Table 4. *Hydrogen-bond parameters*

X–H···Y	X···Y (Å)	H···Y (Å)	∠X–H···Y(°)
N(1)–H(1)···O(1)^{i}	2·988 (2)	2·23 (3)	173 (3)
N(3)–H(3)···O(4)^{ii}	2·997 (2)	2·09 (4)	172 (3)
O(w)–H(w,1)···S(1)	3·218 (2)	2·41 (4)	172 (4)
O(w)–H(w,2)···O(1)^{iii}	3·125 (2)	2·59 (4)	130 (4)
O(w)–H(w,2)···O(2)^{iv}	3·104 (2)	2·54 (4)	134 (3)

Symmetry code for superscripts

None x,y,z
(i) $x, \frac{1}{2} - y, \frac{1}{2} + z$
(ii) $-x, \frac{1}{2} + y, (\frac{1}{2} - z) - 1$
(iii) $x, 1 + y, z$
(iv) $1 - x, 1 - y, -z$

occurring at $x = \frac{1}{2}$, is largely hydrophilic and is where the Na ion and the water molecule are found. The Na atom is nearly on the crystallographic 2_1 screw axis and is surrounded by six O atoms in an octahedral array, with O—Na—O angles ranging from 82·5 to 99·4° (Table 3). The equatorial plane of this octahedron is made by four sulfonate O atoms. The axial positions are occupied by water O atoms. One H of this water molecule is involved in a hydrogen bond with S(1) (Table 4). The other appears to be involved in a bifurcated hydrogen bond, being close to both O(1) of one DHTUS and O(2) of another (Table 4).

Each sheet, in turn, may be considered to be made of long chains. These chains run parallel to **b** and possess crystallographic 2_1 symmetry at $x = 0$, $z = \frac{3}{4}$. The DHTUS anions in a given chain are connected to one another by a strong hydrogen bond between N(3) of one anion and O(4) of its neighbor (Table 4). Neighboring chains in each sheet are related to one another by crystallographic c-glide symmetry (or, equivalently, by crystallographic center of inversion symmetry). There are numerous van der Waals interactions between chains, but also there is one strong hydrogen bond per anion connecting these chains. This hydrogen bond occurs near the surface of the sheet between N(1) of one DHTUS and O(1) of another.

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References

CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
HALL, S. R. & MASLEN, E. N. (1967). *Acta Cryst.* **22**, 216–228.
KOJIĆ-PRODIĆ, B., RUŽIĆ-TOROŠ, Ž. & COFFOU, E. (1976). *Acta Cryst.* B**32**, 1099–1102.
PITMAN, I. H., SHEFTER, E. & ZISER, M. (1970). *J. Am. Chem. Soc.* **92**, 3413–3417.
SECCOMBE, R. C., LEE, B. & HENRY, G. M. (1975). *Inorg. Chem.* **14**, 1147–1153.
SHAPIRO, R., SERVIS, R. E. & WELCHER, M. (1970). *J. Am. Chem. Soc.* **92**, 422–424.

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Calcium Di(hydrogen maleate) Pentahydrate

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Abstract. $Ca(C_4H_3O_4)_2.5H_2O$, orthorhombic, $Pnam$, $a = 11·737$ (2), $b = 6·477$ (1), $c = 19·593$ (2) Å, $Z = 4$, $D_m = 1·590$, $D_c = 1·586$ g cm^{-3}, $\mu = 1·40$ cm^{-1}, final $R(F^2)$ of 0·060. Ca is seven coordinate with distorted monocapped trigonal prismatic geometry (Ca—O ranges from 2·359 to 2·469 Å). The hydrogen maleate ion is coordinated to Ca through one O and possesses a short intramolecular O···O hydrogen bond [O···O 2·426 (1), O—H 1·13 (3) and 1·31 (3) Å].

Introduction. The title compound was prepared by titrating a saturated aqueous solution of maleic acid with calcium hydroxide to pH = 3·95. Solvent was then removed by slow evaporation at room temperature to produce crystals suitable for diffraction studies. Precession photographs gave the systematic absences $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$, which indicated that the space group was either $Pnam$ or $Pna2_1$. The former was indicated by statistical examination of the distribution of E values and was confirmed by the structure refinement. Any deviation from $Pnam$ would be necessarily small because of the very successful refinement in $Pnam$. A crystal (0·7 × 0·6 × 0·3 mm) was mounted on a programmed Picker four-circle

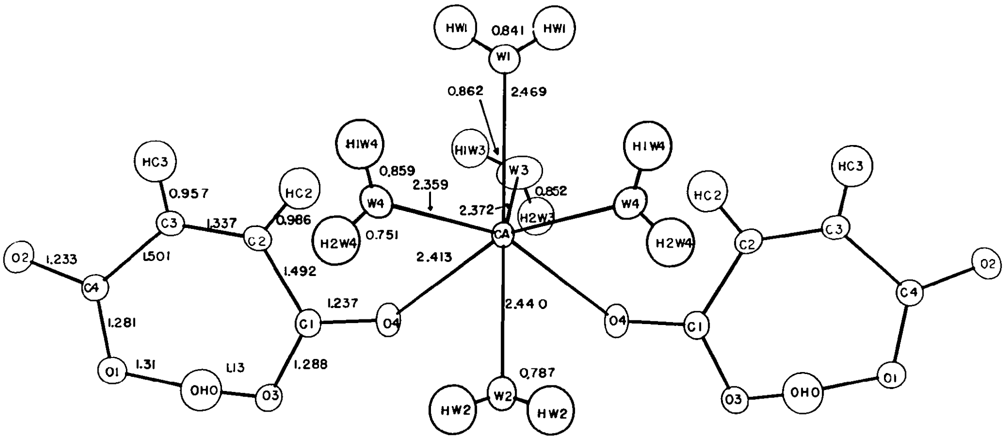

Fig. 1. Bond distances (Å) in $Ca(C_4H_3O_4)_2.5H_2O$. The standard deviations are: Ca–O 0·001–0·003, O–C and C–C 0·002, C–H 0·02, O–H 0·02–0·05 Å.

Table 1. *Final atomic positional parameters for* $Ca(C_4H_3O_4)_2.5H_2O$ ($\times 10^4$)

The estimated standard deviations from the least-squares refinement are given in parentheses in this table and other parts of the manuscript.

	x	*y*	*z*
Ca	1068 (1)	1100 (1)	−2500
W(1)	−1021 (1)	654 (3)	−2500
W(2)	2866 (1)	−793 (3)	−2500
W(3)*	239 (2)	4415 (4)	−2366 (4)
W(4)	712 (1)	−1373 (2)	−3358 (1)
O(1)	2849 (1)	2872 (2)	549 (1)
O(2)	1392 (1)	2645 (2)	1256 (1)
O(3)	3184 (1)	2923 (2)	−673 (1)
O(4)	2168 (1)	2739 (2)	−1612 (1)
C(1)	2217 (1)	2803 (2)	−982 (1)
C(2)	1134 (1)	2750 (2)	−584 (1)
C(3)	951 (1)	2711 (2)	89 (1)
C(4)	1779 (1)	2740 (2)	672 (1)
OHO	3096 (21)	2980 (45)	−101 (14)
H(C2)	458 (15)	2683 (26)	−883 (9)
H(C3)	184 (14)	2695 (26)	245 (9)
H(*W*1)	−1393 (19)	985 (29)	−2850 (10)
H(*W*2)	2988 (17)	−1436 (38)	−2833 (11)
H(1*W*3)	−315 (31)	4644 (63)	−2355 (26)
H(2*W*3)	774 (39)	5269 (73)	−2286 (22)
H(1*W*4)	38 (20)	−1785 (37)	−3462 (12)
H(2*W*4)	1131 (19)	−1636 (33)	−3635 (12)

* The position is only half populated.

diffractometer. Accurate cell dimensions and orientation matrix were obtained by a least squares fit to the setting angles of 16 manually centered reflections (λ = 0·7107 Å and 2θ = 20–40°), and a complete data set was collected with Mo $K\alpha$ radiation (Zr filtered) for $2\theta \le 60°$. 2508 independent reflections were measured of which 1657 were considered observed [$I \ge 2{\cdot}5\sigma(I)$].

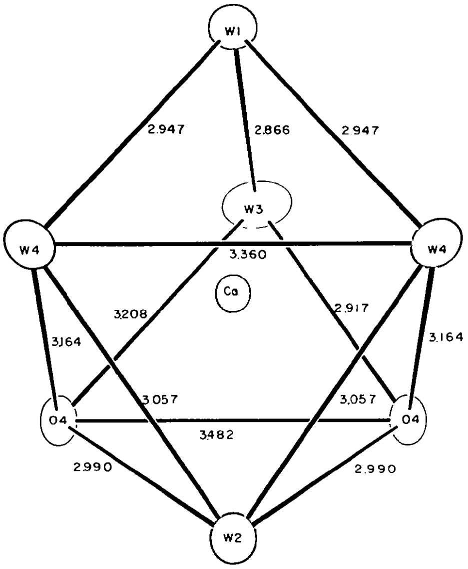

Fig. 2. The surroundings of the calcium ion, showing the O–O distances in the monocapped trigonal prism.

Lorentz and polarization corrections were applied as was an analytical absorption correction (μ = 1·40 cm^{-1} and the transmission factor ranged from 0·805 to 0·876).

The structure was solved by direct methods (Germain, Main & Woolfson, 1971) and refined, without H atoms, by full-matrix least squares [minimizing $\Sigma w(F_o^2 - F_c^2)^2$] to $R(F^2)$ = 0·187 with isotropic temperature factors. Further refinement, including anisotropic thermal parameters followed by a difference Fourier analysis, led to the location of all the H atoms. Refinement including the H atoms with isotropic temperature factors gave a final $R(F^2)$ = 0·060 and $wR(F^2)$ = 0·084. The weights ($1/\sigma^2$) were assigned on

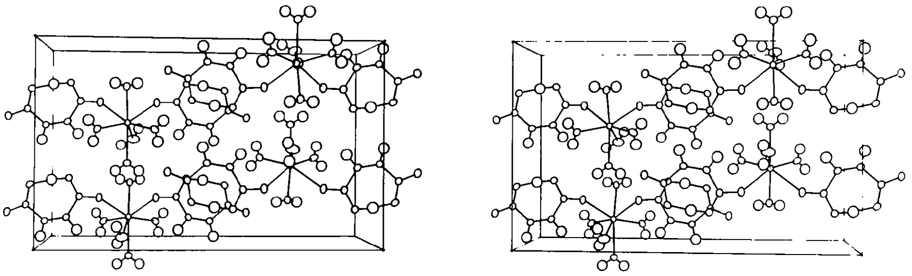

Fig. 3. Stereoscopic drawing of the contents of one unit cell.

Table 2. *Bond angles* (°) *for* $Ca(C_4H_3O_4)_2.5H_2O$

W(1)–Ca–*W*(3)	72·45 (8)	O(4)–Ca–*W*(4)*	83·09 (4)
W(1)–Ca–*W*(2)	143·10 (6)	Ca–O(4)–C(1)	139·44 (9)
W(1)–Ca–*W*(4)	75·20 (4)	O(4)–C(1)–O(3)	120·8 (1)
W(1)–Ca–O(4)	125·66 (3)	O(3)–C(1)–C(2)	120·5 (1)
W(2)–Ca–*W*(4)	79·16 (4)	O(4)–C(1)–C(2)	118·7 (1)
W(2)–Ca–*W*(3)	144·06 (8)	C(1)–C(2)–C(3)	130·7 (1)
W(2)–Ca–O(4)	76·02 (4)	C(2)–C(3)–C(4)	130·3 (1)
W(3)–Ca–*W*(4)	128·37 (17)	C(4)–O(1)–OHO	114 (1)
W(3)–Ca–*W*(4)*	117·59 (17)	O(1)–OHO–O(3)	171 (3)
W(3)–Ca–O(4)	75·02 (15)	OHO–O(3)–C(1)	113 (1)
W(3)–Ca–O(4)*	84·33 (15)	O(1)–C(4)–O(2)	122·7 (1)
W(4)–Ca–*W*(4)*	90·86 (6)	O(1)–C(4)–C(3)	119·4 (1)
O(4)–Ca–O(4)*	92·29 (5)	O(2)–C(4)–C(3)	117·9 (1)
O(4)–Ca–*W*(4)	155·14 (4)		

* In a position related to that in Table 1 by mirror symmetry.

the basis of $\sigma^2(F_o^2) = \sigma^2_{\text{counting}} + (0{\cdot}035 \times F_o^2)^2$. The standard deviation of an observation of unit weight was 1·97. The largest residual on a final difference Fourier map was 0·3 e Å^{-3}.

The final positional parameters are given in Table 1[*] and the bond angles in Table 2. Fig. 1 shows the molecular geometry and bond distances. Fig. 2 presents the coordination of the Ca atom. A stereoscopic view of the unit-cell contents is shown in Fig. 3.

Discussion. The Ca atom is in a somewhat distorted, seven-coordinate, monocapped trigonal prismatic environment, as shown in Fig. 2. The O atoms for *W*(1) and *W*(2) as well as the Ca ion are in the mirror plane. Water molecule *W*(3) is equally distributed over two sites, each of which is about 0·26 Å from the mirror plane. This is apparently mainly because of the steric crowding between *W*(1) and *W*(3). The short *W*(1)–*W*(3) distance (2·866 Å) would be even shorter if *W*(3) were not off the plane to enlarge the *W*(1)–*W*(3) distance. When refinement was performed with *W*(3) restricted to the mirror, the best agreement was $R(F^2) = 0{\cdot}101$, and the thermal motion perpendicular to the mirror was about four times that in the mirror. There are hydrogen bonds from *W*(2) and *W*(4) to the carboxyl oxygens O(1) and O(2) [*W*(2)···O(2) 2·779, *W*(4)···O(2) 2·711, *W*(4)···O(1) 2·771 Å].

The bond lengths and angles of the maleate moiety agree with those reported for other maleate mono-anion derivatives: KH maleate (Darlow, 1961); KH chloromaleate (Ellison & Levy, 1965); CuH maleate (Prout, Carruthers & Rossotti, 1971); LiH maleate (Gupta, Prasad & Gupta, 1975); and imidazolium hydrogen maleate (James & Matsushima, 1976). However, the distance between the intramolecular hydrogen-bonded O atoms is 2·426 (1) Å, which is longer than that found in either CuH maleate or imidazolium hydrogen maleate (2·409 Å) but shorter than in the KH maleate case (2·44 Å). The distance from OHO to O(1) is 1·31 (3) Å and that to O(3) is 1·13 (3) Å. The O(1)–OHO–O(3) angle is 171°. From these observations, it would seem that this intramolecular hydrogen bond is asymmetric. Since the nuclear positions of H atoms may not be the same as the centroid of the electronic distribution, a neutron diffraction study of this compound is under way to establish the hydrogen nuclear positions, as well as to examine the difference electron density in the maleate ion and, in particular, in the short hydrogen bond.

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References

Darlow, S. F. (1961). *Acta Cryst.* **14**, 1257–1259.

Ellison, R. D. & Levy, H. A. (1965). *Acta Cryst.* **19**, 260–268.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

Gupta, M. P., Prasad, S. M. & Gupta, T. N. P. (1975). *Acta Cryst.* **B31**, 37–40.

James, M. N. G. & Matsushima, M. (1976). *Acta Cryst.* **B32**, 1708–1713.

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

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[*] Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33144 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Di-μ-oxo-bis[oxo(η^5-cyclopentadienyl)molybdenum(V)]

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Abstract. (η^5-C_5H_5)$_2$$Mo_2O_4$, $C_{10}H_{10}O_4Mo_2$, M_r = 386·1, orthorhombic, a = 18·500 (3), b = 8·993 (2), c = 6·731 (1) Å, U = 1119·8 Å^3. Systematic extinctions: 0kl, $k + l = 2n + 1$; hk0, $h = 2n + 1$. Space group *Pnma* or $Pn2_1a$; *Pnma* from structure analysis. D_c = 2·29 g cm^{-3} for Z = 4; Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 22 cm^{-1}. The structure contains discrete molecules of crystallographic point group symmetry C_s, the mirror plane passing through the two *cis* terminal oxo ligands, the two Mo atoms and the centroid of each η^5-cyclopentadienyl ring. The two bridging O atoms complete the distorted octahedral coordination of each Mo atom.

Introduction. Small brown hexagonal plates of (η^5-C_5H_5)$_2$$Mo_2O_4$ were kindly supplied by Dr M. L. H. Green and Mr M. Bunker. They were sensitive to air and moisture and were sealed under dry nitrogen in glass capillary tubes. It was not possible to measure their density. After survey precession photography, the selected crystal was set up on a Nonius CAD-4F PDP8-controlled κ geometry diffractometer; cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflexions.

The intensities of reflexions with $\sin\theta/\lambda < 0·70$ Å^{-1} were measured by an $\omega/2\theta$ scan, a variable scan rate and an ω-scan angle of $(1·00 + 0·35 \tan\theta)^\circ$. Mo $K\alpha$ radiation was used with a graphite monochromator. Reflexions with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on simple counting statistics, were not included in subsequent calculations. Corrections were made for Lorentz and polarization effects, but not for absorption. A set of 1512 independent structure amplitudes was obtained.

The structure was solved by Patterson and Fourier techniques, with full-matrix least-squares refinement. All non-H atoms had anisotropic temperature factors. Difference syntheses permitted the location of the H atoms in their expected positions. They were positioned geometrically (C–H = 1·0 Å; $U_{\rm iso}$ = 0·05 Å^2) and included in the structure factor calculations, their location being readjusted after each cycle. In the final stages an overall isotropic extinction parameter (109·5) was introduced (Larson, 1967). Each reflexion was assigned a weight $w^{-1} = 1 + (0·1|F_o| - 1·5)^2$, chosen to minimize the variation of $w(|F_o| - |F_c|)^2$ with F_o. The final R_w was 0·038 for 1512 reflexions. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1975). Complex neutral-atom

Table 1. *Fractional atomic coordinates, with estimated standard deviations in parentheses*

	x	y	z
Mo(1)	0·20457 (2)	0·2500	0·09131 (7)
Mo(2)	0·07013 (2)	0·2500	−0·02220 (7)
O(1)	0·2025 (2)	0·2500	0·3441 (6)
O(2)	0·0210 (2)	0·2500	0·1904 (6)
O(3)	0·1430 (1)	0·4060 (3)	−0·0103 (4)
C(1)	0·2861 (4)	0·2500	−0·180 (1)
C(2)	0·3035 (3)	0·1262 (7)	−0·057 (1)
C(3)	0·3308 (3)	0·1770 (8)	0·115 (1)
C(4)	0·0594 (4)	0·2500	−0·373 (1)
C(5)	0·0227 (3)	0·3764 (7)	−0·3029 (8)
C(6)	−0·0381 (2)	0·3273 (5)	−0·1995 (7)
H(1)	0·2664	0·2500	−0·3179
H(2)	0·2966	0·0192	−0·0934
H(3)	0·3484	0·1131	0·2266
H(4)	0·1037	0·2500	−0·4580
H(5)	0·0374	0·4826	−0·3228
H(6)	−0·0755	0·3921	−0·1361

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Mo(1)–Mo(2)	2·602 (1)		
Mo(1)–O(1)	1·702 (4)	Mo(2)–O(2)	1·695 (4)
Mo(1)–O(3)	1·932 (3)	Mo(2)–O(3)	1·948 (3)
Mo(1)–C(1)	2·366 (7)	Mo(2)–C(4)	2·370 (7)
Mo(1)–C(2)	2·364 (5)	Mo(2)–C(5)	2·373 (5)
Mo(1)–C(3)	2·430 (5)	Mo(2)–C(6)	2·433 (4)
C(1)–C(2)	1·422 (9)	C(4)–C(5)	1·406 (7)
C(2)–C(3)	1·345 (10)	C(5)–C(6)	1·394 (7)
C(3)–C(3$^{\rm i}$)	1·313 (14)	C(6)–C(6$^{\rm i}$)	1·390 (10)
Mo(1)–O(3)–Mo(2)	84·2 (1)		
O(1)–Mo(1)–O(3)	109·9 (1)	O(2)–Mo(2)–O(3)	109·7 (1)
O(3)–Mo(1)–O(3$^{\rm i}$)	93·1 (2)	O(3)–Mo(2)–O(3$^{\rm i}$)	92·2 (2)
C(1)–C(2)–C(3)	108·6 (5)	C(4)–C(5)–C(6)	107·6 (5)
C(2)–C(3)–C(3$^{\rm i}$)	109·9 (4)	C(5)–C(6)–C(6$^{\rm i}$)	108·5 (3)
C(2$^{\rm i}$)–C(1)–C(2)	103·1 (7)	C(5$^{\rm i}$)–C(4)–C(5)	107·9 (6)

Symmetry code

None x,y,z (i) $x, \frac{1}{2} - y, z$