

Structure of Manganese(II) (+)-1-Malate Trihydrate and Comparison with Other Malates

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(Received 9 April 1980; accepted 1 September 1980)

Abstract. $\text{Mn}(\text{C}_4\text{H}_4\text{O}_5)\cdot 3\text{H}_2\text{O}$, $P2_12_12_1$, $a = 9.152$ (1), $b = 9.357$ (3), $c = 10.448$ (2) Å, $Z = 4$, $d(\text{calc}) = 1.790$ Mg m $^{-3}$; $R = 0.033$ for 1241 observed reflections. The Mn^{2+} ion is coordinated by six O atoms arranged in an octahedron. The conformation of the $^-\text{OOC}-\text{C}-\text{COO}^-$ chain is *trans* and differs from that of other malates, which have a *gauche* conformation. A comparison with other malates shows that some important conformational features of the anion are lattice dependent.

Introduction. Crystals of $\text{Mn}(\text{C}_4\text{H}_4\text{O}_5)\cdot 3\text{H}_2\text{O}$ were grown by slow evaporation of an aqueous solution at room temperature. Reflections up to $\theta = 30^\circ$ were measured on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo radiation. An ω/θ scan with a speed ratio of 2:1 was applied. The scan angle was given by $(0.7 + 0.35 \tan \theta)^\circ$ and the aperture of the detection unit was set to $(1.0 + 1.0 \tan \theta)$ mm.

From the systematic extinctions the space group $P2_12_12_1$ was inferred. The reflections were corrected for absorption effects (crystal size $0.2 \times 0.2 \times 0.01$ mm, $\mu = 1.57$ mm $^{-1}$) by an empirical method in which a Gaussian grid is superposed on the crystal (Coppens, 1969). The structure was solved using heavy-atom Fourier procedures. From a total of 1534 reflections, 1241 with $I > 2\sigma(I)$ were used in the refinement, employing the Gauss–Seidel block method (Sparks, 1974), in which each reflection was given a weight based on counting statistics. During the refinement the Debye–Waller temperature parameter of the H atoms was kept fixed at 2.0 Å 2 ($B_{\text{Wilson}} = 1.9$ Å 2). After refinement of the isotropic extinction parameter (Zachariasen, 1963) to $r = 0.19 \times 10^{-5}$ mm the R factor converged to 0.033 $\{R = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ where the summations extend over observed reflections only}. The maximum noise level in the final difference Fourier map was 0.3 e Å $^{-3}$. The refined parameters are listed in Table 1.*

The absolute configuration of the compound was tested and proved to be in accordance with the (+) configuration of the malate ion.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35622 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The Mn^{2+} ion is coordinated by six O atoms forming a slightly distorted octahedron (Table 2 and Fig. 1). Two O atoms, O(1) and O(5), are donated by one malate ion, and two other O atoms are donated by two other malate ions, which are symmetry related. The remainder of the coordination is formed by two water molecules.

A survey of the crystal structure is given in Fig. 1. The packing of the title compound is largely dominated by Coulomb interactions with extra stabilization owing to hydrogen bridges. Short $\text{OH}\cdots\text{O}$ interactions are presented in Table 3.

Groth (1910) reported the existence of two forms of manganese(II) 1-malate: a monoclinic trihydrate and an orthorhombic tetrahydrate. Note that we found an orthorhombic form with three water molecules of crystallization. However, Groth's statement that the monoclinic form is a trihydrate is in all likelihood correct since the reported axial ratios are practically identical to those of the isomorphous zinc 1-malate

Table 1. Refined positional parameters of the title compound

Estimated standard deviations are in parentheses. Isotropic temperature parameters are calculated from the anisotropic thermal ellipsoids assuming equal volume for the 50% probability region. None of the anisotropic values was physically unacceptable.

	x	y	z	B_{iso} (Å 2)
Mn	-0.26913 (6)	-0.15854 (7)	0.11084 (5)	1.75
O(1)	-0.2661 (3)	0.0336 (3)	-0.0044 (2)	2.12
O(2)	-0.2182 (4)	0.2665 (3)	-0.0030 (3)	2.78
O(3)	-0.2650 (3)	0.2742 (3)	0.4399 (2)	1.85
O(4)	-0.4997 (3)	0.3267 (4)	0.4294 (2)	2.10
O(5)	-0.2946 (3)	0.0187 (3)	0.2437 (2)	2.06
O(W1)	-0.2695 (3)	-0.3286 (3)	0.2478 (2)	2.86
O(W2)	-0.0319 (3)	-0.1250 (4)	0.1434 (3)	3.34
O(W3)	-0.0827 (3)	0.4791 (3)	0.1330 (3)	2.64
C(1)	-0.2470 (4)	0.1518 (5)	0.0494 (3)	1.79
C(2)	-0.2629 (4)	0.1569 (5)	0.1964 (3)	1.76
C(3)	-0.3793 (5)	0.2631 (5)	0.2353 (4)	2.00
C(4)	-0.3827 (4)	0.2884 (4)	0.3790 (4)	1.76
H1(C2)	-0.168 (4)	0.195 (4)	0.230 (4)	2.0
H1(O5)	-0.304 (4)	0.012 (4)	0.324 (3)	2.0
H1(C3)	-0.367 (4)	0.351 (4)	0.199 (3)	2.0
H2(C3)	-0.472 (4)	0.227 (4)	0.216 (3)	2.0
H1(W1)	-0.252 (4)	-0.311 (4)	0.326 (3)	2.0
H2(W1)	-0.210 (4)	-0.390 (3)	0.220 (3)	2.0
H1(W2)	-0.022 (4)	-0.090 (4)	0.215 (3)	2.0
H2(W2)	0.034 (4)	-0.180 (4)	0.107 (3)	2.0
H1(W3)	-0.048 (4)	0.517 (4)	0.082 (3)	2.0
H2(W3)	-0.122 (4)	0.407 (4)	0.082 (3)	2.0

Table 2. The coordination of Mn^{2+} ; the estimated standard deviations are 0.002 Å in the distances and 0.1° in the angles

O in molecule at			
Mn—O(1)	1	2.164 Å	
Mn—O(4)	3	2.162	
Mn—O(3)	2	2.111	
Mn—O(5)	1	2.175	
Mn—O(W1)	1	2.140	
Mn—O(W2)	1	2.220	
O(A) at	O(B) at	O(A)—Mn—O(B)	
1	1	O(1)—Mn—O(5)	73.9°
1	2	O(1)—Mn—O(4)	87.3
1	3	O(1)—Mn—O(4)	87.6
1	1	O(1)—Mn—O(W1)	171.8
1	1	O(1)—Mn—O(W2)	87.5
1	2	O(5)—Mn—O(3)	161.1
1	3	O(5)—Mn—O(4)	93.9
1	1	O(5)—Mn—O(W1)	98.1
1	1	O(5)—Mn—O(W2)	84.2
2	3	O(3)—Mn—O(4)	87.0
2	1	O(3)—Mn—O(W1)	100.7
2	1	O(3)—Mn—O(W2)	93.3
3	1	O(4)—Mn—O(W1)	94.7
3	1	O(4)—Mn—O(W2)	175.0
1	1	O(W1)—Mn—O(W2)	90.2

Symmetry code: (1) x, y, z ; (2) $-\frac{1}{2} - x, \bar{y}, -\frac{1}{2} + z$; (3) $-1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

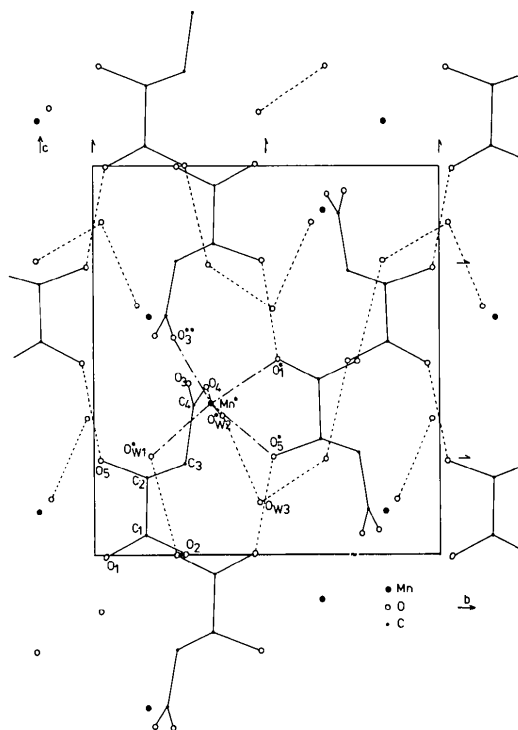


Fig. 1. The crystal structure projected onto the bc plane, showing the coordination of the Mn^{2+} ion, the hydrogen-bonding scheme and the numbering of the atoms. Atoms designated with an asterisk are at $-x, \frac{1}{2} + y, \frac{1}{2} - z$ with respect to the positions given in Table 1; those with a double asterisk are at $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

Table 3. Short $OH \cdots O$ interactions in $Mn(C_4H_4O_5) \cdot 3H_2O$

Donor D	Acceptor A	A at	D—H (Å)	D...A (Å)	D—H...A (°)	A—H (Å)
O(5)—H	O(1)	2	0.85	2.734	154	1.95
O(W1)—H(1)	O(2)	2	0.85	2.670	161	1.85
O(W1)—H(2)	O(W3)	3	0.84	2.757	172	1.91
O(W2)—H(1)	O(W3)	4	0.82	2.740	157	1.96
O(W2)—H(2)	O(4)	5	0.88	2.940	127	2.33
O(W2)—H(2)	O(3)	4	0.88	3.005	150	2.22
O(W3)—H(1)	O(1)	6	0.72	3.195	124	2.74
O(W3)—H(1)	O(4)	7	0.72	2.897	163	2.21
O(W3)—H(2)	O(2)	1	0.93	2.741	173	1.81
e.s.d.			0.03	0.003	2	0.03

Symmetry code: (1) x, y, z ; (2) $-\frac{1}{2} - x, -y, \frac{1}{2} + z$; (3) $x, y - 1, z$; (4) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (5) $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$; (6) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (7) $-\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$.

(Lenstra & Van de Mierop, 1976) and cobalt(II) 1-malate (Kryger & Rasmussen, 1972), which are known to be trihydrates. Therefore, manganese(II) 1-malate is an example of a compound crystallizing in two different crystal packing arrangements with identical stoichiometry.

The most outstanding difference between the title compound and the monoclinic trihydrates is the conformation of the $^-OOC-C-C-COO^-$ moiety, which is *trans* in the title compound and *gauche* in the other cases. This is in direct contrast to the findings of Kanters, Kroon, Peerdeman & Schoone (1967). They claim that the conformation of (di)carboxylic acids, α -hydroxycarboxylic acids and their salts is independent of the cation and of the type of crystal packing.

The influence of lattice interactions on the geometry of the organic anion can be further studied by comparing the malate moieties in $Mn(C_4H_4O_5) \cdot 3H_2O$ with those of $Co(C_4H_4O_5) \cdot 3H_2O$ (Kryger & Rasmussen, 1972), $Zn(C_4H_4O_5) \cdot 3H_2O$ (Lenstra & Van de Mierop, 1976), $Mg(C_4H_4O_5) \cdot 5H_2O$ (Van Havere & Lenstra, 1980b) and $Ca(C_4H_4O_5) \cdot 2H_2O$ (Bränden & Söderberg, 1966). Salts of malic acid are excellent test cases for this purpose. First, the malate anion contains all the functional groups on which Kanters *et al.* performed their statistical survey. Second, the above salts show a wide variety of packing types, *e.g.* in hydrogen-bonding schemes and the way in which the malate ions are involved in the cation coordination. Bond distances, valence angles and torsion angles are collected in Tables 4, 5 and 6, respectively. From a statistical analysis (the tests were performed at the significance level $\alpha = 0.05$) we conclude:

(1) The malate moiety does *not* show conformational stability under various packing conditions. In the Mn salt we find an antiperiplanar (= *trans*) conformation for the $OOC-C-C-COO$ chain, in contrast to the synclinal (= *gauche*) form observed in the other salts. Other torsion angles also show large spread.

(2) Bond distances show no significant deviations from the mean values, *i.e.* they are lattice independent.

Table 4. Bond lengths (Å) of Mn malate and some other malates, with *e.s.d.*'s in parentheses

	Mn malate	Co malate	Zn malate	Mg malate	Ca malate	Mean value	Standard deviation of mean
C(1)—C(2)	1.544 (3)	1.534 (6)	1.531 (6)	1.527 (3)	1.529 (13)	1.533	0.007
C(2)—C(3)	1.512 (4)	1.517 (5)	1.527 (6)	1.517 (3)	1.503 (17)	1.515	0.009
C(3)—C(4)	1.521 (4)	1.521 (5)	1.516 (6)	1.519 (3)	1.512 (10)	1.518	0.004
O(1)—C(1)	1.253 (3)	1.262 (5)	1.266 (6)	1.263 (2)	1.243 (11)	1.257	0.009
O(2)—C(1)	1.233 (3)	1.237 (5)	1.241 (4)	1.246 (2)	1.256 (10)	1.243	0.009
O(3)—C(4)	1.258 (3)	1.251 (5)	1.255 (6)	1.250 (2)	1.251 (13)	1.253	0.003
O(4)—C(4)	1.246 (3)	1.257 (5)	1.283 (6)	1.253 (2)	1.241 (12)	1.256	0.016
O(5)—C(2)	1.414 (3)	1.435 (5)	1.436 (6)	1.434 (2)	1.434 (10)	1.431	0.009

Table 5. Valence angles (°) of Mn malate and some other malates, with *e.s.d.*'s in parentheses

	Mn malate	Co malate	Zn malate	Mg malate	Ca malate	Mean value	Standard deviation of mean
O(1)—C(1)—O(2)	126.8 (2)	124.4 (3)	123.9 (3)	124.9 (2)	124.8 (9)	125.0	1.1
O(1)—C(1)—C(2)	117.4 (3)	119.2 (3)	117.2 (3)	116.9 (2)	118.3 (7)	117.8	0.9
O(2)—C(1)—C(2)	115.8 (3)	116.4 (3)	118.9 (3)	118.1 (2)	116.9 (8)	117.2	1.3
C(1)—C(2)—C(3)	110.7 (2)	110.9 (3)	111.2 (3)	114.2 (2)	113.4 (8)	112.1	1.6
C(1)—C(2)—O(5)	109.8 (2)	107.6 (3)	107.2 (3)	107.7 (2)	111.1 (8)	108.7	1.7
O(5)—C(2)—C(3)	111.2 (2)	111.4 (3)	112.0 (3)	112.6 (2)	109.7 (7)	111.4	1.1
C(2)—C(3)—C(4)	112.4 (2)	117.8 (3)	116.4 (3)	116.5 (2)	116.5 (8)	115.9	2.0
O(3)—C(4)—O(4)	123.5 (2)	123.0 (3)	122.8 (3)	124.4 (2)	120.5 (9)	122.8	1.4
O(3)—C(4)—C(3)	117.8 (2)	115.6 (3)	114.7 (3)	116.5 (2)	118.6 (9)	116.6	1.6
O(4)—C(4)—C(3)	118.7 (2)	121.4 (3)	122.6 (3)	119.1 (2)	120.9 (7)	120.6	1.5

Table 6. Torsion angles (°) of Mn malate and some other malates, with *e.s.d.*'s in parentheses

	Mn (+)-1-malate	Co (-)-1-malate	Zn (-)-1-malate	Mg (+)-1-malate	Ca (-)-1-malate
O(1)—C(1)—C(2)—C(3)	-121.9 (4)	+94.8 (5)	+95.5 (5)	-128.7 (4)	+108.1 (10)
O(1)—C(1)—C(2)—O(5)	+1.3 (4)	-26.5 (5)	-25.8 (5)	-2.9 (4)	-16.0 (10)
C(1)—C(2)—C(3)—C(4)	-171.2 (4)	-64.9 (5)	+64.4 (5)	+68.8 (4)	-69.6 (10)
O(3)—C(4)—C(3)—C(2)	+29.2 (4)	-12.8 (5)	-13.0 (5)	-30.3 (4)	-0.3 (10)

Furthermore, Kanters *et al.* (1967) had claimed that in the COO⁻ groups of α -hydroxy acids the C—O bonded to the cation is shorter than the other C—O bond lengths. In the above-cited malates we observe an average of 1.256 (11) Å for the C—O involved in the cation coordination and an average of 1.245 (11) Å for those not involved. In fact, our data do not allow us to reject the hypothesis that all C—O bonds of the COO⁻ groups are equal.

However, C(1)—C(2) is significantly longer than C(2)—C(3) = C(3)—C(4). A similar conclusion could be drawn from an analysis of hydrogen malates (Van Havere & Lenstra, 1980a).

(3) Except for the angle C(2)—C(3)—C(4) in Mn 1-malate, the valence angles do not deviate significantly from their mean values and therefore they can be considered as lattice independent.

We speculate that a small value for the angle C(2)—C(3)—C(4) is related to an antiperiplanar (=trans) conformation of the anion, since we note a similar phenomenon in hydrogen malates. In those hydrogen malates that are in the trans form, the angle C(2)—C(3)—C(4) is also smaller than the corresponding angle in Li hydrogen 1-malate, *i.e.* in the synclinal (=gauche) form (Van Havere & Lenstra, 1980a).

One of the authors (WVH) thanks the Belgian Organization IWONL for a predoctoral fellowship.

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