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Magnesium (+)-Malate Pentahydrate

BY W. VAN HAVERE AND A. T. H. LENSTRA

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Abstract. $Mg(C_4H_4O_5).5H_2O$, $P2_12_12_1$, $a = 5.923$ (3), $b = 11.340$ (2), $c = 15.397$ (3) Å, $Z = 4$, $d_{calc} = 1.583$ Mg m^{-3}. The conformation of the $^-OOC-C-C-COO^-$ chain is *gauche*. Mg^{2+} is coordinated by a slightly distorted octahedron of O atoms. The title compound is compared with cobalt(II) and zinc malate trihydrate; these latter salts are expected to be isomorphous with magnesium malate trihydrate. In the trihydrates the malic acid moiety behaves as a tridentate ligand to the metal, whereas in the title compound it behaves as a bidentate ligand with one COO^- group coordinated by water molecules and not by a Mg^{2+} ion.

Introduction. The crystals of $Mg(C_4H_4O_5).5H_2O$ were grown by slow evaporation of an aqueous solution at room temperature. Reflections up to $\theta = 30°$ were measured on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo radiation. An ω/θ scan with a 6:1 speed ratio was applied. The scan angle was given by $0.6° + 0.35°$ tan θ 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. In view of the crystal size ($0.25 \times 0.20 \times 0.15$ mm) and the linear absorption coefficient ($\mu = 0.222$ mm^{-1}) no absorption correction was applied.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971); the most likely E map with 200 terms showed all non-hydrogen atoms. A subsequent difference electron density map revealed the positions of the H atoms.

From a total of 1772 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 factor of the H atoms was kept fixed at 3.0 Å^2 ($B_{Wilson} = 2.6$ Å^2). After refinement of the isotropic extinction parameter (Zachariasen, 1963), $r = 0.54 \times 10^{-8}$ m, the R value converged to 0.027. R is defined by $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for observed reflections only. The maximum noise level in the final difference Fourier map is 0.30 e Å^{-3}.

Refined parameters are listed in Table 1 and the numbering of the atoms is illustrated in Fig. 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35376 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
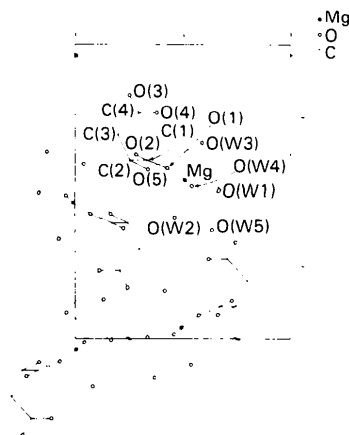

Fig. 1. Crystal packing of Mg (+)-malate pentahydrate projected on to the *yz* plane. The octahedral coordination of Mg is shown by dotted lines.

Discussion. The Mg^{2+} cation is coordinated by six O atoms forming a slightly distorted octahedron (see Table 2). Two O atoms, O(1) and O(5), of the coordination sphere are donated by the malate ion, the four other O atoms are donated by water molecules.

The $^-OOC-C-C-COO^-$ chain of the malate ion has the *gauche* conformation. Although intuitively one would expect the *trans* conformation to be more stable, the *gauche* form seems rather common (see below).

Groth (1910) describes the existence of two forms of magnesium malate: the rhombic pentahydrate, which is reported here, and a monoclinic trihydrate, $Mg(C_4H_4O_5)_2.3H_2O$. A direct comparison of the two structures is not possible, since despite considerable effort we did not succeed in obtaining crystals of the monoclinic form. We are, however, in a position to make the comparison in a somewhat indirect manner since the crystal structures of $Co(C_4H_4O_5).3H_2O$ (Kryger & Rasmussen, 1972) and $Zn(C_4H_4O_5).$-$3H_2O$ (Lenstra & Van de Mieroop, 1976) are known. These trihydrates belong to the same crystal class and have almost identical axis ratios to $Mg(C_4H_4O_5).$-$3H_2O$. Also, since the ionic radii of Mg^{2+}, Co^{2+} and Zn^{2+} are similar, we expect Mg malate trihydrate to be

Table 1. *Refined positional parameters (in fractions of the cell edges) of Mg (+)-malate pentahydrate*

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)
Mg	0·2397 (2)	−0·00518 (8)	0·46242 (6)	1·96
O(1)	0·5394 (3)	0·0726 (2)	0·4249 (1)	2·07
O(2)	0·7197 (3)	0·2285 (2)	0·3719 (1)	2·27
O(3)	0·0898 (4)	0·2469 (2)	0·1706 (1)	2·98
O(4)	0·3056 (3)	0·1099 (1)	0·2308 (1)	2·28
O(5)	0·1469 (3)	0·1653 (2)	0·4202 (1)	2·08
C(1)	0·5446 (4)	0·1759 (2)	0·3945 (2)	1·61
C(2)	0·3213 (4)	0·2431 (2)	0·3905 (2)	1·83
C(3)	0·2694 (5)	0·2963 (2)	0·3023 (2)	2·03
C(4)	0·2164 (4)	0·2101 (2)	0·2296 (2)	1·97
O(W1)	0·3571 (4)	−0·1673 (2)	0·4991 (1)	2·94
O(W2)	0·2898 (4)	0·0415 (2)	0·5905 (1)	2·84
O(W3)	0·2105 (4)	−0·0738 (2)	0·3400 (1)	2·92
O(W4)	−0·0904 (3)	−0·0374 (2)	0·4853 (1)	3·07
O(W5)	−0·1882 (4)	−0·1361 (2)	0·6335 (2)	5·14
H(O5)	0·018 (4)	0·185 (2)	0·407 (1)	3·00
H(C2)	0·348 (4)	0·307 (2)	0·433 (1)	3·00
H1(C3)	0·395 (4)	0·343 (2)	0·283 (1)	3·00
H2(C3)	0·138 (4)	0·344 (2)	0·308 (2)	3·00
H1(W1)	0·368 (4)	−0·209 (2)	0·466 (1)	3·00
H2(W1)	0·379 (4)	−0·198 (2)	0·555 (1)	3·00
H1(W2)	0·266 (4)	−0·002 (2)	0·624 (2)	3·00
H2(W2)	0·256 (4)	0·116 (2)	0·611 (1)	3·00
H1(W3)	0·091 (5)	−0·120 (2)	0·331 (1)	3·00
H2(W3)	0·242 (4)	−0·025 (2)	0·304 (1)	3·00
H1(W4)	−0·203 (2)	−0·008 (2)	0·458 (1)	3·00
H2(W4)	−0·121 (4)	−0·058 (2)	0·534 (1)	3·00
H1(W5)	−0·274 (4)	−0·168 (2)	0·654 (1)	3·00
H2(W5)	−0·216 (4)	−0·070 (2)	0·675 (1)	3·00

Table 2. *The coordination of Mg^{2+}*

Distances are in Å, angles in deg. E.s.d.'s are given in parentheses.

Mg–O(1)	2·059 (1)	Mg–O(W2)	2·063 (2)
Mg–O(5)	2·112 (2)	Mg–O(W3)	2·047 (2)
Mg–O(W1)	2·046 (2)	Mg–O(W4)	2·020 (2)

O(1)–Mg–O(5)	75·3 (1)	O(5)–Mg–O(W4)	88·1 (1)
O(1)–Mg–O(W1)	99·8 (1)	O(W1)–Mg–O(W2)	85·3 (1)
O(1)–Mg–O(W2)	92·0 (1)	O(W1)–Mg–O(W3)	86·6 (1)
O(1)–Mg–O(W3)	88·7 (1)	O(W1)–Mg–O(W4)	86·8 (1)
O(1)–Mg–O(W4)	163·3 (1)	O(W2)–Mg–O(W3)	171·9 (1)
O(5)–Mg–O(W1)	175·0 (1)	O(W2)–Mg–O(W4)	91·1 (1)
O(5)–Mg–O(W2)	95·6 (1)	O(W3)–Mg–O(W4)	90·6 (1)
O(5)–Mg–O(W3)	92·4 (1)		

Table 3. *Bond lengths (Å), valence angles (°) and torsion angles (°), with e.s.d.'s in parentheses, of* $Mg(C_4H_4O_5).5H_2O$, $Co(C_4H_4O_5).3H_2O$ *and* $Zn(C_4H_4O_5).3H_2O$

	Mg malate.5H$_2$O^a	Co malate.3H$_2$O^b	Zn malate.3H$_2$O^c
C(1)–C(2)	1·527 (3)	1·534 (6)	1·531 (6)
C(2)–C(3)	1·517 (3)	1·517 (5)	1·527 (6)
C(3)–C(4)	1·519 (3)	1·521 (5)	1·516 (6)
C(1)–O(1)	1·263 (2)	1·262 (5)	1·266 (6)
C(1)–O(2)	1·246 (2)	1·237 (5)	1·241 (6)
C(4)–O(3)	1·250 (2)	1·251 (5)	1·255 (6)
C(4)–O(4)	1·253 (2)	1·257 (5)	1·283 (6)
C(2)–O(5)	1·434 (2)	1·435 (5)	1·436 (6)
C–H	0·97 (2)	0·88 (3)	1·05 (6)
O–H	0·83 (10)	0·83 (8)	0·89 (6)
O(1)–C(1)–O(2)	124·9 (2)	124·4 (3)	123·9 (3)
O(1)–C(1)–C(2)	116·9 (2)	119·2 (3)	117·2 (3)
O(2)–C(1)–C(2)	118·1 (2)	116·4 (3)	118·9 (3)
C(1)–C(2)–C(3)	114·2 (2)	110·9 (3)	111·2 (3)
C(1)–C(2)–O(5)	107·7 (2)	107·6 (3)	107·2 (3)
O(5)–C(2)–C(3)	112·6 (2)	111·4 (3)	112·0 (3)
C(2)–C(3)–C(4)	116·5 (2)	117·8 (3)	116·4 (3)
O(3)–C(4)–O(4)	124·4 (2)	123·0 (3)	122·8 (3)
O(3)–C(4)–C(3)	116·5 (2)	115·6 (3)	114·7 (3)
O(4)–C(4)–C(3)	119·1 (2)	121·4 (3)	122·6 (3)
O(1)–C(1)–C(2)–C(3)	−128·7 (4)*	+94·8 (5)	+95·5 (5)
O(1)–C(1)–C(2)–O(5)	−2·9 (4)*	−26·5 (5)	−25·8 (5)
C(1)–C(2)–C(3)–C(4)	68·8 (4)*	−64·9	−64·4
O(4)–C(4)–C(3)–C(2)	−30·3 (4)	−12·8	−13·0

References: (a) This work. (b) Kryger & Rasmussen (1972). (c) Lenstra & Van de Mieroop (1976).

* The malate ion in $Mg(C_4H_4O_5).5H_2O$ has the $2R$ configuration. In order to compare the values with those of the other salts in the $2S$ configuration the sign has to be reversed.

Table 4. *Charges on atoms (e) in* $[Mg(OH_2)_6]^{2+}$ *and in free* H_2O *calculated by MO methods (Rinaldi, 1975)*

		INDO	CNDO
$Mg(H_2O)_6$	Mg	+1·09	+1·20
	O	−0·33	−0·31
	H	+0·24	+0·22
H_2O	O	−0·32	−0·27
	H	+0·16	+0·14

isomorphous with the Co and Zn salts. Bond lengths, valence angles and torsion angles of the title compound together with those of Co and Zn malate trihydrate are collected in Table 3. There are no significant differences between the title compound and the monoclinic trihydrates as far as bond lengths and valence angles in

Table 5. *Short* OH $\cdots$ O *interactions in the title compound*

| Donor D	Acceptor A	A at	D–H (Å)	A$\cdots$H (Å)	D$\cdots$A (Å)	D–H$\cdots$A (°)
O(5)–H(O5)	O(2)	$-1 + x, y, z$	0·823	1·911	2·733	178·4
O(W1)–H1(W1)	O(W5)	$\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$	0·701	2·353	3·035	164·8
O(W1)–H2(W1)	O(3)	$\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	0·945	1·865	2·807	174·5
O(W2)–H1(W2)	O(4)	$\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	0·722	2·099	2·816	172·5
O(W2)–H1(W2)	O(2)	$-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	0·920	1·800	2·704	166·7
O(W3)–H1(W3)	O(3)	$\bar{x}, -\frac{1}{2} + y, \frac{1}{2} - z$	0·893	1·851	2·707	160·0
O(W3)–H2(W3)	O(4)	x,y,z	0·799	1·943	2·736	171·6
O(W4)–H1(W4)	O(1)	$-1 + x, y, z$	0·855	1·855	2·693	166·4
O(W4)–H2(W4)	O(W5)	x,y,z	0·800	1·821	2·607	167·4
O(W5)–H1(W5)	O(3)	$-\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	0·697	2·089	2·749	160·8
	E.s.d.		0·040	0·040	0·003	2·0
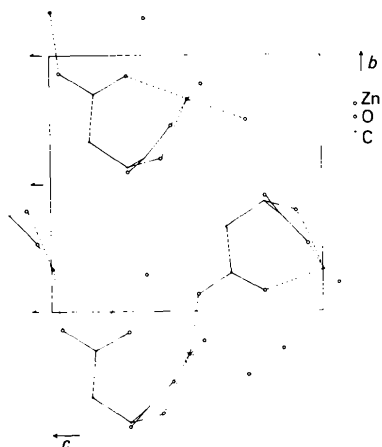
Fig. 2. Crystal packing of Zn malate trihydrate, isomorphous with Mg malate trihydrate, projected on to the *yz* plane.

the malate skeleton are concerned. Also, the differences in the torsion angles are not very important; for example, the *gauche* conformation in $^{-}$OOC–C–C–COO^{-} occurs in all three compounds. Moreover, octahedral coordination of the metal ions is always found.

So far the structures are rather similar, but the way in which the malate skeleton is bound to the cation is totally different. In the monoclinic salts the malate anions behave as tridentate ligands with both charged carboxyl functions and the alcohol group linked to the metal ions. In sharp contrast to this we observe in the rhombic magnesium malate pentahydrate that the malate ion behaves as a bidentate ligand with only the carboxyl function O(1)–C(1)–O(2) and O(5)–H bound to the Mg^{2+} ion. It is even more interesting to note that the second charged carboxyl group is not linked to any metal ion. Surprising as this may seem at

first sight, one must recognize that the COO^{-} group is in close contact with four water molecules [O(W3) at x,y,z; O(W3) at $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; O(W1) at $\frac{1}{2} - x, -y, \frac{1}{2} + z$; O(W2) at $\frac{1}{2} - x, -y, \frac{1}{2} + z$]. Their H atoms can be expected to acquire a substantial positive charge resulting from polarization by the Mg ion. This was tested against calculations which showed (Table 4) the H atoms of water molecules coordinated to Mg to be more positively charged than in free water molecules.

Furthermore, the overall packing of the pentahydrate (Fig. 1) differs from that of the trihydrates (Fig. 2). The packing of the pentahydrate is largely dominated by hydrogen bridges (see Table 5), whereas in the trihydrates one observes ionic-linked spirals of malates along the unique axis, in addition to hydrogen bridges in the other directions.

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