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Structure of a Second Polymorph of Calcium Acetate Monohydrate

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Abstract. Ca(C₂H₃O₂)₂·H₂O, *M_r* = 176.18, triclinic, *P* $\bar{1}$, *a* = 6.700 (2), *b* = 9.801 (2), *c* = 12.257 (2) Å, α = 78.83 (2), β = 86.21 (2), γ = 73.63 (2)°, *V* = 757.6 (3) Å³, *Z* = 4, *D_x* = 1.545 g cm⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 7.7 cm⁻¹, *T* = 295 K, *F*(000) = 368, *R* = 0.029 for 2921 observed reflections with *I* > 2.5 σ (*I*). The structure consists of infinite O-bridged Ca layers that are connected in the third dimension by hydrogen bonds *via* water molecules of crystallization. The Ca atoms are seven and eight coordinated.

Introduction. Two crystal forms of Ca(OAc)₂ were obtained as a result of attempts to obtain good-quality crystals by crystallization under a variety of experimental conditions. Crystallization from pure water yielded needle-shaped crystals of a monohydrate for which the crystal structure has been reported previously (Klop, Schouten, van der Sluis & Spek, 1984). Addition of 10% ethanol resulted in large flat needles. The ethanol was added to decrease the solubility and thereby the viscosity. A high viscosity is known to hamper crystallization. A crystal structure determination of this compound was undertaken to characterize it and to find out whether the ethanol merely changed the habit or changed the complete structure.

Experimental. The colourless transparent crystal (0.2 × 0.4 × 0.6 mm) used in this study, cleaved from a large crystal, was obtained by evaporation from a saturated solution of Ca(OAc)₂ in a 10% ethanol/water mixture. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo *K*α radiation. Cell parameters and estimated standard deviations calculated from the setting

angles of 20 reflections ($10 < \theta < 15^\circ$). Data set: ω -scan mode, $\Delta\omega = 0.5 + 0.35 \tan\theta^\circ$, $1.70 < \theta < 27.50^\circ$, *h*–8→0, *k*–12→12, *l*–15→15, total of 3781 reflections measured, 3480 unique. Standard reflections ($\bar{3}\bar{1}6$, $\bar{3}33$), measured every 2 h, showed a linear decay of 2% and 1% fluctuation during 60 h of X-ray exposure time. Intensity data corrected for decay and *L_p* but not for absorption. Standard deviation calculated following McCandlish, Stout & Andrews (1975); $\sigma^2(I) = \sigma_{cs}^2(I) + (PI)^2$ with *P* = 0.012. 2921 unique reflections considered observed [*I* > 2.5 σ (*I*)]. Structure solved by Patterson and Fourier techniques and refined on *F* by full-matrix least-squares procedures. Anisotropic thermal parameters for all non-hydrogen atoms; isotropic thermal parameters for the water H atoms; one common isotropic temperature parameter for all methyl H atoms. All methyl groups were found to be disordered and refined with rigid methyl groups in two staggered positions with populations ranging from 40 to 60%. An empirical extinction correction was applied: $F^{\text{corr}} = F_{\text{calc}}[1 - (6.5 \times 10^{-7} F_{\text{calc}}^2 / \sin\theta)]$. Refinement converged at *R* = 0.029; ωR = 0.037 [$\omega^{-1} = \sigma^2(F)$]; 227 parameters; *S* = 0.51; (Δ/σ)_{av} = 0.03; (Δ/σ)_{max} = 0.77]. Maximum and minimum residual density 0.32 and –0.46 e Å⁻³ in the final difference Fourier map. Final atomic parameters are listed in Table 1.† Scattering factors of Cromer & Mann (1968). Anomalous-dispersion corrections from Cromer & Liberman (1970). Calculations carried out

† Lists of structure factors, anisotropic thermal parameters, methyl H-atom parameters, additional bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44114 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Final coordinates and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} (Å ²)
Ca(1)	0.21869 (6)	0.05726 (4)	0.40367 (3)	0.0247 (1)
Ca(2)	0.54180 (6)	0.33408 (4)	0.41511 (3)	0.0236 (1)
O(1)	0.6060 (2)	0.1839 (1)	0.6029 (1)	0.0318 (4)
O(2)	0.5656 (3)	0.4128 (1)	0.5987 (1)	0.0365 (5)
O(3)	0.2129 (2)	0.3036 (1)	0.4180 (1)	0.0314 (4)
O(4)	-0.1005 (2)	0.2930 (2)	0.3902 (1)	0.0355 (5)
O(5)	0.5829 (2)	0.0746 (2)	0.3973 (1)	0.0320 (4)
O(6)	0.9174 (2)	-0.0310 (2)	0.4035 (1)	0.0330 (4)
O(7)	0.2041 (3)	0.1135 (2)	0.2138 (1)	0.0452 (5)
O(8)	0.2040 (3)	0.3268 (2)	0.1156 (2)	0.0539 (6)
O(9)	0.5169 (3)	0.3717 (2)	0.2233 (1)	0.0474 (6)
O(10)	0.7768 (4)	0.4994 (3)	0.0896 (2)	0.087 (1)
C(1)	0.6034 (3)	0.2855 (2)	0.6524 (2)	0.0285 (6)
C(2)	0.6413 (5)	0.2549 (3)	0.7745 (2)	0.0487 (8)
C(3)	0.0275 (3)	0.3655 (2)	0.3874 (2)	0.0289 (6)
C(4)	-0.0359 (4)	0.5246 (2)	0.3456 (3)	0.0494 (8)
C(5)	0.7498 (3)	0.0131 (2)	0.3515 (2)	0.0273 (6)
C(6)	0.7467 (4)	-0.0081 (4)	0.2348 (2)	0.0544 (8)
C(7)	0.1916 (4)	0.1993 (3)	0.1251 (2)	0.0415 (6)
C(8)	0.1483 (9)	0.1519 (4)	0.0227 (3)	0.101 (2)
H(91)	0.588 (5)	0.412 (3)	0.166 (3)	0.061 (9)*
H(92)	0.420 (6)	0.370 (4)	0.182 (3)	0.10 (1)*
H(101)	0.762 (6)	0.571 (4)	0.013 (3)	0.10 (1)*
H(102)	0.878 (9)	0.450 (6)	0.092 (5)	0.17 (2)*

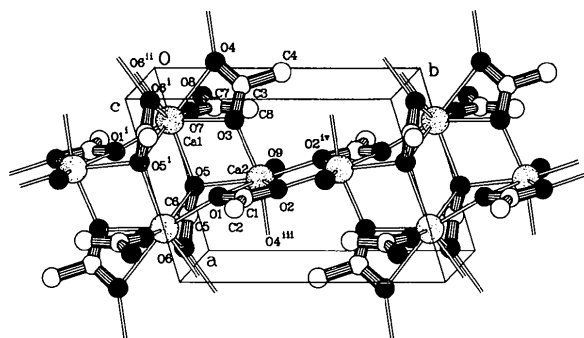
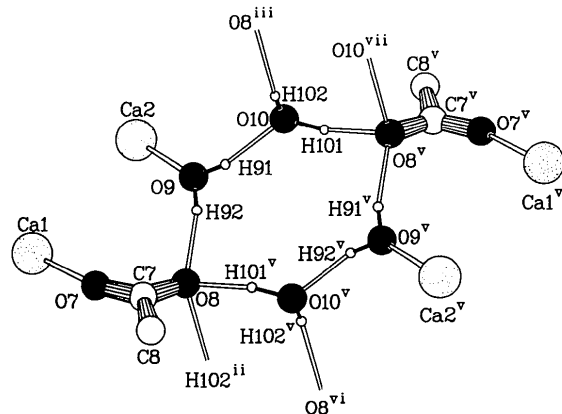
* Isotropic U values.Fig. 1. Projection of the structure illustrating part of an oxygen-bridged Ca sheet parallel to the ab plane, the Ca coordination and atomic numbering. Two neutral clusters are shown. H atoms and part of the water molecules have been omitted. For symmetry code see Table 2.

Fig. 2. Part of the infinite hydrogen-bond chain connecting the Ca ions of two different sheets. For symmetry code see Table 2.

Table 2. Relevant bond distances (Å) and angles (°) for $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, polymorph II

Ca(1)...O(1 ⁱ)	2.339 (1)	O(1)—C(1)	1.258 (2)
Ca(1)...O(3)	2.444 (1)	O(2)—C(1)	1.257 (2)
Ca(1)...O(4)	2.656 (2)	O(3)—C(3)	1.265 (3)
Ca(1)...O(5)	2.489 (2)	O(4)—C(3)	1.254 (3)
Ca(1)...O(5 ⁱ)	2.762 (2)	O(5)—C(5)	1.264 (3)
Ca(1)...O(6 ⁱ)	2.469 (1)	O(6)—C(5)	1.252 (3)
Ca(1)...O(6 ⁱⁱ)	2.410 (2)	O(7)—C(7)	1.231 (3)
Ca(1)...O(7)	2.287 (1)	O(8)—C(7)	1.258 (3)
Ca(2)...O(1)	2.472 (1)	C(1)—C(2)	1.493 (3)
Ca(2)...O(2)	2.544 (1)	C(3)—C(4)	1.490 (3)
Ca(2)...O(2 ^{iv})	2.355 (1)	C(5)—C(6)	1.487 (4)
Ca(2)...O(3)	2.303 (2)	C(7)—C(8)	1.492 (5)
Ca(2)...O(4 ⁱⁱⁱ)	2.325 (2)	O(9)—H(91)	0.91 (4)
Ca(2)...O(5)	2.531 (2)	O(9)—H(92)	0.85 (4)
Ca(2)...O(9)	2.318 (1)	O(10)—H(101)	1.05 (4)
		O(10)—H(102)	0.71 (6)
Ca(1)...O(1 ⁱ)—C(1)	142.3 (1)	O(1)—C(1)—C(2)	120.0 (2)
Ca(1)...O(3)—C(3)	97.9 (1)	O(2)—C(1)—C(2)	120.4 (2)
Ca(1)...O(4)—C(3)	88.3 (1)	O(3)—C(3)—O(4)	120.2 (2)
Ca(1)...O(5)—C(5)	134.5 (1)	O(3)—C(3)—C(4)	119.4 (2)
Ca(1)...O(5 ⁱ)—C(5)	85.9 (1)	O(4)—C(3)—C(4)	120.4 (2)
Ca(1)...O(6 ⁱⁱ)—C(5 ⁱⁱ)	99.9 (1)	O(5)—C(5)—O(6)	120.8 (2)
Ca(1)...O(6 ⁱ)—C(5 ⁱ)	134.5 (1)	O(6)—C(5)—C(6)	119.7 (2)
Ca(1)...O(7)—C(7)	152.2 (2)	O(7)—C(7)—O(8)	124.3 (2)
Ca(2)...O(1)—C(1)	96.2 (1)	O(7)—C(7)—C(8)	118.0 (3)
Ca(2)...O(2)—C(1)	92.8 (1)	O(8)—C(7)—C(8)	117.6 (3)
Ca(2)...O(2 ^{iv})—C(1 ^{iv})	152.9 (1)	H(91)—O(9)—H(92)	94. (3)
Ca(2)...O(3)—C(3)	143.7 (1)	H(101)—O(10)—H(102)	109. (5)
Ca(2)...O(4 ⁱⁱⁱ)—C(4 ⁱⁱⁱ)	115.8 (1)	O(5)—C(5)—C(6)	119.6 (2)
O(1)—C(1)—O(2)	119.6 (2)		

Hydrogen bonds

O—H...O	O...O	O—H	H...O	∠O—H...O
O(9)—H(91)...O(10)	2.709 (3)	0.91 (4)	1.83 (3)	161 (3)
O(9)—H(92)...O(8)	2.728 (3)	0.85 (4)	1.89 (4)	166 (4)
O(10)—H(101)...O(8 ^v)	2.769 (3)	1.05 (4)	1.73 (4)	167 (4)
O(10)—H(102)...O(8 ⁱⁱⁱ)	2.888 (4)	0.71 (6)	2.18 (6)	169 (6)

Symmetry code: (i) $1-x, -y, 1-z$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, -z$; (vi) $-x, 1-y, -z$; (vii) $2-x, 1-y, -z$.

on the CYBER-855 of the University of Utrecht with programs of the *SHELX76* (Sheldrick, 1976) package and on a MicroVAX-II with programs of the *EUCLID* (Spek, 1982) package.

Discussion. The structure (Fig. 1) consists of neutral clusters formed by four Ca cations, eight acetate anions and two coordinating water molecules. Within this cluster two kinds of interactions are observed: a unidentate mode in which the Ca ion coordinates with only one of the acetate O atoms and a bidentate mode in which the acetate ion uses both O atoms to chelate the Ca. All acetate ions that have bidentate interactions are also involved in one or two unidentate bridging interactions. The clusters are connected into chains in the [010] direction *via* oxygen bridges over two inversion centres. These chains are joined into sheets perpendicular to the [001] direction *via* oxygen bridges across two inversion centres and four additional oxygen bridging unidentate interactions. Part of this sheet and the atomic numbering are depicted in Fig. 1. One of the acetate ions and two water molecules join

these sheets into a three-dimensional network by hydrogen bonds. The hydrogen bonds themselves form infinite chains in the [100] directions. This network and the atomic numbering are depicted in Fig. 2. Relevant data on the geometries of the acetate ions, the water molecules, the hydrogen bonds and Ca coordinations are collected in Table 2. Only one of the two crystallographically independent water molecules coordinates to Ca in this polymorph of $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ as opposed to two in the previously studied monohydrate. The carboxyl geometry and Ca–carboxyl interactions are comparable with the results of Einspahr & Bugg (1981). The present bond distances, bond angles and planarity of the acetate ions lie well within the ranges reported there. The two interaction modes found in our study are common to acetate–calcium interactions. For both interaction modes different geometries have been reported previously. The bidentate mode has Ca–O distances between 2.4 and 2.8 Å and Ca–O–C angles between 80 and 100°. The interactions of Ca(1) with O(3) and O(4), Ca(1) with O(5¹) and O(6¹) and of Ca(2) with O(1) and O(2) are also found in the present structure. The unidentate mode has Ca–O distances between 2.2 and 2.6 Å and Ca–O–C angles between 100 and 180°. All non-bidentate Ca–O interactions are unidentate. The distances and angles lie within the ranges reported. For Ca, coordination numbers ranging from six to nine have been reported but the most commonly occurring coordination numbers are seven and eight, the numbers also found in this study. The

slight tendency for the higher coordination numbers to form larger Ca–O distances is also reflected in this study (Table 2). The Ca ions have a closed-shell electronic configuration (p^6). Such ions allow a wide range in angular distortion in the polyhedra formed by the surrounding oxygen atoms. Ca(1) is coordinated by eight acetate O atoms. The coordination can be described as a distorted monocapped pentagonal bipyramid. Ca(2) is coordinated by six acetate O atoms and one water O atom. This coordination can be described as a distorted pentagonal bipyramid. These two coordination types are also found in the previously reported polymorph of calcium acetate monohydrate (Klop, Schouten, van der Sluis & Spek, 1984) and in the structure of the related calcium hydrogen triacetate monohydrate (Klop & Spek, 1984).

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p-Nitrophenoxyacetamide

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Abstract. $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$, $M_r = 197.2$, monoclinic, $P2_1/c$, $a = 7.818$ (2), $b = 7.589$ (2), $c = 14.790$ (2) Å, $\beta = 98.43$ (2)°, $V = 868.02$ Å³, $Z = 4$, $D_m = 1.506$ (3), $D_x = 1.501$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.79$ mm⁻¹, $F(000) = 408$, $T = 426$ (1) K, final $R = 0.0507$ for 798 observed reflections [$I \geq 2\sigma(I)$]. The molecules are hydrogen bonded: N–H...O =

2.886 (3), N–H = 0.97 (7), H–O = 1.92 (6) Å, N–H...O angle = 175.5 (8)°.

Introduction. The title compound is known for its auxion and hypoglycemic activity. Its crystal and molecular structure determination was undertaken as part of a programme to establish structure–activity