130 reflections
θ = 2.5–28.2°
μ = 1.57 mm^{-1}
T = 298 (2) K
Plate, colorless
0.29 × 0.09 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.662, T_{max} = 0.889
5277 measured reflections
1936 independent reflections
1914 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 28.2°
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.094
wR = 0.048
S = 1.21
1936 reflections
160 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 1.1167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.011
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Absolute structure: Flack & Schwarzenbach (1988), 759 Friedel pairs
Flack parameter = 0.05 (3)

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.139 (3)	Mn1—O3^{ii}	2.140 (4)
Mn1—O2	2.292 (3)	Mn1—O4	2.195 (3)
Mn1—O2^{i}	2.142 (3)	Mn1—O1*w*	2.166 (3)
O1—Mn1—O2	72.4 (1)	O3^{ii}—Mn1—O2	163.6 (1)
O1—Mn1—O2^{i}	178.4 (1)	O3^{ii}—Mn1—O2^{i}	89.9 (1)
O1—Mn1—O3^{ii}	91.6 (1)	O3^{ii}—Mn1—O4	95.9 (1)
O1—Mn1—O4	83.5 (1)	O3^{ii}—Mn1—O1*w*	92.0 (1)
O1—Mn1—O1*w*	92.4 (1)	O4—Mn1—O2	79.2 (1)
O2^{i}—Mn1—O2	106.15 (9)	O1*w*—Mn1—O2	92.2 (1)
O2^{i}—Mn1—O1*w*	87.1 (1)	O1*w*—Mn1—O4	171.2 (1)
O2^{i}—Mn1—O4	96.9 (1)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*o*···O5^{iii}	0.85	1.75	2.594 (4)	178
O6—H6*o*···O5^{iv}	0.85	1.81	2.652 (4)	173
O1*w*—H1*w*2···O4^{i}	0.85	2.10	2.871 (4)	152
O1*w*—H1*w*1···O7^{v}	0.85	1.90	2.737 (4)	172

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

H atoms of the hydroxyl group and the water molecule and C-bound H atoms were located and refined, subject to O—H = 0.85 (1) Å, C—H = 0.85 (1) Å and H···H = 1.39 (1) Å, and their displacement parameters were set to 1.2 times those of their parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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