*Acta Cryst.* (1980). B**36**, 156–158

# Calcium Di(hydrogen 1-malate) Hexahydrate

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(*Received* 27 *February* 1979; *accepted* 21 *September* 1979)

**Abstract.** $Ca(C_4H_5O_5)_2.6H_2O$, $C_8H_{10}O_{10}^{2-}.Ca^{2+}.6H_2O$, $P2_12_12_1$, $a = 7{\cdot}067\,(1)$, $b = 15{\cdot}010\,(2)$, $c = 15{\cdot}692\,(2)$ Å, $Z = 4$, $d_c = 1{\cdot}66$ Mg m$^{-3}$. The conformations of the two independent hydrogen malate ions in the crystal are different. The $Ca^{2+}$ ion is coordinated by eight oxygens.

**Introduction.** The crystals of $Ca(C_4H_5O_5)_2.6H_2O$ were prepared 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. From the systematic extinctions the space group $P2_12_12_1$ was inferred. In the subsequent structure analysis 1982 reflections with $I > 3\sigma(I)$ were used. In view of the crystal size ($0{\cdot}10 \times 0{\cdot}13 \times 0{\cdot}11$ mm) and the linear absorption coefficient ($0{\cdot}45$ mm$^{-1}$) no absorption correction was applied. The structure was solved using heavy-atom Fourier procedures. Each reflection was weighted according to its reliability in the intensity measurement. After refinement of the relevant parameters of the non-hydrogen atoms, the difference electron density showed larger maxima at expected positions for the H atoms. The Debye–Waller temperature factors of the H atoms were fixed at a value of $2{\cdot}0$ Å$^2$ (the value of $B_{all}$ in the Wilson plot). The values of the refined parameters are listed in Table 1.* The numbering of the atoms is illus-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34733 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final parameter values in* $Ca(C_4H_5O_5)_2.6H_2O$

See Fig. 1 for the numbering of the atoms. O(21) through O(26) represent the six water molecules of crystallization, H(1C2) is a hydrogen atom attached to the C(2). Isotropic temperature factors are calculated from the anisotropic temperature parameters assuming equal volume of the 50% probability region.

| | $x$ | $y$ | $z$ | $B_{eq.}$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|---|
| Ca | 0·1838 (1) | 0·48810 (3) | 0·45892 (3) | 1·53 | H(1C2) | 0·664 (4) | 0·422 (1) | 0·587 (1) |
| O(1) | 0·4128 (3) | 0·3701 (1) | 0·4394 (1) | 1·86 | H(1C3) | 0·418 (3) | 0·280 (1) | 0·631 (1) |
| O(2) | 0·6908 (3) | 0·3092 (1) | 0·4703 (1) | 1·87 | H(2C3) | 0·620 (3) | 0·275 (1) | 0·630 (1) |
| O(3) | 0·4041 (3) | 0·3060 (1) | 0·7811 (1) | 2·36 | H(1O3) | 0·401 (3) | 0·326 (1) | 0·835 (1) |
| O(4) | 0·6441 (3) | 0·3983 (1) | 0·7579 (1) | 2·40 | H(1O5) | 0·410 (3) | 0·486 (1) | 0·609 (1) |
| O(5) | 0·3802 (3) | 0·4497 (1) | 0·5881 (1) | 1·80 | H(1C12) | −0·185 (4) | 0·645 (1) | 0·574 (1) |
| C(1) | 0·5489 (4) | 0·3552 (1) | 0·4887 (1) | 1·29 | H(1C13) | 0·158 (4) | 0·732 (1) | 0·643 (1) |
| C(2) | 0·5384 (4) | 0·3921 (2) | 0·5796 (1) | 1·48 | H(2C13) | −0·051 (3) | 0·770 (1) | 0·641 (1) |
| C(3) | 0·5213 (4) | 0·3144 (2) | 0·6412 (2) | 1·82 | H(1O13) | 0·064 (3) | 0·686 (1) | 0·836 (1) |
| C(4) | 0·5285 (4) | 0·3441 (2) | 0·7326 (1) | 1·65 | H(1O15) | 0·012 (3) | 0·543 (1) | 0·614 (1) |
| O(11) | 0·0783 (3) | 0·6388 (1) | 0·4330 (1) | 1·84 | H(1O21) | −0·410 (3) | 0·607 (1) | 0·690 (1) |
| O(12) | −0·0312 (3) | 0·7710 (1) | 0·4716 (1) | 2·25 | H(2O21) | −0·532 (3) | 0·640 (1) | 0·641 (1) |
| O(13) | 0·0784 (3) | 0·7115 (1) | 0·7928 (1) | 2·33 | H(1O22) | 0·293 (3) | 0·512 (1) | 0·287 (1) |
| O(14) | −0·1522 (3) | 0·6228 (1) | 0·7466 (1) | 2·22 | H(2O22) | 0·168 (3) | 0·452 (1) | 0·278 (1) |
| O(15) | 0·0553 (3) | 0·5695 (1) | 0·5799 (1) | 2·16 | H(1O23) | −0·153 (3) | 0·519 (1) | 0·361 (1) |
| C(11) | 0·0079 (4) | 0·6925 (2) | 0·4863 (1) | 1·55 | H(2O23) | −0·212 (3) | 0·442 (2) | 0·376 (1) |
| C(12) | −0·0392 (4) | 0·6536 (2) | 0·5741 (1) | 1·61 | H(1O24) | −0·080 (3) | 0·349 (1) | 0·505 (1) |
| C(13) | 0·0172 (4) | 0·7149 (2) | 0·6462 (2) | 1·84 | H(2O24) | 0·092 (3) | 0·321 (1) | 0·527 (1) |
| C(14) | −0·0306 (4) | 0·6775 (2) | 0·7330 (2) | 1·63 | H(1O25) | 0·900 (3) | 0·426 (1) | 0·722 (1) |
| O(21) | −0·5079 (3) | 0·6018 (1) | 0·6693 (1) | 2·70 | H(2O25) | 1·043 (3) | 0·403 (1) | 0·668 (1) |
| O(22) | 0·2212 (3) | 0·4823 (1) | 0·3076 (1) | 2·52 | H(1O26) | 0·571 (3) | 0·557 (2) | 0·432 (1) |
| O(23) | −0·1545 (3) | 0·4824 (1) | 0·3948 (1) | 2·70 | H(2O26) | 0·480 (3) | 0·619 (1) | 0·455 (1) |
| O(24) | 0·0328 (3) | 0·3622 (1) | 0·5259 (1) | 2·27 | | | | |
| O(25) | 1·0071 (3) | 0·4393 (1) | 0·7005 (1) | 2·67 | | | | |
| O(26) | 0·4717 (3) | 0·5716 (1) | 0·4391 (1) | 2·79 | | | | |

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Table 2. *Bond lengths* (Å) *and valency angles* (°) *in the hydrogen malate ions*

Estimated standard deviations are 0·003 Å for the bond lengths and 0·3° for the angles.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1)–C(2) | 1·533 | C(1)–O(2) | 1·250 | C(11)–C(12) | 1·534 | C(11)–O(12) | 1·233 |
| C(2)–C(3) | 1·520 | C(4)–O(3) | 1·296 | C(12)–C(13) | 1·512 | C(14)–O(13) | 1·317 |
| C(3)–C(4) | 1·502 | C(4)–O(4) | 1·220 | C(13)–C(14) | 1·511 | C(14)–O(14) | 1·207 |
| C(1)–O(1) | 1·254 | C(2)–O(5) | 1·420 | C(11)–O(11) | 1·265 | C(12)–O(15) | 1·430 |

| | | | | | |
|---|---|---|---|---|---|
| O(1)–C(1)–O(2) | 124·9 | O(3)–C(4)–O(4) | 123·9 | C(11)–C(12)–C(13) | 112·6 |
| O(1)–C(1)–C(2) | 118·1 | C(3)–C(4)–O(3) | 114·0 | C(13)–C(12)–O(15) | 111·5 |
| O(2)–C(1)–C(2) | 117·0 | C(3)–C(4)–O(4) | 122·1 | C(12)–C(13)–C(14) | 112·9 |
| C(1)–C(2)–O(5) | 110·3 | O(11)–C(11)–O(12) | 125·1 | O(13)–C(14)–O(14) | 123·6 |
| C(1)–C(2)–C(3) | 108·5 | O(11)–C(11)–C(12) | 115·9 | C(13)–C(14)–O(13) | 111·6 |
| C(3)–C(2)–O(5) | 110·2 | O(12)–C(11)–C(12) | 118·9 | C(13)–C(14)–O(14) | 124·8 |
| C(2)–C(3)–C(4) | 112·1 | C(11)–C(12)–O(15) | 107·0 | | |

Table 3. *The coordination of* $Ca^{2+}$; *all* Ca–O *distances less than* 3 Å *are given*

The standard deviations are 0·001 Å in the distances and 0·1° in angles.

| | | | |
|---|---|---|---|
| Ca–O(1) | 2·419 Å | Ca–O(22) | 2·390 Å |
| Ca–O(5) | 2·523 | Ca–O(23) | 2·595 |
| Ca–O(11) | 2·414 | Ca–O(24) | 2·411 |
| Ca–O(15) | 2·434 | Ca–O(26) | 2·410 |

| | | | |
|---|---|---|---|
| O(1)–Ca–O(5) | 64·3° | O(22)–Ca–O(11) | 84·3° |
| O(1)–Ca–O(22) | 76·9 | O(22)–Ca–O(24) | 117·0 |
| O(1)–Ca–O(15) | 135·7 | O(22)–Ca–O(26) | 78·3 |
| O(1)–Ca–O(11) | 150·5 | O(22)–Ca–O(23) | 73·5 |
| O(1)–Ca–O(24) | 77·1 | O(15)–Ca–O(11) | 63·0 |
| O(1)–Ca–O(26) | 78·5 | O(15)–Ca–O(24) | 83·6 |
| O(1)–Ca–O(23) | 122·9 | O(15)–Ca–O(26) | 98·9 |
| O(5)–Ca–O(22) | 136·8 | O(15)–Ca–O(23) | 88·6 |
| O(5)–Ca–O(15) | 72·1 | O(11)–Ca–O(24) | 132·2 |
| O(5)–Ca–O(11) | 121·2 | O(11)–Ca–O(26) | 75·5 |
| O(5)–Ca–O(24) | 73·4 | O(11)–Ca–O(23) | 71·5 |
| O(5)–Ca–O(26) | 76·0 | O(24)–Ca–O(26) | 146·9 |
| O(5)–Ca–O(23) | 144·2 | O(24)–Ca–O(23) | 74·7 |
| O(22)–Ca–O(15) | 146·6 | O(26)–Ca–O(23) | 138·1 |

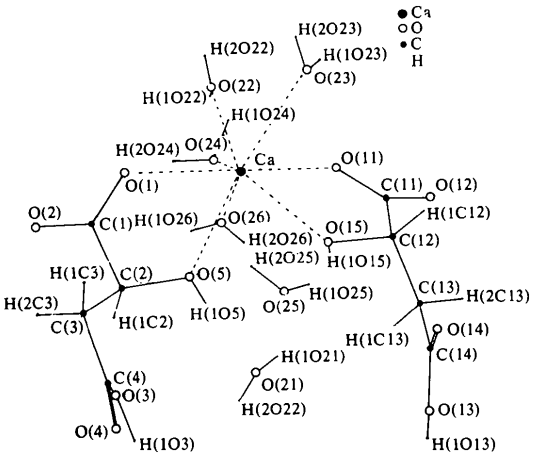


Fig. 1. The numbering of the atoms in the title compound. The oxygen atoms of the water molecules are numbered from O(21) to O(26).

trated in Fig. 1. The refinement converged to a final $R$ of 0·024; the maximum noise level in the difference Fourier function was ~0·2 e $Å^{-3}$. Bond distances and valency angles in the two crystallographically independent hydrogen malate ions are summarized in Table 2. The $Ca^{2+}$ coordination is shown in Table 3 and Fig. 2.

**Discussion.** The bond angles and bond distances in the two crystallographically independent hydrogen malate ions are practically equal to the corresponding values found in ammonium hydrogen 1-malate (Versichel, Van de Mieroop & Lenstra, 1978) and in the monoclinic form of copper hydrogen 1-malate (Van Havere & Lenstra, 1978). In the present compound the average O–H and C–H distances are 0·78 (4) and 0·98 (5) Å. The valency angles H–O–H, C–C–H, H–C–H and C–O–H have average values of 110 (4), 109 (3), 103 (3) and 111 (3)° respectively. In Fig. 3 a view of the crystal structure is given.

It seems logical to compare the present structure with that of calcium malate dihydrate (Bränden & Söderberg, 1966). A first difference is found in the conformation of the malic acid moiety itself. In the title compound the C(1)–C(2)–C(3)–C(4) chains are staggered, whereas they are *gauche* in calcium malate dihydrate. Fig. 4 depicts Newman projections from which this and some other details concerning the malic acid conformation can be seen.

A second difference is noted in the way in which the malic acid moieties contribute to the $Ca^{2+}$ coor-

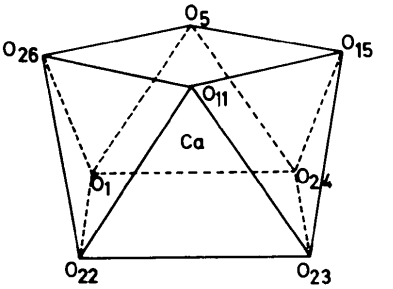


Fig. 2. The coordination of the $Ca^{2+}$ ion.

Table 4. *Short* O—H···O *interactions in the title compound*

Average e.s.d.'s for $D\cdots A$ 0·003 Å, for $D$—H 0·004 Å, for H···$A$ 0·04 Å and for $D$—H···$A$ 3°.

| Donor group ($D$) | Acceptor ($A$) | | $D\cdots A$ | $D$—H | H···$A$ | $D$—H···$A$ |
|---|---|---|---|---|---|---|
| O(3)—H(1) | O(11) | $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ | 2·53 Å | 0·90 Å | 1·63 Å | 173·4° |
| O(13)—H(1) | O(1) | $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ | 2·61 | 0·78 | 1·84 | 167·2 |
| O(5)—H(1) | O(21) | $1+x, y, z$ | 2·73 | 0·66 | 2·07 | 177·2 |
| O(15)—H(1) | O(25) | $x-1, y, z$ | 2·74 | 0·74 | 2·07 | 153·3 |
| O(21)—H(1) | O(14) | $x, y, z$ | 2·81 | 0·77 | 2·04 | 178·7 |
| O(21)—H(2) | O(12) | $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$ | 2·93 | 0·75 | 2·21 | 160·1 |
| O(22)—H(1) | O(25) | $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$ | 2·81 | 0·76 | 2·08 | 161·1 |
| O(22)—H(2) | O(21) | $-\frac{1}{2}-x, 1-y, z-\frac{1}{2}$ | 2·93 | 0·76 | 2·20 | 163·2 |
| O(23)—H(1) | O(4) | $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$ | 2·80 | 0·77 | 2·04 | 171·7 |
| O(23)—H(2) | O(14) | $-\frac{1}{2}-x, 1-y, z-\frac{1}{2}$ | 3·13 | 0·79 | 2·45 | 144·7 |
| O(24)—H(1) | O(2) | $1-x, y, z$ | 2·69 | 0·88 | 1·81 | 173·6 |
| O(24)—H(2) | O(2) | $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$ | 2·81 | 0·75 | 2·08 | 165·1 |
| O(25)—H(1) | O(4) | $x, y, z$ | 2·79 | 0·86 | 1·94 | 173·0 |
| O(25)—H(2) | O(24) | $1+x, y, z$ | 2·98 | 0·79 | 2·32 | 142·2 |
| O(26)—H(1) | O(23) | $1+x, y, z$ | 3·04 | 0·75 | 2·31 | 166·7 |
| O(26)—H(2) | O(12) | $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ | 2·75 | 0·76 | 2·00 | 163·2 |

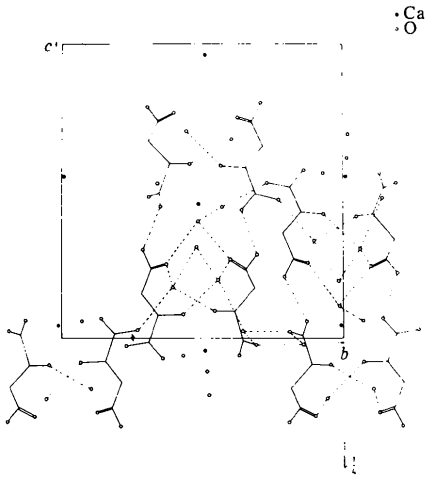


Fig. 3. A view of the structure of $Ca(C_4H_5O_5)_2.6H_2O$.

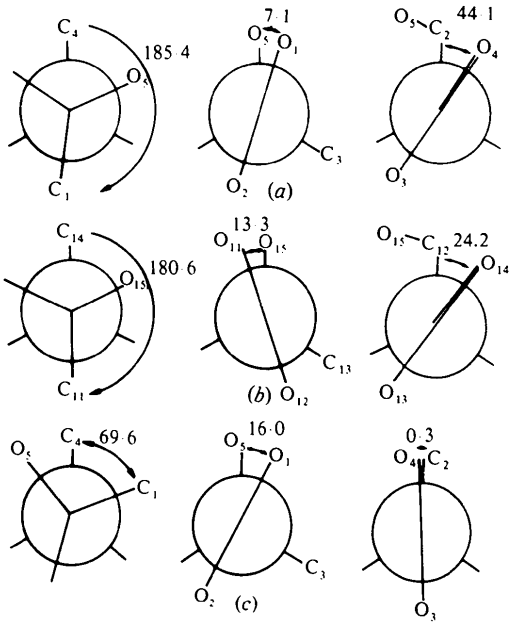


Fig. 4. Dihedral angles (*a*) and (*b*) in the two crystallographically independent hydrogen malate moieties of $Ca(C_4H_5O_5)_2.6H_2O$ compared with (*c*) the malate moiety of $Ca(C_4H_4O_5).2H_2O$. The average e.s.d. is 0·5°.

dination. In both compounds each $Ca^{2+}$ ion is coordinated by eight O atoms, but the factors dominating the three-dimensional networks are different. In the case of calcium malate dihydrate, on the one hand, Coulomb interactions are the dominating factor, *e.g.* three different $Ca^{2+}$ ions show short Coulomb interactions with one single $COO^-$ group. On the other hand, in the structure of calcium di(hydrogen 1-malate) the short-range Coulomb interaction is located within one single stoichiometric unit of $Ca(C_4H_5O_5)_2$. The direct contacts with the nearest neighbours are formed by large numbers of hydrogen bonds. The hydrogen bridges are listed in Table 4.

The acid salts of malic acid with divalent ions are not necessarily all stacked in the same way as calcium di(hydrogen 1-malate) hexahydrate. It should be noted that in the packing of $Cu(C_4H_5O_5)_2.2H_2O$ the nearest-neighbour interactions are not limited to hydrogen bonds. Complexation between the $Cu^{II}$ ion and two different COOH groups provides a strong link between two of the nearest neighbours.

One of the authors (WVH) thanks the Belgian Organization IWONL for financial support.

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