Acta Cryst. (1983). C**39**, 39–41

Structure of Manganese(II) Maleate Trihydrate, $[Mn(C_4H_2O_4)].3H_2O$ (I), and Reinvestigation of the Structure of Manganese(II) Hydrogen Maleate Tetrahydrate, $[Mn(C_4H_3O_4)_2].4H_2O$ (II)

By T. Lis

Institute of Chemistry, The University, 50–383 *Wroclaw, Poland*

(*Received* 14 *June* 1982; *accepted* 23 *July* 1982)

Abstract. (I): $M_r = 223{\cdot}0$, monoclinic, Cc, $a = 8{\cdot}260\,(7)$, $b = 13{\cdot}341\,(13)$, $c = 7{\cdot}731\,(5)$ Å, $\beta = 115{\cdot}35\,(6)^\circ$, $V = 769{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}89$, $D_x = 1{\cdot}92$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = 1·8 mm^{-1}, final $R = 0{\cdot}031$ and $R_w = 0{\cdot}041$ for 1517 non-zero reflexions. (II): $M_r = 357{\cdot}1$, triclinic, $P\bar{1}$, $a = 7{\cdot}374\,(3)$, $b = 9{\cdot}755\,(4)$, $c = 5{\cdot}325\,(4)$ Å, $\alpha = 106{\cdot}65\,(4)$, $\beta = 86{\cdot}68\,(4)$, $\gamma = 115{\cdot}44\,(4)^\circ$, $V = 330{\cdot}5$ Å^3, $Z = 1$, $D_m = 1{\cdot}78$, $D_x = 1{\cdot}79$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·12 mm^{-1}, final $R = 0{\cdot}035$ and $R_w = 0{\cdot}043$ for 1254 non-zero reflexions. In both crystalline compounds the Mn atoms have distorted octahedral coordination. In contrast to an almost planar hydrogen maleate residue the carboxylate groups of the maleate anion are strongly twisted out of the plane through the C-atom chain.

Introduction. This investigation was undertaken as part of our study on the stereochemistry of Mn$^{\rm II}$ carboxylate salts.

Experimental. A mixture of crystals of salts (I) and (II) obtained when manganese(II) carbonate was dissolved in an aqueous solution of maleic acid and the solution was left to evaporate; pure compound (I) prepared by addition of excess manganese(II) carbonate to aqueous solution of maleic acid and boiling until pH increased to ~7, unreacted manganese carbonate was then removed and the solution left to evaporate when nearly colorless crystals grew as monoclinic plates; Weissenberg photographs showed the space group to be Cc or $C2/c$; compound (II) has been studied by Gupta & Mahanta (1978), who solved the crystal structure by photographic methods ($R = 0{\cdot}097$). For (I) and (II): Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation and graphite monochromator for lattice-parameter and intensity measurements; 2θ–ω scan technique, $T = 299 \pm 2$K; a specimen 0·4 × 0·4 × 0·35 mm of (I) was cut from a large crystal, for (II) a crystal 0·2 × 0·2 × 0·35 mm was selected; for (I) 1517 intensities measured in the range $10 \le \theta \le 35^\circ$, for (II) 1254 in the range $5 \le \theta \le 30^\circ$; intensities measured only for reflexions above background; for both compounds empirical absorption corrections made from φ-scan data; all calculations performed on a NOVA 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of the anomalous dispersion included for Mn and O atoms. In (I) Mn atoms found from a Patterson map and noncentrosymmetric Cc assumed, x and z coordinates of Mn held invariant to fix origin, all other atoms from difference syntheses, full-matrix least-squares refinement, anisotropic thermal parameters (positional and isotropic temperature parameters for H atoms fixed), $R = 0{\cdot}031$, $R_w = 0{\cdot}041$ (refinement of the parameters for the inverted structure gave $R = 0{\cdot}035$, $R_w = 0{\cdot}048$);* final difference synthesis featureless; $F(000) = 452$. For (II), unit-cell parameters obtained by least-squares refinement of 15 accurately centered reflections: $a = 7{\cdot}374\,(3)$, $b = 9{\cdot}682\,(4)$, $c = 5{\cdot}325\,(4)$ Å, $\alpha = 105{\cdot}15\,(4)$, $\beta = 93{\cdot}32\,(4)$, $\gamma = 113{\cdot}64\,(4)^\circ$; these parameters are rather similar to those reported by Gupta & Mahanta (1978): $a = 7{\cdot}35\,(2)$, $b = 9{\cdot}77\,(2)$, $c = 5{\cdot}18\,(1)$ Å, $\alpha = 106{\cdot}9\,(2)$, $\beta = 94{\cdot}6\,(2)$, $\gamma = 116{\cdot}6\,(3)^\circ$, intensity measurements were made on the basis of the unit-cell parameters determined by us, and the structure was then refined with the known atomic coordinates (Gupta & Mahanta, 1978) as initial parameters; a high R value was obtained and the refinement failed. After detailed investigation of solutions from centering data, an alternative unit cell was proposed (see *Abstract*) which differs strongly from the Gupta & Mahanta cell in β-angle value only; all hkl were then transformed into the new values by matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & -1\,; \\ 0 & 0 & 1 \end{pmatrix}$$

isotropic refinement gave $R = 0{\cdot}09$ suggesting that these unit-cell parameters should be assumed; after

---

* Lists of structure factors, anisotropic thermal parameters and least-squares-plane data for (I) and (II) and H-atom parameters for (I) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38094 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/010039-03$01.50

anisotropic refinement of non-H atoms, all H-atom positions were found from a difference synthesis; these positions were essentially similar to those postulated geometrically by Gupta & Mahanta (1978); further refinement with isotropic thermal factors for H atoms gave $R = 0{\cdot}035$, $R_w = 0{\cdot}043$; $F(000) = 183$.

Discussion. Final atomic parameters are in Tables 1 and 2, hydrogen-bonding data and bond distances and angles in Tables 3 and 4, and views of the structures down **c** with the atom numbering are in Figs. 1 and 2, for (I) and (II) respectively. In crystals of (I) the Mn atoms are octahedrally coordinated by four carboxylate O atoms from three different maleate ions and by two *cis* water O atoms. All four O atoms of a maleate ligand participate in binding Mn^{2+} ions. Thus, each maleate ligand is coordinated to three different Mn atoms (Fig. 1), forming an extensive net. In addition there is a network of hydrogen bonds utilizing the uncoordinated water molecule $H_2O(7)$. Five out of six H atoms from three different water molecules are involved in hydrogen bonding (Table 3).

Table 1. *The final atom coordinates and equivalent isotropic thermal parameters of* (I)

$B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq}(Å^2)
Mn	0	0·14331 (2)	0·25	1·18 (1)
O(1)	−0·1685 (4)	−0·1234 (2)	−0·0914 (4)	1·75 (12)
O(2)	−0·0368 (4)	−0·0079 (2)	0·1319 (5)	2·28 (15)
O(3)	−0·2353 (4)	0·1756 (2)	−0·0090 (4)	1·90 (13)
O(4)	−0·5208 (4)	0·1984 (2)	−0·2008 (4)	1·75 (12)
O(5)	0·2163 (4)	0·0895 (2)	0·5121 (4)	1·90 (13)
O(6)	0·1856 (5)	0·1634 (4)	0·1213 (5)	3·23 (20)
O(7)	0·5344 (4)	0·2473 (3)	0·2575 (5)	2·60 (16)
C(1)	−0·1727 (4)	−0·0541 (2)	0·0188 (4)	1·34 (13)
C(2)	−0·3519 (4)	−0·0361 (2)	0·0170 (5)	1·60 (14)
C(3)	−0·4475 (4)	0·0483 (2)	−0·0276 (5)	1·61 (14)
C(4)	−0·3931 (4)	0·1468 (2)	−0·0803 (4)	1·30 (13)

Table 2. *The final atom coordinates and isotropic thermal parameters of* (II)

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq} or B(Å^2)
Mn	0	0	0	1·85 (4)
O(1)	0·1495 (4)	0·2089 (3)	−0·1496 (4)	2·39 (13)
O(2)	0·1188 (4)	0·3845 (3)	0·1950 (4)	3·13 (15)
O(3)	0·2121 (4)	0·6662 (3)	0·3398 (4)	3·33 (16)
O(4)	0·4013 (4)	0·8741 (3)	0·2084 (5)	3·17 (16)
O(5)	0·2353 (4)	0·0994 (3)	0·3235 (4)	2·47 (14)
O(6)	0·1940 (4)	−0·0805 (3)	−0·2455 (5)	2·59 (15)
C(1)	0·1784 (4)	0·3486 (3)	−0·0306 (5)	1·95 (16)
C(2)	0·2891 (5)	0·4710 (4)	−0·1656 (5)	2·39 (18)
C(3)	0·3512 (5)	0·6283 (4)	−0·0810 (6)	2·40 (18)
C(4)	0·3225 (4)	0·7300 (3)	0·1702 (6)	2·16 (17)
H(2)	0·332 (7)	0·430 (5)	−0·324 (8)	5·3 (10)
H(3)	0·420 (6)	0·680 (4)	−0·186 (7)	3·3 (7)
H(32)	0·139 (9)	0·513 (8)	0·264 (10)	10·2 (16)
H(51)	0·223 (6)	0·140 (5)	0·490 (8)	4·4 (9)
H(52)	0·276 (6)	0·042 (5)	0·320 (8)	4·1 (10)
H(61)	0·335 (9)	−0·022 (6)	−0·210 (9)	7·3 (13)
H(62)	0·186 (8)	−0·150 (6)	−0·341 (9)	5·8 (12)

Table 3. *Bond lengths* (Å) *and angles* (°) *and* H-*bonding data for* (I)

Mn—O(1^{i})	2·230 (3)	Mn—O(2)	2·181 (3)
Mn—O(3)	2·154 (3)	Mn—O(4^{ii})	2·165 (2)
Mn—O(5)	2·171 (3)	Mn—O(6)	2·172 (4)
C(1)—O(1)	1·268 (4)	C(1)—O(2)	1·250 (4)
C(4)—O(3)	1·239 (4)	C(4)—O(4)	1·270 (4)
C(1)—C(2)	1·494 (5)	C(3)—C(4)	1·501 (4)
C(2)—C(3)	1·334 (4)		
O(1^{i})—Mn—O(2)	96·4 (2)	O(1^{i})—Mn—O(3)	90·4 (2)
O(1^{i})—Mn—O(4^{ii})	84·5 (2)	O(1^{i})—Mn—O(5)	84·6 (2)
O(1^{i})—Mn—O(6)	174·7 (2)	O(2)—Mn—O(3)	83·5 (2)
O(2)—Mn—O(4^{ii})	165·5 (2)	O(2)—Mn—O(5)	89·8 (2)
O(2)—Mn—O(6)	85·5 (2)	O(3)—Mn—O(4^{ii})	82·0 (2)
O(3)—Mn—O(5)	171·2 (2)	O(3)—Mn—O(6)	94·7 (2)
O(4^{ii})—Mn—O(5)	104·7 (2)	O(4^{ii})—Mn—O(6)	94·9 (2)
O(5)—Mn—O(6)	90·5 (2)		
Mn^{iii}—O(1)—C(1)	131·2 (3)	Mn—O(2)—C(1)	132·2 (3)
Mn—O(3)—C(4)	135·3 (3)	Mn^{iv}—O(4)—C(4)	123·6 (3)
O(1)—C(1)—O(2)	123·7 (3)	O(3)—C(4)—O(4)	123·0 (3)
O(1)—C(1)—C(2)	115·0 (3)	O(3)—C(4)—C(3)	122·1 (3)
O(2)—C(1)—C(2)	121·1 (3)	O(4)—C(4)—C(3)	115·0 (3)
C(1)—C(2)—C(3)	127·8 (3)	C(4)—C(3)—C(2)	126·6 (3)

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

H-bond distances (Å) and angles (°)

O—H···O	O···O	O—H	H···O	∠O—H···O
O(5)—H(51)···O(4^{i})	2·762 (4)	0·83	1·98	158
O(5)—H(52)···O(2^{ii})	2·841 (4)	1·13	1·77	156
O(6)—H(61)···O(7^{iii})	2·807 (5)	0·97	1·86	165
O(7)—H(71)···O(1^{iv})	2·768 (4)	0·79	2·02	157
O(7)—H(72)···O(6)	2·840 (5)	1·07	2·02	131

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

Table 4. *Bond lengths* (Å) *and angles* (°) *and* H-*bonding data for* (II)

Mn—O(1)	2·214 (2)	Mn—O(5)	2·205 (2)
Mn—O(6)	2·128 (3)	C(2)—C(3)	1·338 (4)
C(1)—C(2)	1·482 (4)	C(3)—C(4)	1·485 (4)
C(1)—O(1)	1·256 (3)	C(4)—O(4)	1·225 (3)
C(1)—O(2)	1·261 (3)	C(4)—O(3)	1·291 (3)
C(2)—H(2)	0·93 (5)	C(3)—H(3)	0·86 (4)
O(1)—Mn—O(5)	92·5 (1)	O(1)—Mn—O(6)	83·0 (1)
O(5)—Mn—O(6)	87·3 (1)	C(1)—O(1)—Mn	126·3 (2)
O(1)—C(1)—O(2)	121·9 (3)	O(4)—C(4)—O(3)	121·4 (3)
O(1)—C(1)—C(2)	117·0 (3)	O(4)—C(4)—C(3)	118·6 (3)
O(2)—C(1)—C(2)	121·1 (3)	O(3)—C(4)—C(3)	120·0 (3)
C(1)—C(2)—C(3)	129·9 (3)	C(4)—C(3)—C(2)	130·4 (3)

H-bond distances (Å) and angles (°)

O—H···O	O···O	O—H	H···O	∠O—H···O
O(3)—H(32)···O(2)	2·417 (3)	1·29 (7)	1·15 (7)	165 (7)
O(5)—H(51)···O(1^{i})	2·841 (3)	0·88 (4)	1·97 (4)	171 (4)
O(5)—H(52)···O(4^{ii})	2·857 (3)	0·74 (5)	2·14 (5)	166 (5)
O(6)—H(61)···O(4^{iii})	2·771 (3)	0·95 (7)	1·85 (7)	162 (6)
O(6)—H(62)···O(3^{iv})	2·851 (3)	0·70 (5)	2·16 (5)	169 (6)

Symmetry code: (i) $x,y,1+z$; (ii) $x,y-1,z$; (iii) $1-x, 1-y,-z$; (iv) $x,y-1,z-1$.

In crystals of (II) the Mn^{2+} ions (which lie on the symmetry points of the crystal) are octahedrally coordinated by four water O atoms and two O atoms from two monodentate hydrogen maleate ligands. The structure is stabilized by hydrogen bonds utilizing all

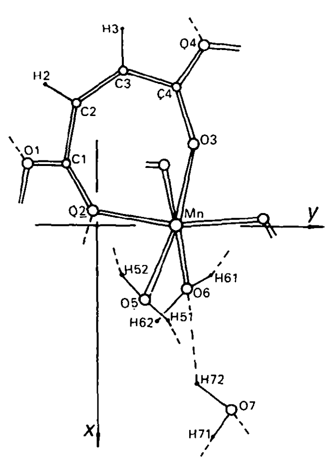

Fig. 1. The crystal structure of (I) projected on the (001) plane.

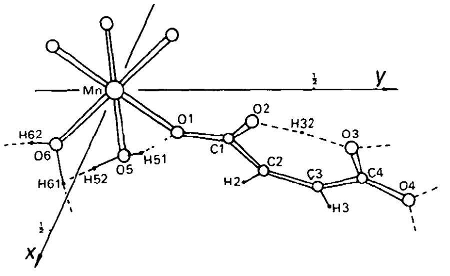

Fig. 2. The crystal structure of (II) projected on the (001) plane.

O-bonded H atoms (Table 4). The crystal structure of (II) has been discussed previously (Gupta & Mahanta, 1978) and the atomic parameters in the present work do not differ significantly from the previous refinements (though e.s.d.'s are considerably lower). It is notable that although the β-angle value is incorrect in Gupta & Mahanta's (1978) data, the bond lengths and angles in both works are comparable [except for the Mn—O(5) bond length: 2·205 (2) Å in the present work and 1·98 (2) Å in Gupta & Mahanta (1978)] because of the specific alignment of the hydrogen maleate residue in the crystal (Fig. 2). (The maleate monoanions lie almost along the **b** direction.)

The distorted octahedral coordination of Mn atoms in (I) and (II) is similar to that found in most Mn^{2+} carboxylate salts. The Mn—O distances range between 2·128 (3) and 2·230 (3) Å and are comparable to those found in related compounds (Lis & Matuszewski, 1979).

In both crystals the C-atom chain of maleate ligands is planar. In the case of (II), the carboxyl groups are slightly twisted out of the C-atom plane [2·6 (8) and 5·5 (8)°] so that the two central O atoms are on the same side of the plane of the C atoms. This situation is analogous to that found in other hydrogen maleate salts: Cu Hmaleate (Prout, Carruthers & Rossotti, 1971), Li Hmaleate (Gupta, Prasad & Gupta, 1975), Ca di(hydrogen maleate) (Hsu & Schlemper, 1978). The stabilization of this conformation is due to the strong intramolecular hydrogen bond of 2·417 (3) Å [O(3)···O(2)]. Unlike (II), both carboxylate groups of the maleate dianion in (I) are strongly twisted with respect to the C-atom plane, by 60·0 (8)° for the group C(2),C(1),O(1),O(2) and 34·7 (8)° for C(3),C(4),O(3),O(4). The conformation of the maleate ligand is such that the O atoms chelating the Mn^{2+} ions are displaced from the C-atom plane in the same direction. It is notable that the twist angles in other maleate dianion salts are different: 66 and −17° in disodium maleate monohydrate (James & Williams, 1974); 88 and 4° in tin(II) maleate monohydrate (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977); 79 and 17° in cadmium(II) maleate dihydrate (Hempel, Hull, Ram & Gupta, 1979).

The bond lengths and angles of the hydrogen maleate moiety and of the maleate dianion agree with those reported for other derivatives of this ligand cited above.

The author thanks Mr Andrzej Kowalski for technical assistance.

References

Dewan, J. C., Silver, J., Andrews, R. H., Donaldson, J. D. & Laughlin, D. R. (1977). *J. Chem. Soc. Dalton Trans.* pp. 368–371.

Gupta, M. P. & Mahanta, B. (1978). *Cryst. Struct. Commun.* **7**, 179–182.

Gupta, M. P., Prasad, S. M. & Gupta, T. N. P. (1975). *Acta Cryst.* B**31**, 37–40.

Hempel, A., Hull, S. E., Ram, R. & Gupta, M. P. (1979). *Acta Cryst.* B**35**, 2215–2216.

Hsu, B. & Schlemper, E. O. (1978). *Acta Cryst.* B**34**, 930–932.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

James, M. N. G. & Williams, G. J. B. (1974). *Acta Cryst.* B**30**, 1257–1262.

Lis, T. & Matuszewski, J. (1979). *Acta Cryst.* B**35**, 2212–2214.

Prout, C. K., Carruthers, J. R. & Rossotti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3342–3349.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.