

The elusive crystals of calcium acetate hemihydrate: Chiral rods linked by parallel hydrophilic strips[†]

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Abstract

Calcium acetate hemihydrate is found in the efflorescent salts that form on pottery and other calcareous heritage artefacts. The formation of these salts can lead to deterioration of these objects. A recent analysis of the structure of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ by X-ray powder diffraction (XRPD) has revealed it has a remarkable and surprisingly complex structure. Although the compound usually exists in powder or microcrystalline form, often in mixtures with other salts, we have serendipitously managed to grow crystals of a size suitable for single crystal X-ray diffraction. Our single crystal data show the structure is based on infinite supramolecular polymeric rods that are chiral. Each rod has a minimum diameter of 1.75 nm and the external surface of each rod features four parallel, hydrophobic domains separated by hydrophilic strips. Each hydrophilic strip consists of acetate oxygen atoms and coordinated water molecules that are able to form hydrogen bonding interactions with symmetry-related strips on a neighbouring rod in an arrangement that resembles a zipper. Within the extended crystal structure each rod is bound to four rods of opposite handedness to give a racemic mixture.

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For ESI and crystallographic data in CIF or other electronic format see DOI: xxxx/xxxx

Introduction

Whilst calcium acetate may be thought of as a simple salt, it exists in a range of polymorphs in both anhydrous and hydrated solid phases. Anhydrous calcium acetate, $\text{Ca}(\text{OAc})_2$ ($\text{OAc} = \text{CH}_3\text{COO}$), exists in three polymorphic forms, designated as α , β and γ .^{1,2} Whilst the structures of the β and γ polymorphs are unknown, a study of the α form using XRPD was published in 2020.¹ This compound is formed by thermal dehydration of calcium acetate monohydrate and exists in both high and low temperature phases. Both phases contain channels formed by calcium centres bridged by acetate units. The phase change is reversible and involves a monodentate acetate group in the low temperature form becoming bidentate in the high temperature form.

Calcium acetate forms a number of different solid phases in association with water with known crystal structures.³⁻⁶ The different forms of hydrated calcium acetate were catalogued by Miller *et al* in 2019.^{6,7} Structures of derivatives of calcium acetate that contain both coordinated and uncoordinated acetic acid molecules are also known, with formulas $\text{Ca}(\text{OAc})_2(\text{HOAc})^6$ and $\text{Ca}(\text{OAc})_2(\text{HOAc})\cdot\text{H}_2\text{O}$.^{6,8}

The most common form of hydrated calcium acetate is the monohydrate, $\text{Ca}(\text{OAc})_2\cdot\text{H}_2\text{O}$, which is obtained by crystallization of calcium acetate from aqueous solution. Its structure consists of double-stranded O-bridged Ca chains with bridging and monodentate acetate groups, held together by hydrogen bonding interactions between coordinated water molecules and the oxygen atoms of acetate units.⁴

The commercially available hemihydrate of calcium acetate, $\text{Ca}(\text{OAc})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ ⁹, is an intermediate product in the synthesis of the anhydrous form.² It is also found in the white or grey efflorescent salt deposits on the exterior of porous calcareous heritage artefacts, which include shell collections in museums¹⁰ and ancient pottery such as the ceramic collection from the Agora of Athens.¹¹ The salts are thought to form as a result of reaction of calcium compounds in the artefacts with acetic acid vapour released by wooden storage cabinets.¹² The efflorescence can cause deterioration of the artefacts, affecting both their exteriors and interiors, and intervention strategies may be required to conserve them. It is particularly likely to form in cracks and structural defects, which can damage the artefacts further.^{10,11}

As an efflorescent salt, the hemihydrate usually exists in powder or microcrystalline form, often in mixtures with other salts.¹¹ Despite the fact that the compound is well known, the difficulty in obtaining suitable crystals has prevented structural characterization by single crystal X-ray diffraction. A recent, elegant analysis of a sample of $\text{Ca}(\text{OAc})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ by XRPD by Bette *et al*¹³ has shown that it possesses a remarkable rod-like structure with Ca(II) centres located within a cylindrical surface and bridged by acetate anions.

As part of an investigation into porous crystalline networks, we recently reported a series of polymeric materials synthesised from metal acetates and 4-hydroxybenzoic acid (H_2hba).^{14,15} The acetate ion acted as a base in the formation of metal-hba polymeric networks. In an attempt to generate a calcium-hba coordination polymer, we suspended a mixture of calcium acetate monohydrate and 4-hydroxybenzoic acid in 1,4-dioxane. A small number of colourless, block-shaped crystals formed after several days. X-ray diffraction data were collected and we were surprised to find the crystals were not the expected product, but rather calcium acetate hemihydrate. Presumably the serendipitous crystallization from the non-aqueous solvent, 1,4-dioxane, has promoted the growth of the elusive $\text{Ca}(\text{OAc})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ crystals.

The crystals we obtained have provided the rare opportunity for the analysis of the structure of $\text{Ca}(\text{OAc})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ by single crystal X-ray diffraction. Our single crystal data confirm the key details of the structural analysis from the XRPD study and in addition provide accurate molecular geometries.

Furthermore, the single crystal structure determination yields detailed information regarding interrod interactions.

Experimental section

Synthesis

4-hydroxybenzoic acid (0.552 g, 4.00 mmol) was dissolved in 1,4-dioxane (8 mL) and added to a suspension of $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.316 g, 1.88 mmol) in 1,4-dioxane (4 mL). The resulting suspension was allowed to stand for 7 days, over which time colourless, block-shaped crystals formed. Yield: <1%.

Details relating to the attempted synthesis of the crystals using alternative approaches are included in the Supplementary Information.

X-ray crystallography

Data were collected on an Oxford Diffraction SuperNova diffractometer with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) at 130 K. Gaussian absorption corrections were carried out using a multifaceted crystal model and the ABSPACK routine within the CrysAlisPro software package.¹⁶ The structure was solved using SHELXT and refined using a full matrix least-squares procedure based on F^2 (SHELXL)^{17, 18} using the OLEX2 program.^{19, 20} Anisotropic displacement parameters were applied to all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions on the carbon atoms and refined using the riding model. The positions of disordered hydrogen atoms on the coordinated water molecules were located from residual electron density maps and restrained to standard bond lengths and angles.

Crystallographic data and structural refinement parameters are presented in Table 1. Full details of crystal structure refinements in CIF format are available as Supplementary Information.

Table 1 Crystal data and structure refinement parameters for $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Empirical formula	$\text{C}_8\text{H}_{14}\text{Ca}_2\text{O}_9$
Formula weight	334.35
Temperature	130.01(10)
Crystal system	tetragonal
Space group	$I4_1/acd$
a (\AA)	33.1757(4)
c (\AA)	10.5521(2)
V (\AA^3)	11613.9(4)
Z	32
Crystal dimensions (mm)	0.15 x 0.137 x 0.061
ρ_{calc} (g cm^{-3})	1.530
μ (mm^{-1})	7.182
2θ range for data collection ($^\circ$)	7.538 to 140.068
Measured refls.	12099
Independent refls.	2761 [$R_{\text{int}} = 0.0277$, $R_{\text{sigma}} = 0.0220$]
Goodness-of-fit on F^2	1.180
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0293$, $wR_2 = 0.0794$
Largest diff. peak/hole (e \AA^{-3})	0.31/-0.34

Results and discussion

As indicated in the introduction, crystals of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ suitable for single crystal diffraction analysis were obtained from a mixture of calcium acetate monohydrate and 4-hydroxybenzoic acid in 1,4-dioxane. XRPD analysis of the starting material indicated a trace quantity of the hemihydrate in addition to the monohydrate (see supplementary information). Microscopic inspection of the calcium acetate reactant failed to reveal any of the characteristic, relatively large block-shaped crystals of the hemihydrate which were isolated from the 1,4-dioxane solution. To confirm that the generation of the crystals was not an isolated occurrence, the original reaction was repeated and usable crystals of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ were again obtained.

Following the initial success in generating usable crystals of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, it was found that it was not possible to produce $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystals in the absence of 4-hydroxybenzoic acid. Attempts to form the hemihydrate crystals involving the dissolution of species chemically related to 4-hydroxybenzoic acid, phenol and benzoic acid, also failed to yield crystals of the hemihydrate.

Crystals of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ are tetragonal, with cell dimensions: $a = 33.1757(4) \text{ \AA}$, $c = 10.5521(2) \text{ \AA}$; $V = 11\,613.9(3) \text{ \AA}^3$, measured at 130K. This compares favourably with the cell determined by XRPD¹³ at room temperature of $a = 33.4102(4) \text{ \AA}$, $c = 10.5662(1) \text{ \AA}$; $V = 11\,794.5(3) \text{ \AA}^3$. As noted by Bette *et al*, the volume of the unit cell is remarkably large for such a relatively simple salt.¹³

The structure of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ is presented in Figure 1. The 1-D polymer has a rod-like shape with a minimum diameter (van der Waals surface to van der Waals surface) of 1.75 nm and a maximum diameter of 2.1 nm (corresponding to a diagonal in Figure 1(a)). A four-fold screw axis runs through the centre of each rod. Each rod is chiral and has four near neighbours. These adjacent, parallel rods are of the opposite hand and form a racemic mixture, as shown in Figure 2.

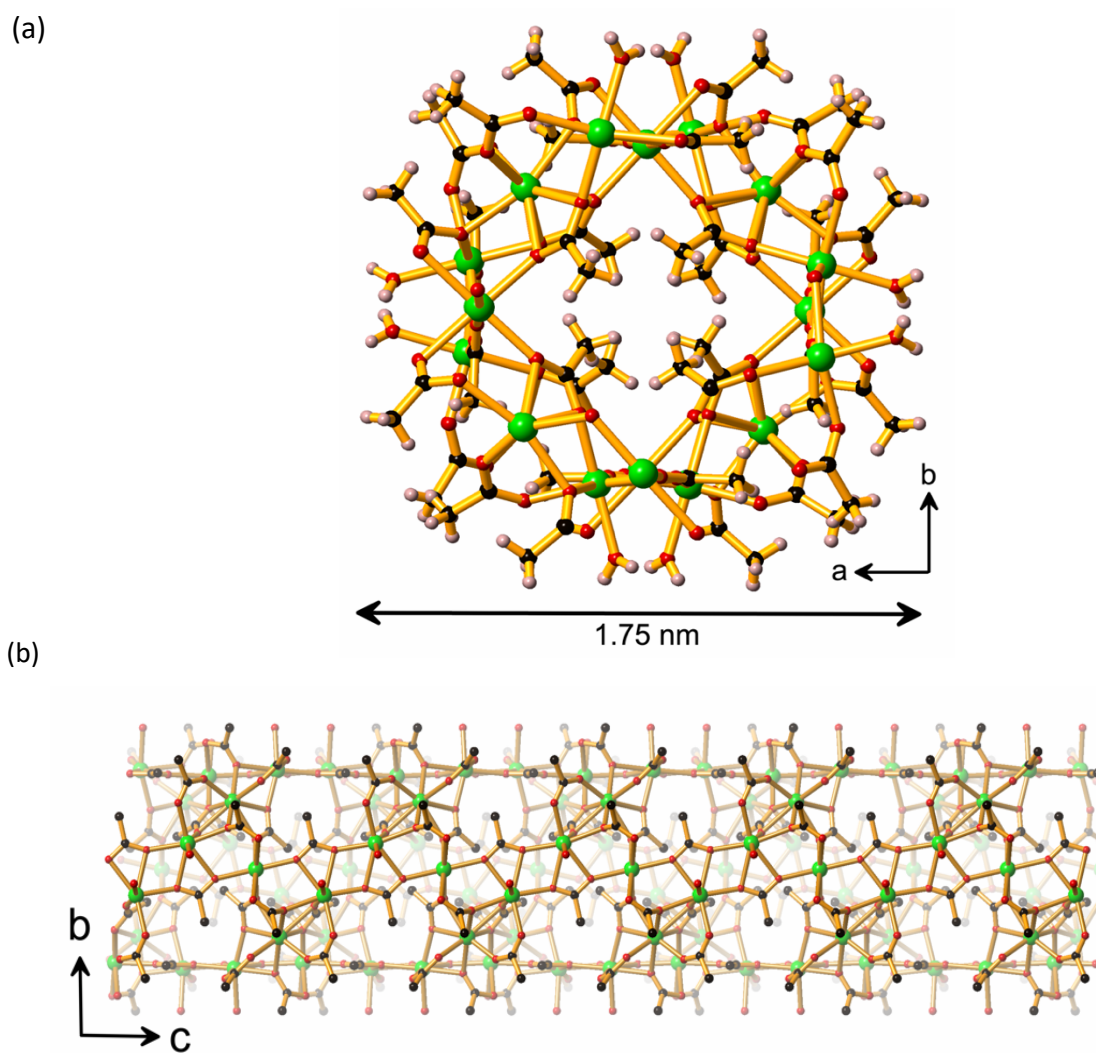


Figure 1 A single rod of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ viewed along the (a) c -axis and (b) a -axis. Hydrogen atoms are omitted in part (b). Colour code: Ca green, O red, C black, H pale pink.

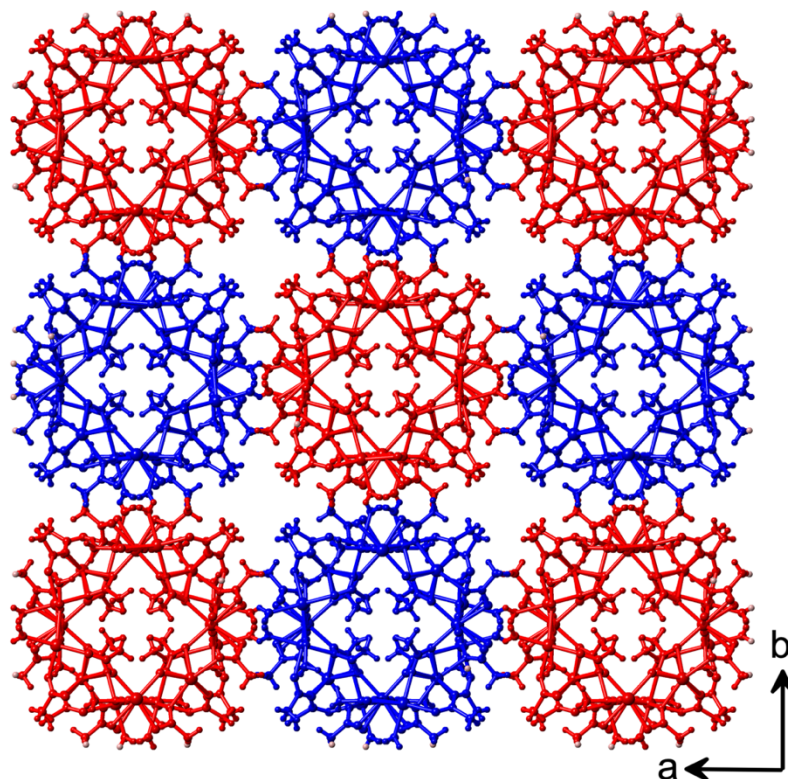


Figure 2 The crystal packing of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ viewed along the c -axis. The rods are chiral, with adjacent rods of opposite hand (coloured red and blue). There are four rods per unit cell.

There are four different acetate units, which we can identify by referring to their methyl carbons C2, C4, C6 and C8. The acetate units link calcium atoms by the μ_2 and μ_3 bridging modes which are often observed in coordination complexes containing this ligand (Figure 3).

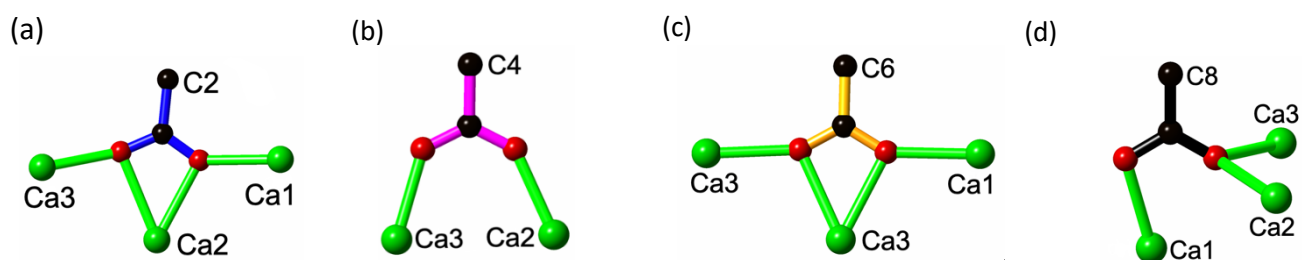


Figure 3 Coordination modes of the four independent acetate units (a) - (d) in $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$. The acetate units are colour coded to indicate their locations in the structure (see text). Hydrogen atoms have been omitted.

There are three different Ca centres, Ca1, Ca2 and Ca3 (Figure 4). Both Ca1 and Ca2 are coordinated to eight acetate oxygen atoms, with two chelating acetate ligands. Ca3 is seven coordinate and bonded to a water molecule and five acetate units, one of which is chelating. The calcium centres may be considered to lie in a coaxial inner shell within each rod.

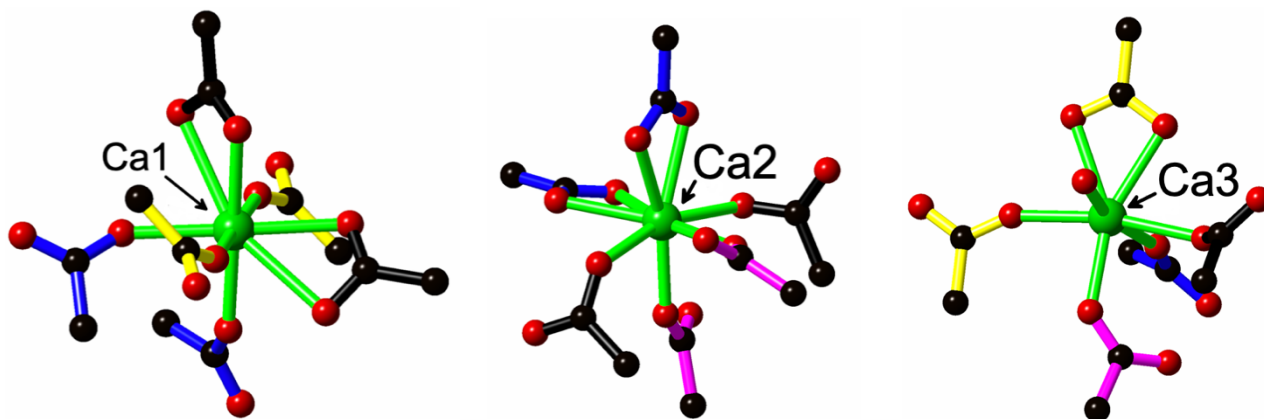


Figure 4 The coordination environments of the three crystallographically independent Ca sites, Ca1, Ca2 and Ca3, in $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$. Hydrogen atoms have been omitted.

The locations of the four acetate units in the structure can be seen in Figure 5. Acetates with C2 methyl groups (in blue) are directed towards the centre of the rod and form its core. Whilst the ball and stick model shown in Figure 5 gives the impression of an internal, central channel in the rod, it is important to note that no significant void is present when the structure is represented with a space filling model with the C2 methyl hydrogen atoms included. Acetates with C6 methyl groups (yellow) link calcium centres (green) in a cylindrical inner shell of the rod, whilst those with C4 and C8 methyl groups (purple and black, respectively) point outwards.

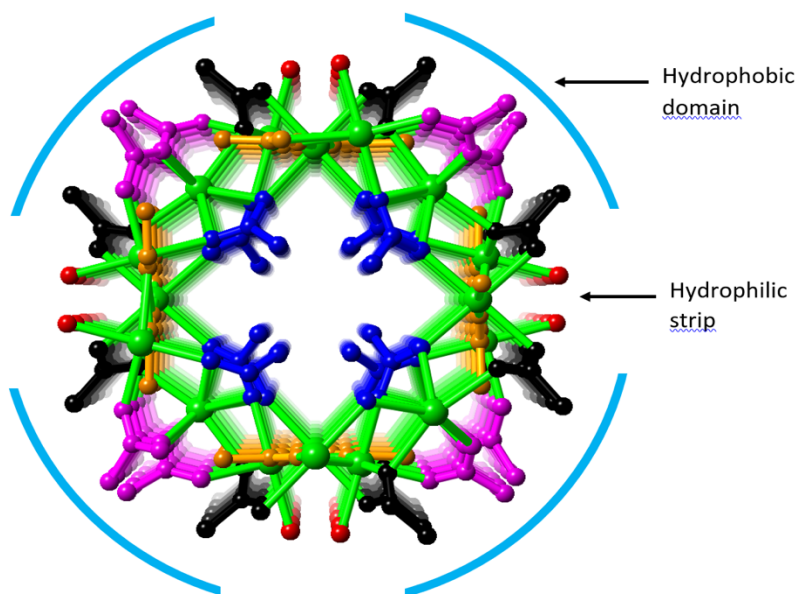


Figure 5 Perspective view of a rod showing the roles of the four acetate units in $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$. The units are colour coded: C2 blue, C4 purple, C6 yellow and C8 black. Four axial hydrophobic domains and four axial hydrophilic strips are present along the tube axis. Calcium centres (green) and the acetates with a C6 methyl group form a coaxial layer within the tube.

The coaxial, cylindrical structure of the rods is shown diagrammatically in Figure 6(a). The internal and external regions of the rods are dominated by the highly ordered, repeating arrangement of acetate units (Figure 6(b)). The outward pointing C4 and C8 methyl groups create non-polar domains along four sides of the axis of the rod. Between these non-polar domains lie polar strips containing coordinated water molecules and the oxygen atoms of one of the acetate units (Figure 6(b)).

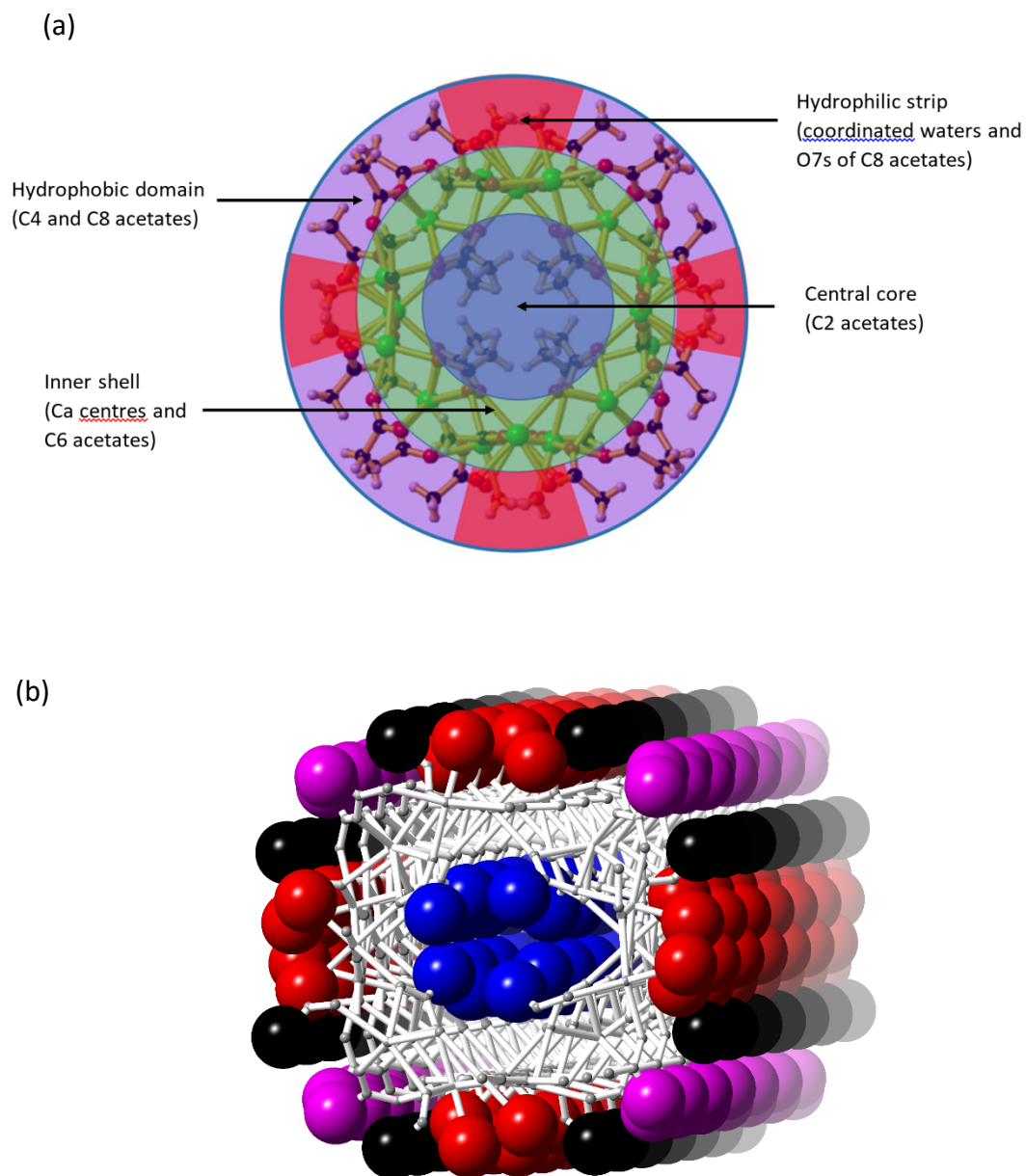


Figure 6 (a) A cross section through a rod of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, showing the coaxial, shell-like arrangement of acetate units, calcium centres and water molecules. (b) The arrangement of atoms on the internal and external surfaces of each rod. The outward pointing C4 and C8 methyl groups (purple and black) form hydrophobic axial domains. Four hydrophilic strips (red) are formed by water molecules and one of the oxygen atoms (O7) from the C8 acetate units. Hydrogen atoms have been omitted.

The four axial polar strips along the external surface of each rod are responsible for the hydrogen-bonded assembly of the rods in the crystal. Water molecules and oxygen atoms of one of the acetate units interact with neighbouring chains in a zipper-like fashion (Figure 7).

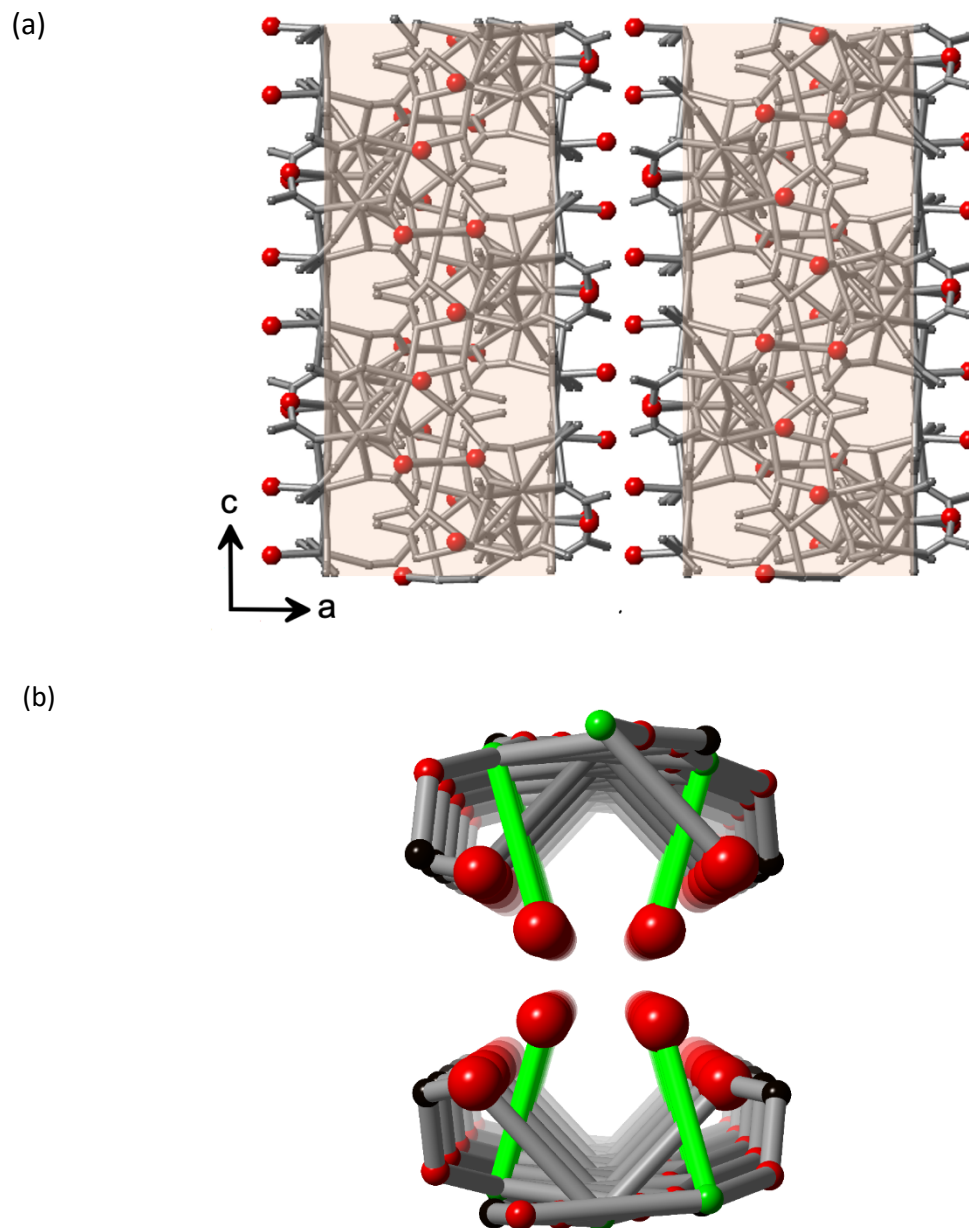


Figure 7 (a) The staggered, zipper-like arrangement of oxygen atoms in coordinated water molecules (O9) between two rods. (b) Perspective view of the interface between two rods, viewed along the *c*-axis. Bonds between Ca centres and the O atoms of water are shown in green. Hydrogen atoms are omitted in both diagrams.

Difference Fourier maps indicate the two hydrogen atoms on each coordinated water molecule are disordered between three positions which align with the directions to the closest oxygen atoms (Figure 8). 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. Other hydrogen bonds are formed between the hydrogen atoms of the water and the oxygen atoms on adjacent acetate groups.

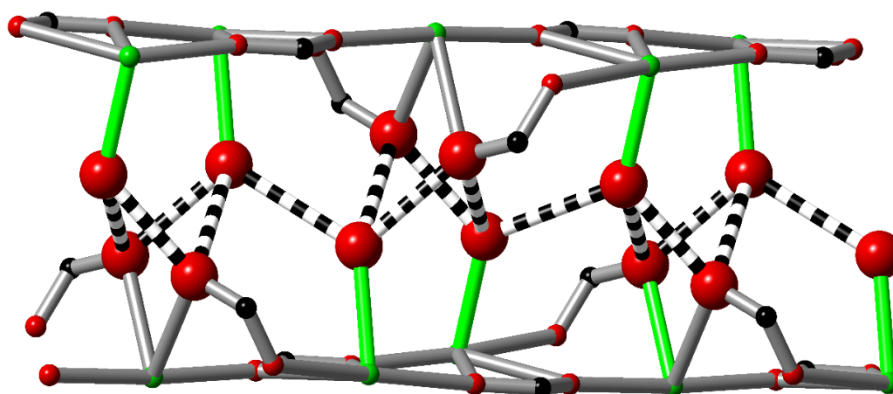


Figure 8 Hydrogen bonds are formed at the interface of two rods by disordered hydrogen atoms on coordinated water molecules and acetate oxygen atoms. Bonds between Ca centres and the O atoms of water are shown in green. Hydrogen atoms are omitted.

The acetate oxygen involved in hydrogen bonding in the hydrophilic strips is disordered between two positions (labelled as O7A and O7B). O7A is displaced 0.28 Å from the mean plane formed by the two carbon atoms while O7B is 0.31 Å from the other side of this plane. This is presumably associated with the disorder of the hydrogen atoms belonging to the coordinated water molecule.

Bette *et al* noted that by selecting certain Ca centres, it is possible to identify an interesting triple helix motif within each rod and compared it to the triple helix of collagen.¹³ The calcium centres can be regarded as being arranged in a pattern of three separate homochiral helices, as shown in Figure 9. These helices are created by a sequence of -Ca3-Ca3-Ca2- centres. The Ca3-Ca3 and Ca3-Ca2 distances are 4.042 Å and 3.786 Å, respectively, and the helical pitch is equal to three times the length of the c-axis (31.6563 Å). A fourth helix of the opposite hand crosses over his triple helix, formed by a -Ca1-Ca2- sequence with separations of 4.139 Å. The helical pitch of this fourth helix is equal to the length of the c-axis (10.5521 Å). There are, therefore, three complete turns of the -Ca1-Ca2- helix per turn of the other helices.

In combination with metal centres, the acetate ion is known to form a wide variety of multi-nuclear structures that commonly exhibit beautifully symmetric architectures. Notable examples include basic zinc acetate $[\text{Zn}_4\text{O}(\text{OAc})_6]^{21}$ and the Mn_{12} wheel complex, $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{AcOH} \cdot 4\text{H}_2\text{O}$.²² In these two examples, methyl groups extend outwards from the metal-oxygen aggregate resulting in the generation of circular or spherical type assemblies. In the case of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, the methyl groups extend not only outwards from a cylindrical Ca-O surface but also toward the cylindrical axis to generate this remarkable structure.

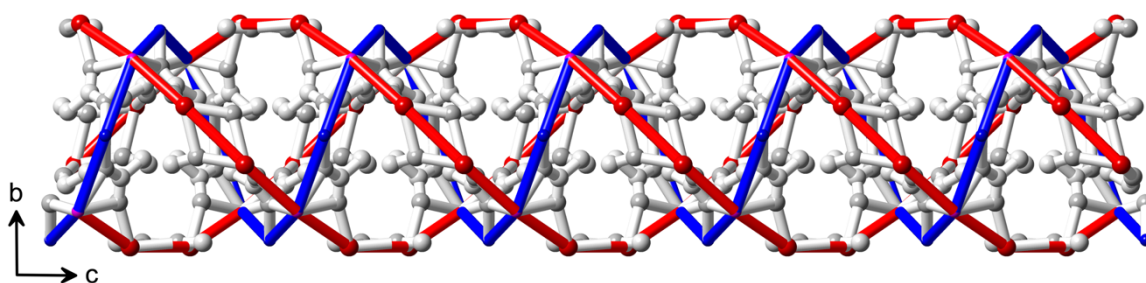


Figure 9 View down the a -axis, showing the pattern of three helices formed from the Ca2 and Ca3 centres (red) and the fourth helix formed from the Ca1 and Ca2 centres (blue). Hydrogen atoms and selected carbon and oxygen atoms are omitted for clarity.

The crystal packing of $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ leads to channels between the rods. The channels are parallel to the rods, with diameters of about 2.5 Å in projection (Figure 2). Since they are bounded by the acetate C4 and C8 methyl groups, the channels have a non-polar hydrophobic surface. Difference Fourier maps show no localised solvent in the channels of the crystal we studied. The PLATON SQUEEZE tool²³ indicates the solvent accessible volume is 136 Å³ per unit cell with negligible electron density (15 electrons per unit cell which equates to 0.23 electrons per $\text{Ca}(\text{OAc})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ unit). Using automated electron diffraction tomography, Bette *et al*¹³ found evidence to suggest that small numbers of additional disordered water molecules may be present within the rods. However, as mentioned earlier, there is no void of significant size within the rods in our crystal.

Conclusions

Calcium acetate hemihydrate is known to be a component of the efflorescent salts that slowly form on the surface of calcareous heritage objects stored in museums and similar institutions. Single crystal X-ray diffraction analysis of this compound shows it is composed of extended chains with a rod-like shape. Each chain is chiral, with a minimum diameter of 1.75 nm. The calcium centres within a chain can be considered to be located in an inner coaxial shell and arranged in a triple helix pattern. The highly directional orientation and repeating pattern of the four different types of acetate units result in rods with an outer surface made up of four axial hydrophobic domains interleaved with hydrophilic strips. Each hydrophilic strip interacts with a hydrophilic strip on an adjacent rod via hydrogen bonding to form a zipper-like arrangement. These interactions are responsible for the self-assembly of the rods into a racemic mixture.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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