The elusive crystals of calcium acetate hemihydrate: chiral rods linked by parallel hydrophilic strips

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Electronic supplementary information

Contents

1. XRPD data and discussion relating to the calcium acetate starting material

X-ray powder diffraction analysis was performed on the $Ca(OAc)_2 \cdot H_2O$ ($OAc^- = CH_3COO^-$) to determine the purity of the starting material. As is apparent from inspection of Figure S1, there is a good match between the experimentally determined powder pattern (black) and the calculated pattern of the monohydrate (blue). There are some very small additional peaks in the experimentally determined powder pattern which match intense peaks in the calculated powder pattern of the hemihydrate (red). This is consistent with the presence of a trace quantity of the hemihydrate in the monohydrate sample. Inspection of the bulk monohydrate under a microscope failed to identify the block-like crystals of the type isolated from 1,4-dioxane, indicating that the original hemihydrate was present as a microcrystalline solid.

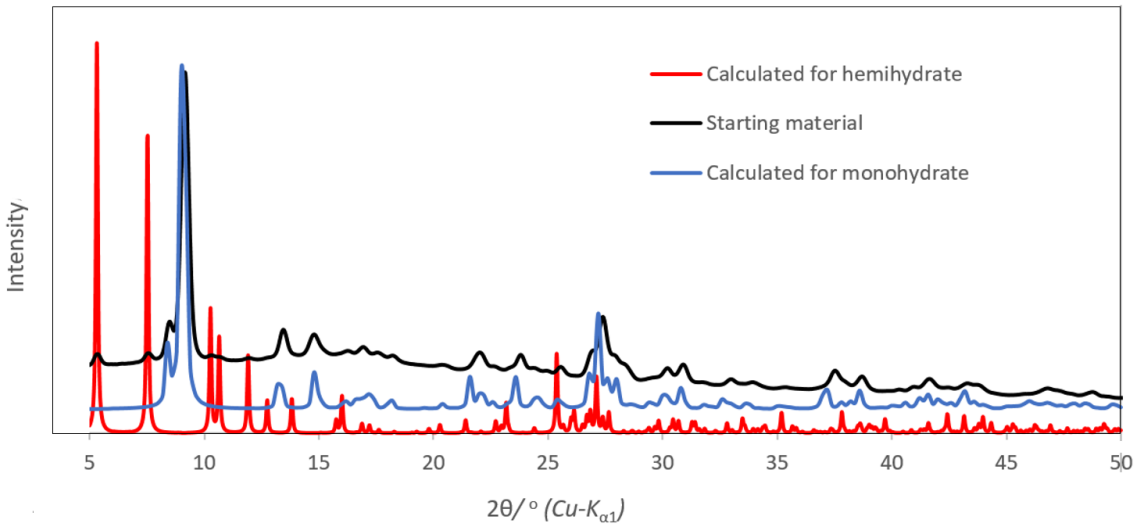


Figure S1 Measured XRPD pattern of the starting material (black) , measured at 100 K, and the calculated patterns of $Ca(OAc)_2 \cdot H_2O$ (blue) and $Ca(OAc)_2 \cdot ½H_2O$ (red). Whilst the starting material is composed mainly of the monohydrate, trace amounts of the hemihydrate are present.
The calculated pattern of $Ca(OAc)_2 \cdot H_2O$ is based on the room temperature structure reported by E. Klop *et al*, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 51-53.

2. Experimental details relating to alternative attempted synthetic procedures

The formation of the hemihydrate in a 1,4-dioxane solution containing dissolved 4-hydroxybenzoic acid prompted an investigation to determine the importance of the 4-hydroxybenzoic acid in the generation of the hemihydrate crystals. The following reactions were performed to determine whether the hemihydrate could be formed under similar conditions that yielded $Ca(OAc)_2 \cdot ½H_2O$ but in the absence of the 4-hydroxybenzoic acid or using different solvents.

i) Benzoic acid (0.488 g, 4.00 mmol) was dissolved in 1,4-dioxane (8 mL) and added to a suspension of $Ca(OAc)_2 \cdot H_2O$ (0.316 g, 1.80 mmol) in 1,4-dioxane (4 mL).

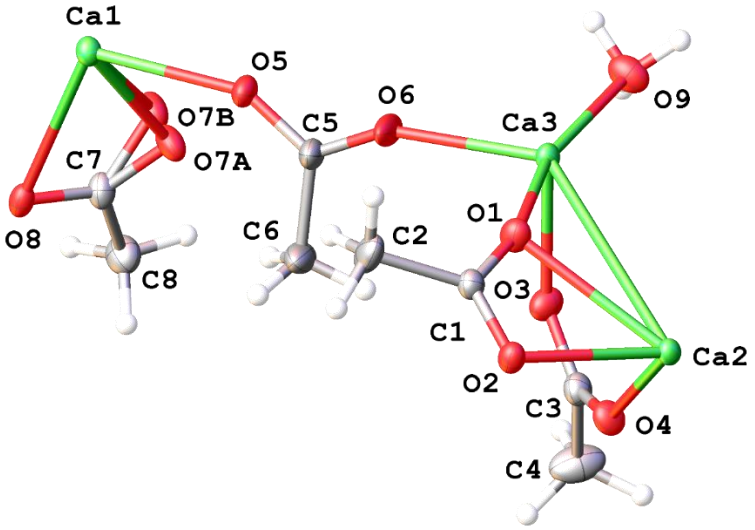
ii) Phenol (0.376 g, 4.00 mmol) was dissolved in 1,4-dioxane (8 mL) and added to a suspension of $Ca(OAc)_2 \cdot H_2O$ (0.316 g, 1.80 mmol) in 1,4-dioxane (4 mL).

iii) 4-hydroxybenzoic acid (0.552 g, 4.00 mmol) was dissolved in methanol (8 mL) and added to a suspension of $Ca(OAc)_2 \cdot H_2O$ (0.316 g, 1.80 mmol) in methanol (4 mL).

iv) 4-hydroxybenzoic acid (0.552 g, 4.00 mmol) was dissolved in ethanol (8 mL) and added to a suspension of $Ca(OAc)_2 \cdot H_2O$ (0.316 g, 1.80 mmol) in ethanol (4 mL).

v) A suspension of $Ca(OAc)_2 \cdot H_2O$ (0.316 g, 1.80 mmol) was added to 1,4-dioxane (12 mL).

In each of the five cases indicated above, no usable single crystals of the hemihydrate were formed after 7 days.



3. Figure S2 Asymmetric unit of calcium acetate hemihydrate, $Ca(OAc)_2 \cdot ½H_2O$ (OAc = CH_3COO), showing the labelling scheme and 50% probability displacement ellipsoids. Oxygen O7 is disordered between two positions, O7A and O7B. The hydrogen atoms on each coordinated water molecule are disordered between three positions which align with the directions to the closest oxygen atoms. One of the neighbours of the oxygen atom of the coordinated water (labelled O9) is a symmetry-related O9 on a neighbouring rod (O9···O9 distance 2.932 Å). The hydrogen atom bonded to the oxygen oriented along this direction must therefore have a maximum occupancy of 0.5.

4. Table S1 Selected bond lengths for $Ca(OAc)_2 \cdot \frac{1}{2}H_2O$.

Atoms		Length/Å	Atoms		Length/Å
C1	C2	1.504(3)	Ca1	O7B	2.448(7)
C1	O1	1.258(2)	Ca1	O8	2.7898(14)
C1	O2	1.262(2)	Ca2	Ca3	3.7861(4)
C3	C4	1.512(3)	Ca2	O1	2.6203(14)
C3	O3	1.258(2)	Ca2	O2	2.4839(13)
C3	O4	1.256(2)	Ca2	O4	2.3060(13)
C5	C6	1.498(3)	Ca2	$O8^{II}$	2.4447(12)
C5	O5	1.263(2)	Ca3	$Ca3^{I}$	4.0415(7)
C5	O6	1.255(3)	Ca3	O9	2.3765(14)
C7	C8	1.495(3)	Ca3	O1	2.2958(13)
C7	O7A	1.251(7)	Ca3	O3	2.3111(14)
C7	O7B	1.307(12)	Ca3	$O5^{I}$	2.4846(14)
C7	O8	1.264(2)	Ca3	$O6^{I}$	2.5236(16)
Ca1	$O2^{II}$	2.3758(13)	Ca3	O6	2.3459(16)
Ca1	O5	2.3568(14)	Ca3	$O8^{III}$	2.4394(13)
Ca1	O7A	2.464(7)			

$^{I}3/2-X,+Y,1-Z$; $^{II}1/4+Y,-1/4+X,3/4-Z$; $^{III}+X,+Y,1+Z$

5. Table S2 Selected bond angles for $Ca(OAc)_2 \cdot \frac{1}{2}H_2O$.

Atoms			Angle/˚	Atoms			Angle/˚
O4	Ca2	$O1^{V}$	157.27(4)	O5	Ca1	O7B	85.9(6)
O4	Ca2	O1	84.15(4)	O4	Ca2	$O8^{VI}$	81.41(5)
O4	Ca2	$O2^{V}$	151.84(4)	$O4^{V}$	Ca2	$O8^{VI}$	85.70(4)
O4	Ca2	O2	96.78(5)	$O8^{VI}$	Ca2	O1	71.89(4)
$O4^{V}$	Ca2	O4	88.91(7)	$O8^{VI}$	Ca2	$O1^{V}$	119.44(4)
O4	Ca2	$O8^{IV}$	85.70(5)	$O8^{IV}$	Ca2	$O2^{V}$	122.38(4)
O9	Ca3	$O5^{I}$	81.86(5)	$O8^{VI}$	Ca2	$O2^{V}$	71.61(4)
$O2^{III}$	Ca1	$O2^{IV}$	84.08(6)	$O8^{IV}$	Ca2	$O8^{VI}$	161.91(7)
$O2^{IV}$	Ca1	$O7A^{II}$	175.4(6)	O1	Ca3	$O8^{VI}$	77.83(5)
$O2^{III}$	Ca1	$O7A^{II}$	94.5(5)	O9	Ca3	$O6^{I}$	80.43(6)
$O2^{III}$	Ca1	O7B	169.7(8)	O9	Ca3	$O8^{VI}$	86.44(5)
$O2^{IV}$	Ca1	O7B	105.3(6)	O1	Ca3	O9	162.98(6)
$O2^{III}$	Ca1	$O8^{II}$	67.32(4)	O1	Ca3	O3	92.47(5)
$O2^{IV}$	Ca1	$O8^{II}$	134.27(4)	O1	Ca3	$O5^{I}$	87.22(5)
$O5^{II}$	Ca1	$O2^{III}$	83.20(5)	O1	Ca3	$O6^{I}$	102.88(6)
O5	Ca1	$O2^{III}$	99.71(5)	O1	Ca3	O6	101.43(6)
O5	Ca1	$O5^{II}$	176.12(8)	O5	Ca1	$O7B^{II}$	90.9(6)
O5	Ca1	$O7A^{II}$	101.3(5)	$O5^{II}$	Ca1	$O8^{II}$	110.80(4)
O5	Ca1	O7A	75.8(5)	$O5^{II}$	Ca1	O8	68.33(4)
$O5^{II}$	Ca1	O7B	90.9(6)	$O7A^{II}$	Ca1	O7A	87.3(11)
O7A	Ca1	$O8^{II}$	111.18(18)	O6	Ca3	O9	95.24(7)

Atoms			Angle/˚	Atoms			Angle/˚
O7A^{II}	Ca1	O8^{II}	48.26(12)	O6	Ca3	O5^{I}	118.25(5)
O7B^{II}	Ca1	O7B	65.8(11)	O6	Ca3	O6^{I}	67.02(7)
O7B	Ca1	O8^{II}	107.4(3)	O6	Ca3	O8^{VI}	169.23(5)
O7B^{II}	Ca1	O8^{II}	49.3(2)	O8^{VI}	Ca3	O5^{I}	72.51(5)
O8	Ca1	O8^{II}	155.72(5)	Ca1^{VII}	O2	Ca2	116.76(5)
O1^{V}	Ca2	O1	109.84(6)	O2^{V}	Ca2	O1	80.03(4)
O8^{VI}	Ca3	O6^{I}	123.72(5)	O2^{V}	Ca2	O1^{V}	50.82(4)
Ca3	O1	Ca2	100.52(5)	O2	Ca2	O2^{V}	91.11(6)
O3	Ca3	O9	91.77(5)	Ca1	O5	Ca3^{I}	115.51(5)
O3	Ca3	O5^{I}	154.22(5)	Ca3	O6	Ca3^{I}	112.14(6)
O3	Ca3	O6^{I}	151.89(5)	Ca2^{VIII}	O8	Ca1	104.30(5)
O3	Ca3	O6	87.09(5)	Ca3^{VIII}	O8	Ca1	102.90(5)
O3	Ca3	O8^{VI}	82.22(5)	Ca3^{VIII}	O8	Ca2^{VIII}	101.65(5)
O5^{I}	Ca3	O6^{I}	51.59(5)				

^{I}3/2-X,+Y,1-Z; ^{II}3/2-X,+Y,-Z; ^{III}5/4-Y,-1/4+X,-3/4+Z; ^{IV}1/4+Y,-1/4+X,3/4-Z; ^{V}1/4+Y,-1/4+X,7/4-Z; ^{VI}+X,+Y,1+Z; ^{VII}1/4+Y,5/4-X,3/4+Z; ^{VIII}+X,+Y,-1+Z