How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 9438–9442
International Edition: doi.org/10.1002/anie.202001609
German Edition: doi.org/10.1002/ange.202001609

Helical Structures

Corrosion of Heritage Objects: Collagen-Like Triple Helix Found in the Calcium Acetate Hemihydrate Crystal Structure

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Abstract: *Helical motifs are common in nature, for example, the DNA double or the collagen triple helix. In the latter proteins, the helical motif originates from glycine, the smallest amino acid, whose molecular confirmation is closely related to acetic acid. The combination of acetic acid with calcium and water, which are also omnipresent in nature, materializing as calcium acetate hemihydrate, was now revealed to exhibit a collagen-like triple helix structure. This calcium salt is observed as efflorescence phase on calcareous heritage objects, like historic Mollusca shells, pottery or marble reliefs. In a model experiment pure calcium acetate hemihydrate was crystallized on the surface of a terracotta vessel. Calcium acetate hemihydrate crystallizes in a surprisingly large unit cell with a volume of 11,794.5(3) Å*^{3} *at ambient conditions. Acetate ions bridge neighboring calcium cations forming spiral chains, which are arranged in a triple helix motif.*

Helical structures, in particular double and triple helices are omnipresent in the living nature, for example, in the DNA,[1] in polysaccharides like amylose[2] or in proteins like collagen.[3] But also synthetic organic compounds like helicenes,[4] inorganic materials like $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$[5] or inorganic-organic hybrid materials like $Cd_3(OH)_2(TCBA)H_2O)$[6] (H_4TCBA = 3,4,5-tris(carboxymethoxy)-benzoic acid) show helical motifs. Substances with helical structures are regarded as promising candidates for excellent mechanical, electrical and optical properties.[7] Most helical materials that have been synthesized have very complex constitutions.[5,8] For simple LiP, a double helix structure was predicted but has not been experimentally proven yet.[9] Instead the substance was reported to contain only a P-helix that is coordinated by lithium.[10] By sophisticated preparation methods semiconductors like CdTe or CdS were obtained in helical arrangement.[11] Metals like gold were also crystallized in helical form by DNA-templating techniques.[12] Recently the facile synthesis of simple semiconducting SnIP, which crystallizes in a double helix motif, was reported.[13]

In this study we present the structure of the seemingly simple compound calcium acetate hemihydrate, $Ca(AcO)_2\cdot{}^1\!/_2\,H_2O$ ($AcO = CH_3COO$), that exhibits a triple helical motif analogous to the collagen proteins. In nature, pure calcium acetate hydrate salts do not occur as minerals, only a mixed calcium copper acetate, paceite ($CaCu(AcO)_4\cdot 6H_2O$) has been found, yet.[14] Calcium acetate containing phases were observed to occur as efflorescence salts on calcareous objects in collections already at the end of the 19th century.[15] The acetate originates from wooden furniture used for storage or display as wood emits considerable amounts of formic and acetic acid or its aldehyde precursors.[16] Accordingly, calcium acetates,[17] mixed acetate formates,[17,18] and acetate nitrates[19] were identified as efflorescence salts. Their crystal structures contain characteristic calcium carboxylate zig-zag chain motifs[20] which also enable the intercalation of additional water molecules or chloride ions in between these chains.[21] The efflorescence phases often crystallize in pores and cracks. Due to their needle-like morphology and their reversible de- and rehydration behavior, the crystallization of efflorescence salts can cause significant damage to the artefacts.[22] Calcium acetate hemihydrate is an efflorescence salt identified to occur for example, on ancient pottery found on the Athenian Agora,[22] on Mollusca shells in natural history collections of the British Museum and of the Royal Scottish Museum[17] and on a marble relief (Figure 1 a,b, Supporting Information section 2.2.) stored in the Museum for Byzantine Art in Berlin.[23] Although $Ca(AcO)_2\cdot{}^1\!/_2\,H_2O$ has already been known since 1958[24] and was subject of several studies,[25] for substance identification by X-ray powder diffraction (XRPD) only a PDF-card (019-0199)[25a] evaluated with "low precision" is available and its crystal structure still remains unknown. As the efflorescence phases usually occur in microcrystalline state and as multiphase mixtures, their characterization is not trivial. Calcium salt hemihydrates like $CaSO_4\cdot{}^1\!/_2\,H_2O$[26] or $CaCO_3\cdot{}^1\!/_2\,H_2O$[27] are

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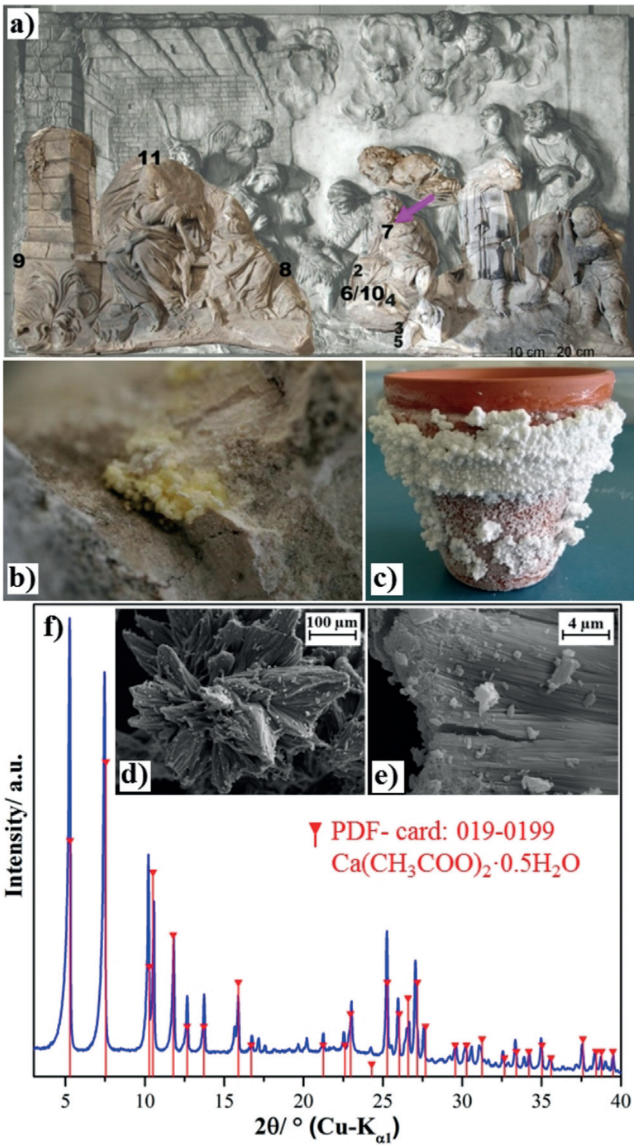

Figure 1. a) "Adoration of the Shepherds' by G. Torretti (1664–1743), the relief exhibits efflorescence phases that were sampled at different (1–11) positions; b) detailed view of the efflorescence phase at sample area 7 (magenta arrow in part a); c) terracotta pot covered with efflorescence crystals from a model experiment, d), e) SEM images of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ obtained by the model experiment, f) measured diffraction pattern of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ including the PDF-card used for phase identification. Figure 1 a,b: © Rathgen Forschungslabor, Staatliche Museen zu Berlin—Preußischer Kulturbesitz.

of vast technological and scientific importance, but their structural characterization was often proven to be challenging.

Two samples of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ were obtained in model experiments in which porous terracotta pots were filled with saturated calcium acetate solutions and stored under a defined relative humidity. All experimental details are given in the Supporting Information. After six weeks of storage at 29% r.H. and 43% r.H., the terracotta pots were completely covered with a white efflorescence phase (Figure 1 c) consisting of strongly aggregated needle-like crystals (Figure 1 d,e). The reflection positions of the measured patterns are in good agreement with the reference data that is commonly used to identify $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ (Figure 1 f, Supporting Information Figure S2). The measured vibrational spectra are also in agreement with literature data (Supporting Information Figures S14, S15). The phase composition was confirmed by elemental analyses (Supporting Information Table S1). All observed reflections could be indexed, hence the obtained samples can be considered as pure. Indexing of the powder pattern led to a surprisingly large tetragonal unit cell with space group $I4_1/acd$, a unit cell volume of 11794.5(3) Å^3 and lattice parameters of $a = 33.4102(4)$ Å and $c = 10.5662(1)$ Å. The crystal structure was finally solved ab initio from the powder data. Automated electron diffraction tomography (ADT)[28] was employed to confirm the structural model (Supporting Information Section 3.2.). The complete substance characterization including elemental, thermal and vibrational spectral analysis and all experimental details are given in the Supporting Information.

In the crystal structure of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$, the cations occupy three crystallographically independent sites. Two calcium cations (Ca(1) and Ca(2)) are situated on special positions (Supporting Information Table S3). These cations are coordinated by eight acetate related oxygen atoms (Figure 2 a,b), with two acetate ions coordinating in bidentate and four acetate ions coordinating in monodentate modes. The calcium site situated on a general position (Ca(3)) is coordinated by six acetate and one water related oxygen atoms (Figure 2 c). Only one acetate ion coordinates to this calcium site in a bidentate way. There are four crystallographically independent acetate sites, three of them are situated in the coordination sphere of three calcium ions and one is located in the coordination sphere of only two cations (Supporting Information Figure S16). Acetate ions bridge Ca(1) and Ca(2) sites forming spiral calcium carboxylate $[(Ca(1)(AcO)_{6/3})(Ca(2)(AcO)_{4/3}\,(AcO)_{2/2})]_n$ chains with Ca-(1)-Ca(2) distances of 4.17 Å (Figure 2 d, turquoise bonds). Spiral, acetate bridged calcium carboxylate $[(Ca(2)(AcO)_{4/3}(AcO)_{2/2})(Ca(3)(AcO)_{4/3})(AcO)_{1/2}H_2O)]_{2n}$ chains are also formed by one Ca(2) and two Ca(3) sites with Ca(3)-Ca(3) distances of 4.10 Å and relatively short Ca(2)-Ca(3) distances of 3.78 Å (Figure 2 e, green bonds). The Ca(1)-Ca(2) carboxylate chain forms a helix (Figure 2 f) running along the c-axis with four chain units per winding, with a repetition lengths of 1c (10.57 Å). At the positions of the Ca(2) sites the Ca(1)-Ca(2) 4_1 helix is interpenetrated by three Ca(2)-Ca(3) carboxylate chains (Figure 2, green, yellow and red dashed bonds) that are helices themselves (Figure 2 g), also running along the c-axis with four chain units per winding and a repetition lengths of 3c (31.70 Å). This leads to an overall triple helix motif in the crystal structure of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$, with three Ca(2)-Ca(3) helices being interpenetrated with a Ca(1)-Ca(2) helix that acts as a bridging backbone (Figure 3 a,b). Accordingly, the crystal structure of this simple calcium acetate hemihydrate reveals strong similarity to the natural protein collagen[3] (Figure 3 c,d). Due to its more complex molecular structure the axial repeat of the collagen triple helix is much higher, which is expected to be 60 Å or 86 Å with the shorter one evaluated to be more likely.[3a] In

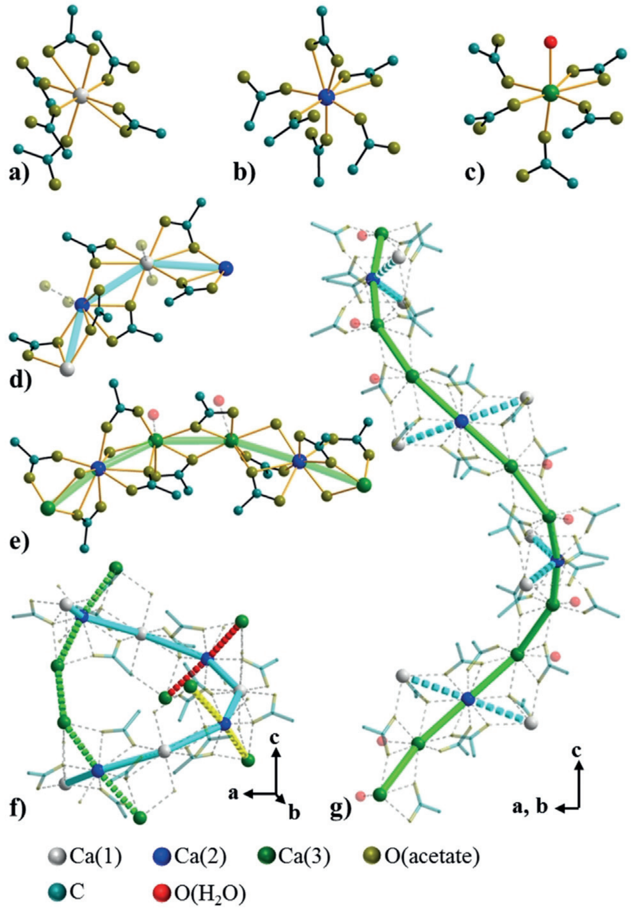

Figure 2. a)–c) Coordination spheres of the calcium cations, d) Ca(1)-Ca(2) chain as structural backbone motif, e) Ca(2)-Ca(3) chain as another structural backbone motif, f) Ca(1)-Ca(2) 4_1-helix (blue bonds) that is interpenetrated with three Ca(2)-Ca(3) chain (green, yellow and red dashed bonds), g) Ca(2)-Ca(3) 4_1-helix (green bonds) that is interpenetrated with a Ca(1)-Ca(2) helix (turquoise dashed bonds).[32]

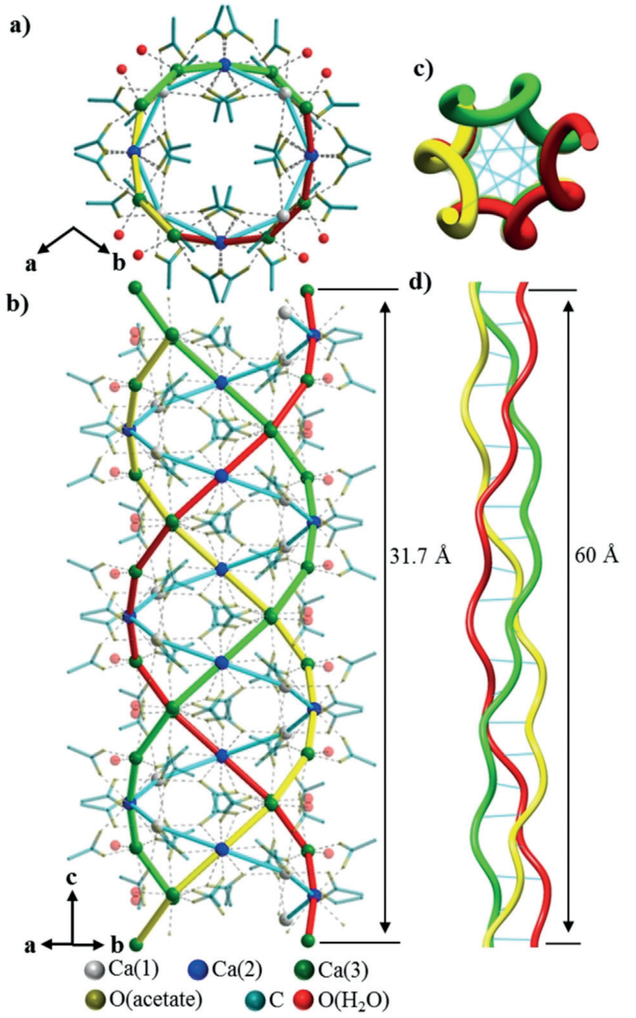

Figure 3. Comparison of triple-helical motifs in the crystal structures of a,b) $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ and of c,d) collagen.[3] The image of collagen was prepared using the UCSF Chimera software.[29]

the collagen proteins, water molecules mediate the interactions within a triple helix rod by hydrogen bonds. The arrangement of the water molecules and the H-bonds form an additional helix that interpenetrates the triple helix.[3b] In the structure of $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ the interpenetrating Ca(1)-Ca(2) helix mediates interactions within the rod. The water molecules are situated exclusively at the outside of the triple helix rods (Figure 4, red atoms). ADT analyses indicate that a small amount of additional, disordered water is situated within the rods (Supporting Information Section 3.2.). Due to short distances between water related oxygen sites of 3.00 Å, the presence of H-bonds appears to be likely. The potential H-bonds interconnect neighboring triple-helix strings (Figure 4, blue, dashed bonds) and direct their orientation. Accordingly, along the crystallographic *a*- and *b*-axes left-handed and right-handed triple helices are arranged in an alternating fashion (Figure 4a). Within a unit cell there are in total four triple helices, two left- and two right-handed (Figure 4b).

The discovery of a triple helical motif analogous to the collagen proteins in such a simple chemical compound like $Ca(AcO)_2\cdot{}^1/_2\,H_2O$ is quite surprising. As this phase can be obtained by crystallization on calcareous or porous materials[22] or by simple isothermal decomposition of $Ca(AcO)_2\cdot H_2O$,[25a] it doesn't need a helical precursor for crystallization, but it may serve as a simple and easy accessible precursor for future works. The collagen proteins played an essential role in tissue evolution, in particular in the transition from unicellularity to multicellularity.[30] Collagen consists to one third of glycine,[3b] which enables the triple helical structure due to its small size. As the constitution of acetate is similar to glycine, the existence of helical calcium glycinates appears to be very likely. Up to now, only the crystal structure of non-helical calcium glycinate trihydrate ($Ca(C_2H_5NO_2)\cdot 3\,H_2O$) has been solved.[31]

Acknowledgements

From the Max Planck Institute for Solid State Research, Alexander M. Pütz is acknowledged for measuring the IR-spectrum, Christine Stefani for the XRPD measurements,

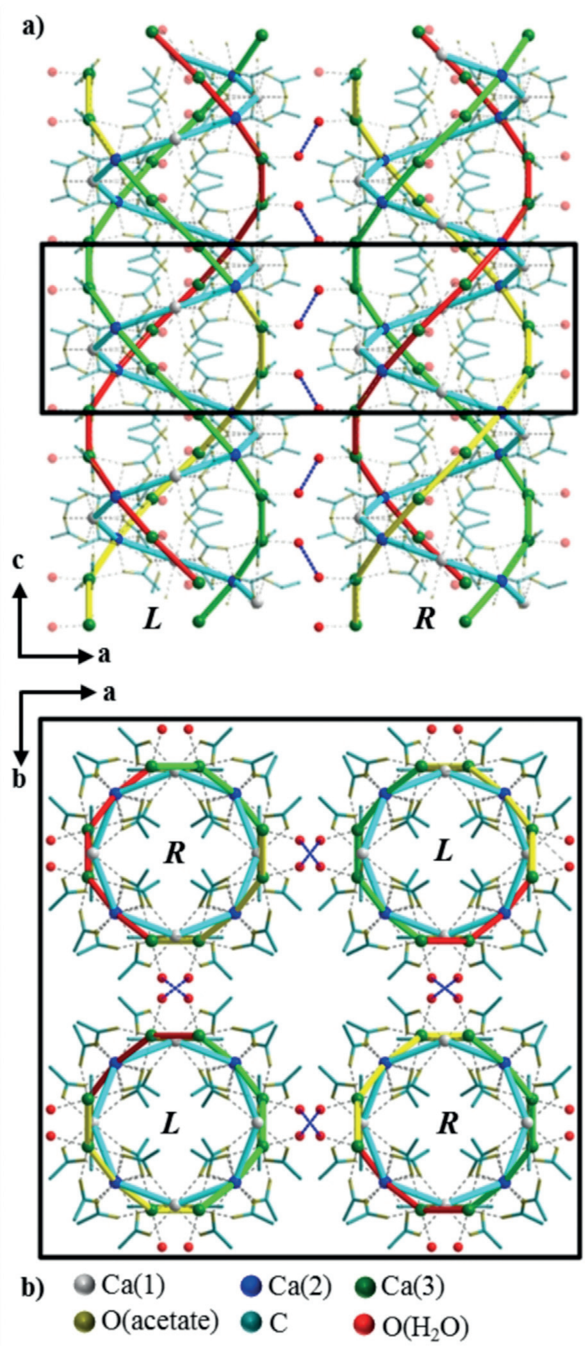

Figure 4. Packing diagram of Ca(AcO)$_2\cdot{}^1/_2$ H$_2$O a) view along the *b*-axis, b) view along the *c*-axis, interactions between neighboring triple helices by potential H-bonds are indicated by blue dashed bonds. Right handed helices are indicated by "R", left handed helices by "L".

Marie-Louise Schreiber for the elemental analysis, and Viola Duppel for taking the SEM images. Stefan Simon from the Rathgen Forschungslabor and Michael Steiger from the University of Hamburg shared their results on the Torretti relief. Funding by DFG for the project "In search of structure" (grant EG 137/9-1) is gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

Keywords: calcium · carboxyalate ligands · helical structures · structure elucidation · X-ray diffraction

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Manuscript received: January 31, 2020
Accepted manuscript online: February 17, 2020
Version of record online: April 15, 2020