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An X-ray and Neutron Study of a Gel-Grown Phase of Calcium Malonate Dihydrate

By J. Albertsson, Å. Oskarsson* and C. Svensson

Inorganic Chemistry, Chemical Center, University of Lund, POB 740, S-220 07 Lund 7, Sweden

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A gel-grown phase of $Ca(C_3H_2O_4).2H_2O$ [monoclinic, space group $P2_1/c$, $a = 8{\cdot}7767$ (6), $b = 7{\cdot}7540$ (5), $c = 9{\cdot}8836$ (6) Å, $\beta = 106{\cdot}406$ (6)°, $Z = 4$] has been investigated with both X-ray and neutron diffraction. The structure refined to $R = 0{\cdot}022$ (X-rays) and 0·066 (neutrons). The malonate ion is coordinated to four different Ca^{2+} ions in layers stacked along **a**. Each Ca^{2+} ion is coordinated by five carboxylate and two water O atoms. The coordination polyhedron is a pentagonal bipyramid. Each water H atom is involved in a hydrogen bond linking the layers along **a**. The thermal parameters obtained in the neutron experiment are compatible with the C—H and O—H···O stretch frequencies obtained from IR spectra.

Introduction

In a previous communication (Briggman & Oskarsson, 1977) the structure of a crystal of calcium malonate dihydrate crystallizing in space group $C2/m$ was described. We denote this as (I). In (I) the Ca^{2+} and malonate ions form layers linked by hydrogen bonds donated by water molecules. The water O atoms are located on the mirror plane and one water molecule appears to have one of its H atoms statistically distributed across the plane. The structure of (I) was solved by X-ray methods. In order to elucidate further the hydrogen-bond system we tried several methods of growing single crystals large enough for neutron diffraction experiments. Only the gel method (see *Experimental*) gave large crystals. Chemical analysis showed that these crystals have the same composition as (I) but X-ray diffraction indicated space group $P2_1/c$. This second phase of $Ca(C_3H_2O_4).2H_2O$ is denoted (II). We report here the crystal structure of (II) determined by both X-ray and neutron diffraction experiments.

Our main reasons for proceeding with the structure determination of (II) were (i) statistical disorder is less apt to occur in space group $P2_1/c$ than in $C2/m$ and (ii) the conformations of the flexible malonate ion could be different in (II) and (I). In (I) both carboxylate groups are perpendicular to the plane through the C atoms. In a planar conformation of the malonate ion there is a severe O···O repulsion resulting in a distortion of the C—C—C angle. The malonate ions (mal) are planar in $(-)[Co(NO_2)en_2](+)[Comal_2en]$ with C—C—C angles close to 125° (Matsumoto & Kuroya, 1972). The malonate residues are also planar in potassium hydrogen malonate, with a C—C—C angle of 119·4° (Sime, Speakman & Parthasarathy, 1970). In (I) the angle has the unstrained value of 109·5 (2)°.

By a systematic study of the malonate salts of Group I and Group II metal ions we aim to elucidate the various influences of inter- and intramolecular forces on the geometry of the malonate ion. The crystal structures of (I), strontium malonate, and disodium malonate hydrate have been reported earlier (Briggman & Oskarsson, 1977; Oskarsson, 1978).

Experimental

Single crystals of (II) were obtained by the gel method (Henisch, Hanoka & Dennis, 1965*a*,*b*) as shown in Fig. 1. Two layers of silica gel were formed in a test tube by mixing sodium silicate with (i) malonic acid and (ii) hydrochloric acid. In the second layer two small single crystals of (I) were introduced as seeds, and on top of this was added calcium chloride solution. The test tube was kept at room temperature and after two days three single crystals had started to grow. They reached a volume of 5–10 mm³ in about ten days. The crystals had the same composition as (I) but belonged to another space group. Seeds of (I) did not grow under the conditions used. The formation of (II) instead of (I) may be a kinetic effect since (II) is transformed into (I) in 0·1 mol l^{-1} hydrochloric acid, *i.e.* (I) is the more stable compound.

Crystals of (II) are colourless with a tabular **a** habit. They are bounded by six to eight well developed faces. The Laue class is $2/m$ and the systematic absences $0k0$: $k \neq 2n$, $h0l$: $l \neq 2n$ uniquely determine

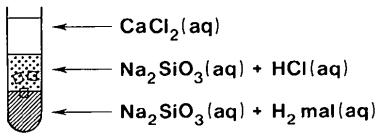

Fig. 1. The preparation of large single crystals of calcium malonate dihydrate (II).

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* To whom correspondence should be addressed.

the space group as $P2_1/c$. Unit-cell dimensions were determined by a least-squares treatment of 40 θ values measured on a four-circle diffractometer (CAD-4), as previously described (Danielsson, Grenthe & Oskarsson, 1976).

The crystal data, experimental parameters pertinent to the collection and reduction of the intensity data sets, and some information about the least-squares refinements are given in Table 1. The X-ray data were collected with Nb-filtered Mo $K\alpha$ radiation on the CAD-4 diffractometer. Neutron intensities were measured on a Hilger & Watts four-circle diffractometer at the R2 reactor, Studsvik, Sweden. The neutron beam was taken from a radial reactor channel and passed through a double monochromator system (Stedman, Almqvist, Raunio & Nilsson, 1969). The (200) planes of two copper crystals were used to give a wavelength of 1·210 Å. The neutron flux at the crystal was about 10^6 s^{-1} cm^{-2}. In both neutron and X-ray experiments three standard reflexions were measured at regular intervals to check the crystal and electronic stabilities; variations in their intensities were negligible. The neutron intensities were calculated with the peak-location method suggested by Lehmann & Larsen (1974). Values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization (X-ray only) and absorption effects, the latter by numerical integration [$\sigma_c(I)$ is based on counting statistics]. The linear absorption coefficient for neutrons was calculated as $\mu = 1{\cdot}50$ cm^{-1} from an assumed incoherent scattering for H of 40 b.

Structure determination and refinement

The positions of the non-H atoms were determined from X-ray data by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). The parameters were refined by full-matrix least squares (Table 1). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $[\sigma_c^2(|F_o|^2)/4|F_o|^2 + C|F_o|^2]^{-1}$. C was adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2\rangle$ were obtained in different $|F_o|$ and $\sin\theta$ intervals. The H atoms were located in a difference map. All non-H atoms were assigned anisotropic and all H atoms isotropic temperature factors. The latter parameters were also refined as a test of the data set. In the last cycle all parameter shifts were $<0{\cdot}05\sigma$. The X-ray scattering factors were taken from Doyle & Turner (1968) (Ca,O,C) and from Stewart, Davidson & Simpson (1965) for H.

The final X-ray parameters were used to begin the neutron refinement. All atoms were now assigned anisotropic temperature factors. This refinement converged towards larger values of R, R_w and S than did the X-ray refinement (Table 1). This was expected since the relatively small crystal (7·14 mm^3) used in the neutron-diffraction experiment gave rather weak inten-

Table 1. *Crystal data* (22°C), *collection and reduction of the intensity data, and the least-squares refinement*

Formula	$Ca(C_3H_2O_4).2H_2O$	a (Å)	8·7767 (6)	V (Å^3)	645·24
FW	178·16	b (Å)	7·7540 (5)	Z	4
Space group	$P2_1/c$ (monoclinic)	c (Å)	9·8836 (6)	D_x (g cm^{-3})	1·77
		β (°)	106·406 (6)		

	X-ray diffraction	Neutron diffraction
Crystal size (mm)	0·13 × 0·20 × 0·22	1·1 × 2·6 × 2·5
λ (Å)	0·71073	1·210
Take-off angle (°)	3	–
θ interval (°)	3–30	2–57
ω–2θ scan width $\Delta\omega$ (°)	0·6 + 1·1 tan θ	2·5–2·7
Minimum number of counts in a scan	3000	–
Maximum recording time (min)	3	~13
μ (cm^{-1})	8·78	1·50
Range of transmission factor (numerical integration)	0·81–0·87	0·71–0·86
Number of measured reflexions	1861	1796
Number of reflexions with zero weight	244 [$I < 3\sigma_c(I)$]*	444 [$I < 1{\cdot}5\sigma_c(I)$]
Number of reflexions used in the final refinements, m	1617	1352
Number of parameters refined, n	116	146
$R = \sum\|\Delta F\|/\sum\|F_o\|$†	0·022	0·066
$R_w = [\sum w(\Delta F)^2/\sum w\|F_o\|^2]^{1/2}$	0·029	0·067
$S = [\sum w(\Delta F)^2/(m-n)]^{1/2}$	1·71	2·04
C (weighting function)	4·9 × 10^{-5}	4 × 10^{-4}
g (×10^{-4}) (extinction)	0·59 (6)	0·10 (3)
Range of correction on $\|F_o\|$	1·00–1·06	1·00–1·07

* 11 strong reflexions were deleted during refinement because of a filter error during the intensity collection.

† $\Delta F = |F_o| - |F_c|$.

sities. In the final cycle the parameter shifts were $<0{\cdot}05\sigma$. The coherent scattering amplitudes for neutrons were taken from Bacon (1972).

Both data sets were tested for isotropic extinction (Zachariasen, 1967). The correction applied to $|F_o|$ differed from 1·00 for *ca* 10% of the X-ray and *ca* 20%

Table 2. *Positional coordinates with e.s.d.'s*

	X-ray			Neutron		
	x	*y*	*z*	*x*	*y*	*z*
Ca	0·23410 (2)	0·47021 (3)	0·61257 (2)	0·23434 (28)	0·47010 (33)	0·61264 (26)
C(1)	0·23147 (13)	0·73877 (15)	0·86496 (12)	0·23139 (21)	0·73880 (27)	0·86454 (19)
C(2)	0·07976 (14)	0·64423 (16)	0·87088 (12)	0·08061 (23)	0·64480 (28)	0·87120 (20)
C(3)	−0·05148 (13)	0·66391 (14)	0·73297 (11)	−0·05138 (21)	0·66409 (24)	0·73288 (19)
O(1)	0·30571 (10)	0·82717 (13)	0·96893 (9)	0·30586 (29)	0·82792 (35)	0·96896 (25)
O(2)	0·27618 (11)	0·71905 (13)	0·75608 (10)	0·27591 (29)	0·71963 (36)	0·75547 (26)
O(3)	−0·03613 (10)	0·58998 (12)	0·62264 (8)	−0·03626 (25)	0·58924 (31)	0·62286 (22)
O(4)	−0·16843 (10)	0·75690 (12)	0·73654 (10)	−0·16821 (26)	0·75683 (34)	0·73645 (25)
O(*W*1)	0·62202 (11)	0·75210 (13)	0·97410 (10)	0·62124 (28)	0·75249 (35)	0·97445 (24)
O(*W*2)	0·49563 (13)	0·45526 (16)	0·77647 (12)	0·49637 (32)	0·45489 (41)	0·77701 (31)
H(*W*11)	0·5251 (27)	0·7809 (33)	0·9695 (22)	0·51486 (58)	0·78732 (71)	0·97641 (53)
H(*W*12)	0·6773 (27)	0·7381 (30)	1·0553 (24)	0·68181 (57)	0·73614 (73)	1·07428 (47)
H(*W*21)	0·5613 (26)	0·3917 (29)	0·7757 (23)	0·57893 (61)	0·37310 (70)	0·77223 (57)
H(*W*22)	0·5409 (28)	0·5370 (28)	0·8344 (25)	0·54405 (61)	0·54472 (78)	0·83962 (60)
H(21)	0·0415 (20)	0·6866 (23)	0·9471 (18)	0·04168 (59)	0·69216 (77)	0·95961 (47)
H(22)	0·1074 (22)	0·5168 (21)	0·8855 (19)	0·11118 (60)	0·50871 (64)	0·88728 (53)

Table 3. *Thermal parameters with e.s.d.'s* ($\times 10^5$)

The form of the temperature factor is $\exp(-\beta_{11}h^2 - 2\beta_{12}hk - \ldots)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(*a*) X-ray experiment*						
Ca	384 (3)	500 (4)	252 (2)	−17 (2)	92 (2)	21 (2)
C(1)	441 (13)	689 (17)	426 (11)	118 (12)	44 (10)	−111 (11)
C(2)	575 (14)	891 (20)	324 (11)	25 (13)	133 (10)	−165 (4)
C(3)	416 (12)	596 (16)	373 (11)	−85 (12)	116 (9)	−80 (11)
O(1)	580 (11)	1169 (17)	486 (9)	57 (11)	35 (8)	−395 (10)
O(2)	690 (12)	1215 (18)	593 (10)	−300 (11)	314 (9)	−408 (11)
O(3)	502 (10)	871 (14)	349 (8)	37 (10)	110 (7)	−166 (9)
O(4)	515 (11)	973 (15)	552 (10)	142 (10)	113 (8)	−278 (10)
O(*W*1)	529 (12)	1077 (16)	479 (10)	−73 (11)	76 (9)	127 (10)
O(*W*2)	639 (13)	1244 (20)	861 (14)	237 (13)	−138 (11)	−311 (13)
(*b*) Neutron experiment						
Ca	454 (28)	588 (35)	341 (22)	−5 (27)	111 (19)	23 (25)
C(1)	439 (21)	773 (30)	319 (17)	42 (21)	65 (15)	200 (19)
C(2)	514 (23)	882 (33)	327 (18)	36 (21)	116 (16)	−25 (20)
C(3)	407 (21)	625 (28)	323 (17)	13 (19)	129 (14)	−96 (18)
O(1)	603 (29)	1152 (44)	427 (22)	35 (29)	59 (19)	−355 (27)
O(2)	668 (30)	1202 (44)	532 (24)	−318 (30)	303 (21)	−380 (27)
O(3)	479 (25)	875 (36)	326 (20)	74 (26)	75 (18)	−160 (23)
O(4)	484 (27)	1088 (41)	482 (22)	143 (28)	80 (19)	−279 (27)
O(*W*1)	606 (31)	1022 (41)	429 (24)	−74 (29)	94 (21)	151 (26)
O(*W*2)	682 (33)	1178 (49)	773 (33)	299 (36)	−144 (26)	−252 (33)
H(*W*11)	912 (66)	1518 (89)	877 (55)	−128 (61)	1961 (43)	−134 (55)
H(*W*12)	988 (59)	1746 (92)	613 (48)	−10 (66)	78 (42)	344 (56)
H(*W*21)	957 (65)	1403 (87)	1069 (60)	405 (65)	93 (49)	31 (60)
H(*W*22)	1055 (67)	1567 (97)	1006 (59)	166 (68)	32 (50)	−224 (67)
H(21)	1080 (63)	2083 (104)	535 (43)	19 (68)	332 (41)	−173 (55)
H(22)	1328 (72)	1139 (81)	866 (51)	151 (64)	257 (47)	319 (53)

* The isotropic temperature factors *B* for H obtained in the X-ray experiments are H(*W*11) 5·1 (5), H(*W*12) 4·2 (5), H(*W*21) 4·2 (5), H(*W*22) 3·8 (5), H(21) 2·6 (3), and H(22) 2·2 (3) Å^2.

of the neutron reflexions. Table 2 gives the atomic coordinates and Table 3 the thermal parameters.* The e.s.d.'s are two to three times larger for the neutron parameters than for those derived in the X-ray case. The two sets of coordinates for the ten non-H atoms are compared in the δp plot shown in Fig. 2 (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972). Ordered values of $\delta p_i = |\Delta p_i|/\sigma(\Delta p_i)$ are plotted *vs* the values expected for a half-normal distribution with zero mean and unit variance. The 30 points in the plot fall approximately on a straight line with slope 1·41 and intercept −0·01. No gross systematic error is indicated, but since $\sigma p(N)_i$ dominates $\sigma(\Delta p_i) = [\sigma^2 p(X)_i + \sigma^2 p(N)_i]^{1/2}$, it is impossible to make any statement about $\sigma p(X)_i$ from the slope of the line; $\sigma p(N)_i$ might on average be underestimated by the factor 1·4.

Description of the structure

Fig. 3 shows the unit-cell contents of (II). The structure is shown projected on the *ac* plane in Fig. 4. The Ca^{2+} ion is coordinated by five carboxylate and two water O atoms. The malonate forms a six-membered chelate ring with the Ca^{2+} ion. The coordination polyhedra are connected in pairs by edge sharing and are linked *via* the malonate ions in layers parallel to the *bc* plane. The layers are connected by hydrogen bonds donated by the water molecules. The packing coefficient, defined as the sum of the van der Waals volumes of the species in a unit cell divided by the cell volume (Kitaigorodsky, 1973; Briggman & Oskarsson, 1977), is 0·78 for (II) and 0·81 for (I). The molar volume of (II) is 4·6% larger than that for (I). The two values of the packing coefficient are compatible with the observation that (I) may be the thermodynamically more stable compound, in spite of the entropy gain when the chelate is formed in (II).

Fig. 5 shows one layer of the structure of (I) projected on the *bc* plane. There is no obvious relation between the structures of (I) and (II). In (I) the coordination polyhedra around the eight-coordinated Ca^{2+} ions form infinite chains along **b** by sharing edges. The coordination polyhedra are connected pairwise in (II), again by edge sharing. The hydrogen-bond system appears to be more efficient in (I) than in (II) as the environment of the hydrogen-bonded carboxylate O atoms is pseudotetrahedral in (I) but trigonal in (II).

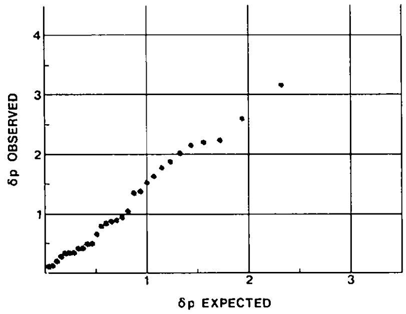

Fig. 2. A half-normal probability plot of the positional coordinates of the non-H atoms from the X-ray and neutron investigation. Slope: 1·41, intercept: −0·01.

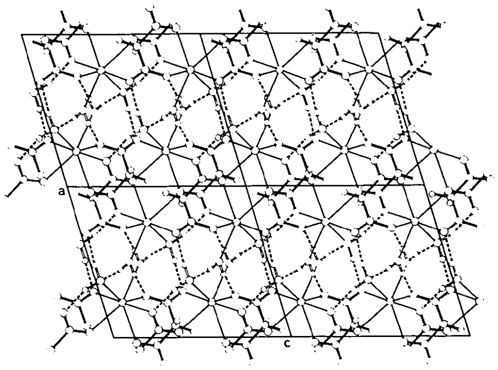

Fig. 4. The crystal packing of calcium malonate dihydrate (II). The structure is projected on the *ac* plane.

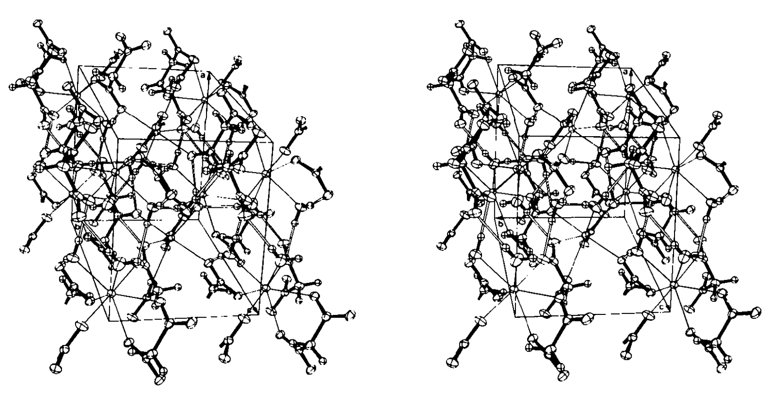

Fig. 3. The unit-cell contents of calcium malonate dihydrate (II).

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* Lists of structure factors for both X-ray and neutron determinations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33574 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The coordination polyhedron

Coordination number seven can usually be described equally well by several polyhedra. We have chosen a pentagonal bipyramid (ideal symmetry D_{5h}) for the Ca^{2+} coordination in (II). Fig. 6 shows the two connected polyhedra and Table 4 describes their geometry. The common edge is O(3)–O(3^{i}) and the distances from these atoms to Ca^{2+} are the longest Ca–O distances in the coordination sphere.

The malonate ion

The malonate ion and its hydrogen bonds are shown in Fig. 7. Table 5 gives intramolecular distances and angles. Each malonate ion is coordinated to four different Ca^{2+} ions. The one bonded in a chelate is included in Fig. 7. The chelate ring may be described as having a boat conformation with Ca^{2+} and C(2) on the same side of a plane through C(1), O(2), C(3), O(3).

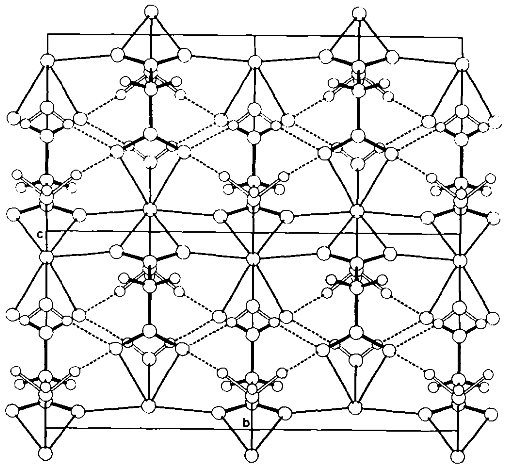

Fig. 5. The structure of a layer of calcium malonate dihydrate (I) projected on the *bc* plane.

The torsion angles in Table 5 show that the conformation of the malonate ion is similar to that observed in strontium malonate (Briggman & Oskarsson, 1977). In disodium malonate hydrate (Oskarsson, 1978) one of the carboxylate groups is in the plane of the three C atoms and the other rotated 60° out of this plane. Both carboxylate groups are perpendicular to the C–C–C plane in (I). The non-bonded O(2)···O(3) distance is 2·87 Å in (II). The corresponding O···O distances are 2·92 Å in the Sr^{2+} salt and 2·97 Å in the Na^{+} salt. In all three compounds

Table 4. *Some geometrical features of the coordination polyhedron*

The superscripts (i)–(vi) give the transformations applied to the x,y,z values in Table 2: (i) $\bar{x}, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (v) $\bar{x}, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$.

(*a*) Selected distances (Å)

	X-ray	Neutron
Ca–O(1^{iv})	2·320 (1)	2·317 (4)
Ca–O(2)	2·361 (1)	2·362 (4)
Ca–O(3)	2·575 (1)	2·577 (3)
Ca–O(3^{i})	2·521 (1)	2·523 (3)
Ca–O(4^{v})	2·404 (1)	2·405 (4)
Ca–O($W1^{iii}$)	2·408 (1)	2·411 (4)
Ca–O($W2$)	2·410 (1)	2·415 (4)
Ca–Ca^{i}	4·109 (1)	4·113 (5)
O(3)–O(3^{i})	3·016 (2)	3·015 (4)

(*b*) Deviations (Å) from the least-squares plane through O(2), O(3), O(3^{i}), O($W1^{iii}$), O($W2$)

O(2)	0·500	0·508
O(3)	−0·544	−0·551
O(3^{i})	0·371	0·372
O($W1^{iii}$)	−0·122	−0·120
O($W2$)	−0·265	−0·209
O(1^{iv})	2·248	2·241
O(4^{v})	−2·472	−2·476
Ca	−0·071	−0·074

The angle between the line O(1^{iv})–O(4^{v}) and the least-squares plane is 85·9° in both the X-ray and neutron determinations.

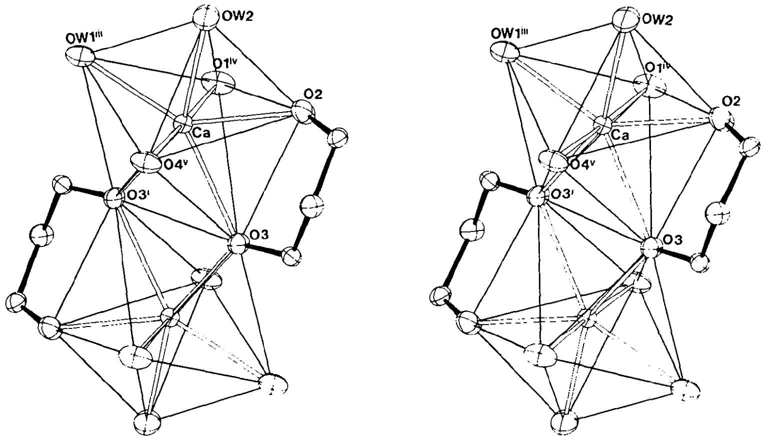

Fig. 6. The pair of connected coordination polyhedra.

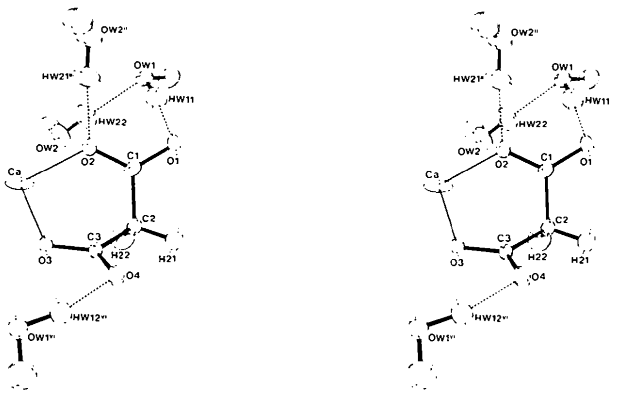

Fig. 7. The malonate ion and the hydrogen bonds in (II).

Table 5. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *in the malonate ion*

	X-ray	Neutron
C(1)–C(2)	1·536 (2)	1·528 (3)
C(2)–C(3)	1·524 (2)	1·529 (3)
C(1)–O(1)	1·254 (1)	1·260 (3)
C(1)–O(2)	1·255 (1)	1·255 (3)
C(3)–O(3)	1·272 (1)	1·272 (3)
C(3)–O(4)	1·263 (1)	1·261 (3)
C(2)–H(21)	0·96 (2)	1·088 (5)
C(2)–H(22)	1·02 (2)	1·089 (5)
C(1)–C(2)–C(3)	111·3 (1)	111·2 (2)
O(1)–C(1)–C(2)	119·0 (1)	118·8 (2)
O(2)–C(1)–C(2)	117·3 (1)	117·6 (2)
O(1)–C(1)–O(2)	123·6 (1)	123·6 (2)
O(3)–C(3)–C(2)	119·0 (1)	118·9 (2)
O(4)–C(3)–C(2)	116·6 (1)	116·6 (6)
O(3)–C(3)–O(4)	124·4 (1)	124·5 (2)
H(21)–C(2)–H(22)	110 (1)	109·3 (4)
O(1)–C(1)–C(2)–C(3)	136·3 (1)	136·3 (2)
O(2)–C(1)–C(2)–C(3)	−45·4 (1)	−45·1 (3)
O(3)–C(3)–C(2)–C(1)	68·7 (1)	68·8 (2)
O(4)–C(3)–C(2)–C(1)	−110·1 (1)	−110·2 (2)
O(2)–O(3)	2·866 (1)	2·867 (3)

the O···O repulsion causes strain in the C–C–C angle, which is 111·3° in (II), 112·5° in Sr(mal), and 114·9° in Na_2(mal).H_2O. There is no strain in (I). The rare-earth malonates are ionic compounds, as are the alkaline-earth malonates. In the rare-earth malonates the angles between the planes through the carboxylate groups and the C-atom chain vary in the range 28–70° (Hansson, 1973). The C–C–C angles are 109–118°. In the chelated compounds K[Mn(H_2O)$_2$(mal)$_2$].-2H_2O and K_3[Mn(mal)$_3$].2H_2O (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977) the torsion angles O–C–C–C are in the range 20–37° for O atoms bonded to Mn. The C–C–C angles are 114–120°.

The two halves of the malonate ion are in quite different environments in (II) (see Figs. 3 and 4). Table 5 shows that when bond lengths and angles around C(1) are compared with those around C(3) the differences are highly significant. The good agreement between chemical coordinates derived from the neutron and X-ray data and their small e.s.d.'s make the detection of these rather minute differences between the ligand halves feasible.

The C–H bond lengths in the methylene group are the same, 1·09 Å.* We have estimated the amplitude of the motion of each H atom relative to C(2) by calculating the difference r.m.s. component $R_{\rm CH}$ in the direction of the C–H bond as shown in Table 6. In this way we approximately remove the intermolecular thermal motion leaving the ground-state C–H stretch motion. If we also assume simple harmonic oscillation of the H atoms along the bonds, we can calculate the C–H stretch frequency from $\nu = h/(8\pi^2\, cR^2_{\rm CH})$ (Table 6). The average value (2850 cm^{-1}) is in the range expected for aliphatic C–H stretchings (2800–3000 cm^{-1}).

The water molecules

Table 7 lists the geometry of the two water molecules in (II) and of the hydrogen bonds they donate. In a survey of water-molecule geometry in crystalline hydrates determined by neutron diffraction, Ferraris & Franchini-Angela (1972) found $\frac{2}{3}$ of O–H lengths between 0·932 and 0·980 Å and $\frac{2}{3}$ of H–O–H angles within 105–111°. The observed geometries in (II) are thus unexceptional.

The four water H atoms are all within hydrogen-bonding distance of O atoms (H···O < 2·2 Å), as shown in Fig. 7. The water molecule *W*(1) donates bonds to the carboxylate O(1) and O(4) and accepts one from *W*(2). *W*(2) is also hydrogen-bonded to O(2). The crystal environment is tetrahedral for *W*(1) and trigonal for *W*(2). Ca^{2+} is near one of the lone-pair directions of *W*(1) but located on the twofold axis of *W*(2) (the bisector of the lone-pair orbitals). This is in contrast to the situation in (I) where, although one of the water molecules has a tetrahedral and the other a trigonal environment, both molecules are coordinated to Ca^{2+} along lone-pair directions.

The asymmetric O–H···O stretch frequencies are estimated in Table 6 in the same manner as the C–H frequencies. Values near 1500 and 2500 cm^{-1} are obtained. The geometry of the hydrogen bonds (Table 7) indicates that O(*W*1)···O(*W*2) is a weak bond and that the other three are of normal strength. In the IR spectra of (I) and (II) the O–H···O stretch frequencies appear to be in the intervals 2900–3300 cm^{-1} in (I) and 3100–3400 cm^{-1} in (II). This shift between (I) and (II) is compatible with more efficient hydrogen bonding in (I), as discussed above, since a stronger O···H bond gives a lower frequency for the

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* Our discussion of the H-atom part of the structure is, of course, based on results derived from the neutron data.

Table 6. *The root-mean-square components of thermal displacement* (Å) *and the corresponding harmonic frequencies* ($\rm cm^{-1}$) *along the* C–H *bonds in the methylene group and the* O···O *hydrogen bonds in the water molecules*

(*a*) The methylene group

	$R_{\rm CH}(\rm H)$	$R_{\rm CH}(\rm C)$	$R_{\rm CH}=[R^2_{\rm CH}(\rm H)-R^2_{\rm CH}(\rm C)]^{1/2}$	$\nu=16{\cdot}86/R^2_{\rm CH}$
C(2)–H(21)	0·1492	0·1259	0·0801	2630
C(2)–H(22)	0·1773	0·1611	0·0740	3080

(*b*) The water molecules

	$R_{\rm OO}(\rm H)$	$R_{\rm OO}(\rm O)$	$R_{\rm OO}=[R^2_{\rm OO}(\rm H)-R^2_{\rm OO}(\rm O)]^{1/2}$	$\nu=16{\cdot}86/R^2_{\rm OO}$
O(*W*1)–H(*W*11)	0·1893	0·1581	0·1041	1560
O(*W*1)–H(*W*12)	0·1600	0·1364	0·0836	2410
O(*W*2)–H(*W*21)	0·1714	0·1514	0·0803	2610
O(*W*2)–H(*W*22)	0·1963	0·1630	0·1094	1410

Table 7. *The geometry of the water molecules and the hydrogen bonds*

Distances are in Å and angles in degrees. The superscripts are explained in Table 4.

	X-ray	Neutron
O(*W*1)–H(*W*11)	0·87 (2)	0·977 (5)
O(*W*1)–H(*W*12)	0·82 (2)	0·988 (5)
H(*W*11)–O(*W*1)–H(*W*12)	113 (2)	105·3 (5)
O(*W*2)–H(*W*21)	0·76 (2)	0·974 (6)
O(*W*2)–H(*W*22)	0·87 (2)	0·947 (7)
H(*W*21)–O(*W*2)–H(*W*22)	106 (2)	108·3 (5)
O(1)···O(*W*1)	2·823 (1)	2·815 (3)
O(1)···H(*W*11)	1·96 (2)	1·842 (5)
O(1)···H(*W*11)–O(*W*1)	175 (2)	173·0 (5)
O(4)···O(*W*$1^{\rm vi}$)	2·724 (1)	2·724 (3)
O(4)···H(*W*$12^{\rm vi}$)	1·92 (2)	1·764 (5)
O(4)···H(*W*$12^{\rm vi}$)–O(*W*$1^{\rm vi}$)	168 (2)	163·0 (5)
O(2)···O(*W*$2^{\rm ii}$)	2·799 (1)	2·791 (4)
O(2)···H(*W*$21^{\rm ii}$)	2·04 (2)	1·820 (6)
O(2)···H(*W*$21^{\rm ii}$)–O(*W*$2^{\rm ii}$)	172 (2)	174·3 (5)
O(*W*1)···O(*W*2)	2·870 (2)	2·873 (4)
O(*W*1)···H(*W*22)	2·15 (2)	2·078 (6)
O(*W*1)···H(*W*22)–O(*W*2)	172 (2)	173·1 (5)

O–H stretching. $R_{\rm OO}$ in Table 6 should have been 0·0715 Å to give $\nu = 3300\ \rm cm^{-1}$. The actual amplitudes are not far from this value but the simple model of harmonic difference motion of the H atoms is not as accurate for the water molecules as it is for the methylene group.

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