Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2019

Efflorescence on calcareous objects in museums: Crystallisation, phase characterisation and crystal structures of calcium acetate formate phases

Sebastian Bette[a,c,*], Michael X. Müller[b], Gerhard Eggert[c], Thomas Schleid[b], Robert E. Dinnebier[a]

[a]Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

[b]Institut für Anorganische Chemie, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

[c]State Academy of Art and Design, Am Weißenhof 1, 70191 Stuttgart, Germany

E-Mail: S.Bette@fkf.mpg.de

Additional Tables and Figures

Table S 1. Crystallographic and Rietveld refinement data of $Ca(CH_3COO)(HCOO)\cdot H_2O$ and $Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$ at ambient conditions.

molecular formula	$Ca(CH_3COO)(HCOO)\cdot 1H_2O$	$Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$
sum formula	$C_3H_6CaO_5$	$C_{10}H_{22}Ca_3O_{16}$
molecular weight (g/mol)	162.15	518.49
space group	$P2_1/c$ (14)	$P4_12_12$(92)
Z	4	4
a /Å	9.2729(1)	6.8655(1)
b /Å	6.8002(1)	6.8655(1)
c /Å	11.2219(2)	45.5454(6)
α /°	90	90
β /°	121.232(1)	90
γ /°	90	90
V /Å³	605.08(1)	2144.77(4)
ρ_{calc}/ g · cm^{-3}	1.78	1.61
Wavelength / Å	1.5406	1.5406
R-p /% *	1.24	4.74
R-wp /% *	1.58	6.34
R-F^2 /% *	0.85	3.39
starting angle (° 2θ)	10	5
final angle (° 2θ)	110	105
step width (° 2θ)	0.01	0.01
time/scan (h)	20	20
no. of variables	68	62

* R-p, R-wp, and R-F^2 as defined in TOPAS (Bruker AXS)

Table S 2. Atomic coordinates of $Ca(CH_3COO)(HCOO)\cdot H_2O$ and $Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$ at ambient conditions.

Atom	Wyck.	Site	S.O.F.	*x/a*	*y/b*	*z/c*	B /Å²
$Ca(CH_3COO)(HCOO)\cdot H_2O$							
Ca(1)	4e	1	1	0.090(1)	0.469(1)	0.873(2)	0.49(8)
O(1)	4e	1	1	0.713(1)	0.900(1)	0.702(1)	2.87(1)
C(1a)	4e	1	1	0.691(2)	0.044(8)	0.331(2)	2.70(1)*
C(2a)	4e	1	1	0.565(5)	0.103(14)	0.178(3)	2.70(1)*
O(1a)	4e	1	1	0.841(1)	0.995(1)	0.376(1)	2.70(1)*
O(2a)	4e	1	1	0.621(4)	0.052(12)	0.406(3)	2.70(1)*
C(1b)	4e	1	1	0.881(8)	0.040(2)	0.055(3)	2.70(1)*
O(1b)	4e	1	1	0.896(1)	0.864(1)	0.095(1)	2.70(1)*
O(2b)	4e	1	1	0.916(13)	0.193(3)	0.135(5)	2.70(1)*
H(1b)	4e	1	1	0.840(10)	0.079(4)	0.957(3)	2.70(1)*
$Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$							
Ca(1)	4a	..2	1	0.278(1)	0.278(1)	0	1.76(8)*
Ca(2)	8b	1	1	0.231(1)	0.747(1)	0.5436(1)	1.76(8)*
O(1)	8b	1	1	0.099(2)	0.763(2)	0.9106(2)	2.11(12)*
O(2)	8b	1	1	0.589(2)	0.236(2)	0.2781(2)	2.11(12)*
C(1a)	8b	1	1	0.272(3)	0.258(7)	0.0627(5)	3.00(26)*
C(2a)	8b	1	1	0.302(7)	0.225(10)	0.0960(6)	3.00(26)*
O(1a)	8b	1	1	0.105(2)	0.289(3)	0.0501(3)	3.00(26)*
O(2a)	8b	1	1	0.429(3)	0.252(12)	0.0498(8)	3.00(26)*
C(1b)	8b	1	1	0.728(4)	0.768(4)	0.2721(3)	3.00(26)*
C(2b)	8b	1	1	0.750(3)	0.743(3)	0.3058(2)	3.00(26)*
O(1b)	8b	1	1	0.564(6)	0.783(6)	0.2583(7)	3.00(26)*
O(2b)	8b	1	1	0.864(6)	0.776(5)	0.2547(5)	3.00(26)*
C(1c)	8b	1	1	0.608(4)	0.734(5)	0.9097(3)	3.00(26)*
O(1c)	8b	1	1	0.601(2)	0.765(2)	0.9378(2)	3.00(26)*
O(2c)	8b	1	1	0.755(6)	0.687(10)	0.8960(6)	3.00(26)*
H(1c)	8b	1	1	0.494(5)	0.744(8)	0.8961(5)	3.00(26)*

*The thermal displacement parameters of acetate related sites were constraint, when multiple Ca- or water related oxygen sites were present, their thermal displacement parameters were refined constrained, as well.

Table S 3. Selected bond lengths and angles of $Ca(CH_3COO)(HCOO)\cdot H_2O$ and $Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$ at ambient conditions.

Atoms	Distance	Atoms	Distance	Atoms	Angle
$Ca(CH_3COO)(HCOO)\cdot H_2O$					
Ca(1)-O(1)	2.44(1) Å	Ca(1)-O(1b)	2.29(1) Å	O(1b)-C(1b)-O(2b)	125(2)°
Ca(1)-O(1a)	2.33(1) Å	Ca(1)-O(1b)	2.92(1) Å	O(1a)-C(1a)-O(2á)	125(1)°
	2.53(1) Å	Ca(1)-O(2b)	2.30(2) Å		
Ca(1)-O(2a)	2.60(3) Å		2.56(5) Å		
$Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$					
Ca(1)-O(1a)	2.57(1) Å	Ca(2)-O(1)	2.34(1)	O(1a)-C(1a)-O(2a)	125(5)°
	2.57(1) Å	Ca(2)-O(2)	2.46(1)	O(1b)-C(1b)-O(2b)	110(3)°
Ca(1)-O(2a)	2.50(1) Å	Ca(2)-O(1a)	2.34(1)	O(1c)-C(1c)-O(2c)	125(2)°
	2.50(1) Å	Ca(2)-O(2a)	2.35(2)		
Ca(1)-O(1b)	2.38(4) Å	Ca(2)-O(1b)	2.63(4)		
	2.38(4) Å	Ca(2)-O(2b)	2.38(2)		
Ca(1)-O(2b)	2.47(4) Å	Ca(2)-O(1c)	2.54(1)		
	2.47(4) Å				

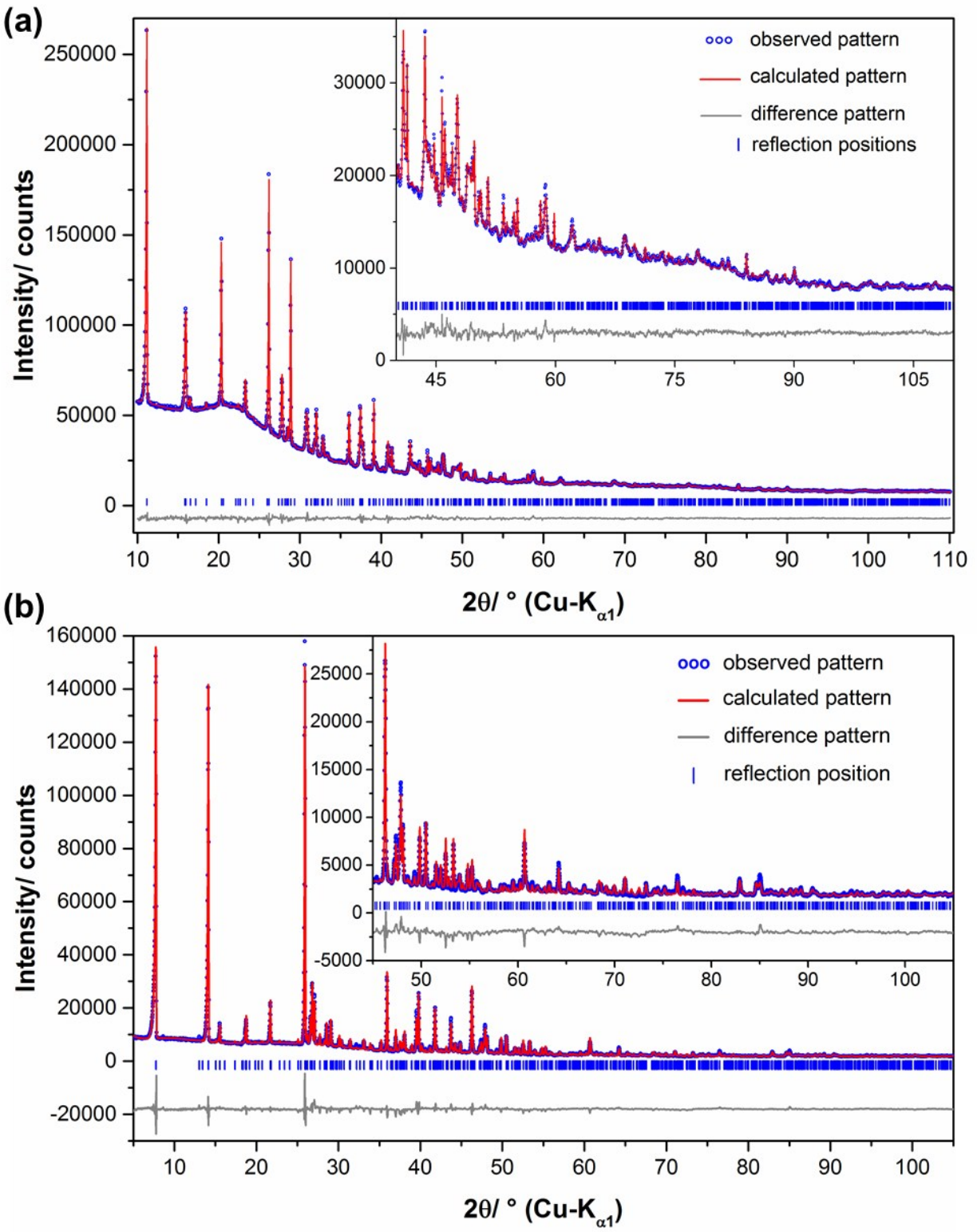

Figure S 1. Scattered X-ray intensities of (a) $Ca(CH_3COO)(HCOO)\cdot H_2O$ and (b) $Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$ at ambient conditions as a function of the diffraction angle 2θ. The observed pattern (circles) measured in Debye-Scherrer geometry, the best Rietveld fit profiles (line) and the difference curve between the observed and the calculated profiles (below) are shown. The high angle part starting at 40.0° and 45.0° in 2θ is enlarged for clarity.

Table S 4 Comparison of the peak positions in the diffraction pattern of $Ca(CH_3COO)(HCOO)\cdot H_2O$ given by Tennent and Baird with the calculated diffraction pattern.

Tennent and Baird[1]	**This study**	
d/ Å	**d/ Å**	**relative intensity**
7.97*	7.93	100
5.54*	5.55	44
	5.36	2
4.35*	4.36	31
3.79	3.81	9
3.39*	3.40	39
	3.40	10
3.22	3.20	22
	3.12	3
3,05	3.09	31
2.89	2.89	23
	2.81	3
2.80	2.79	13
	2.72	2
2.70	2.72	6
	2.68	2
2.46	2.49	15
	2.40	18
2.38*	2.38	11
2.29	2.30	13
	2.29	3
2.20	2.21	11
	2.19	3
	2.18	5

*strongest lines

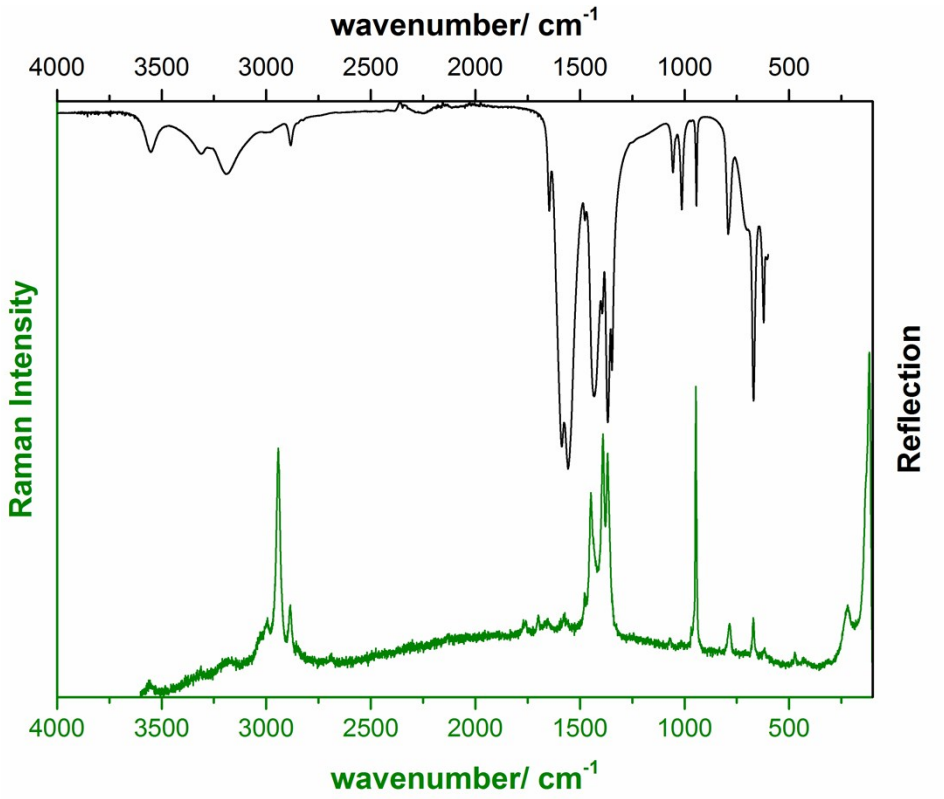

Figure S 2. IR (black line) and Raman spectrum (green line) of $Ca(CH_3COO)(HCOO)\cdot H_2O$.

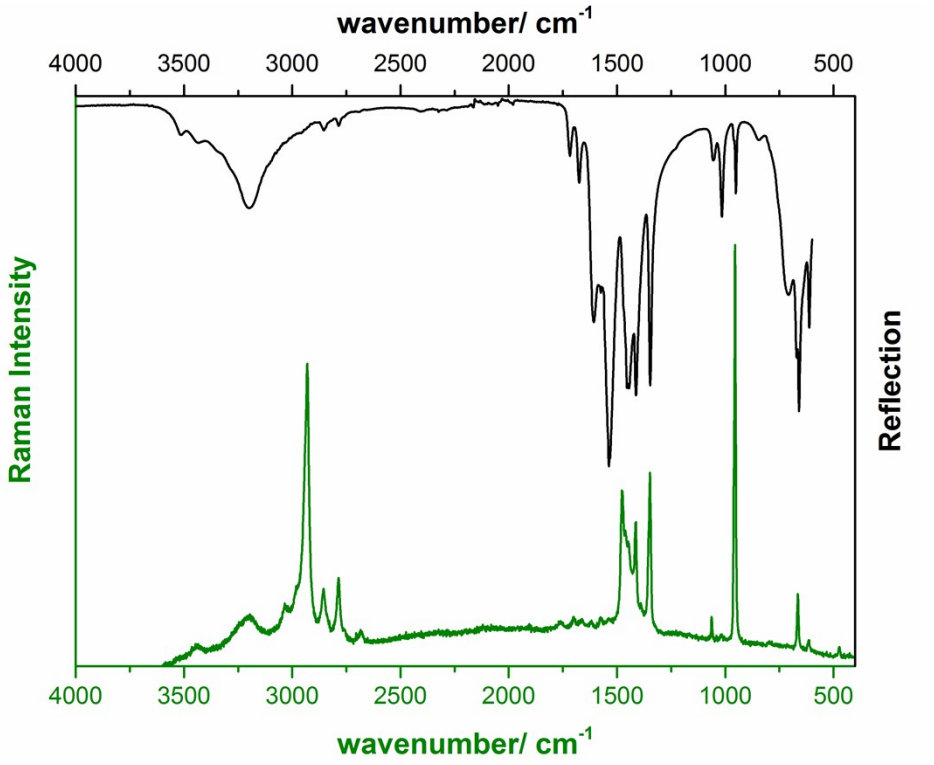

Figure S 3. IR (black line) and Raman spectrum (green line) of $Ca_3(CH_3COO)_4(HCOO)_2\cdot 4H_2O$.

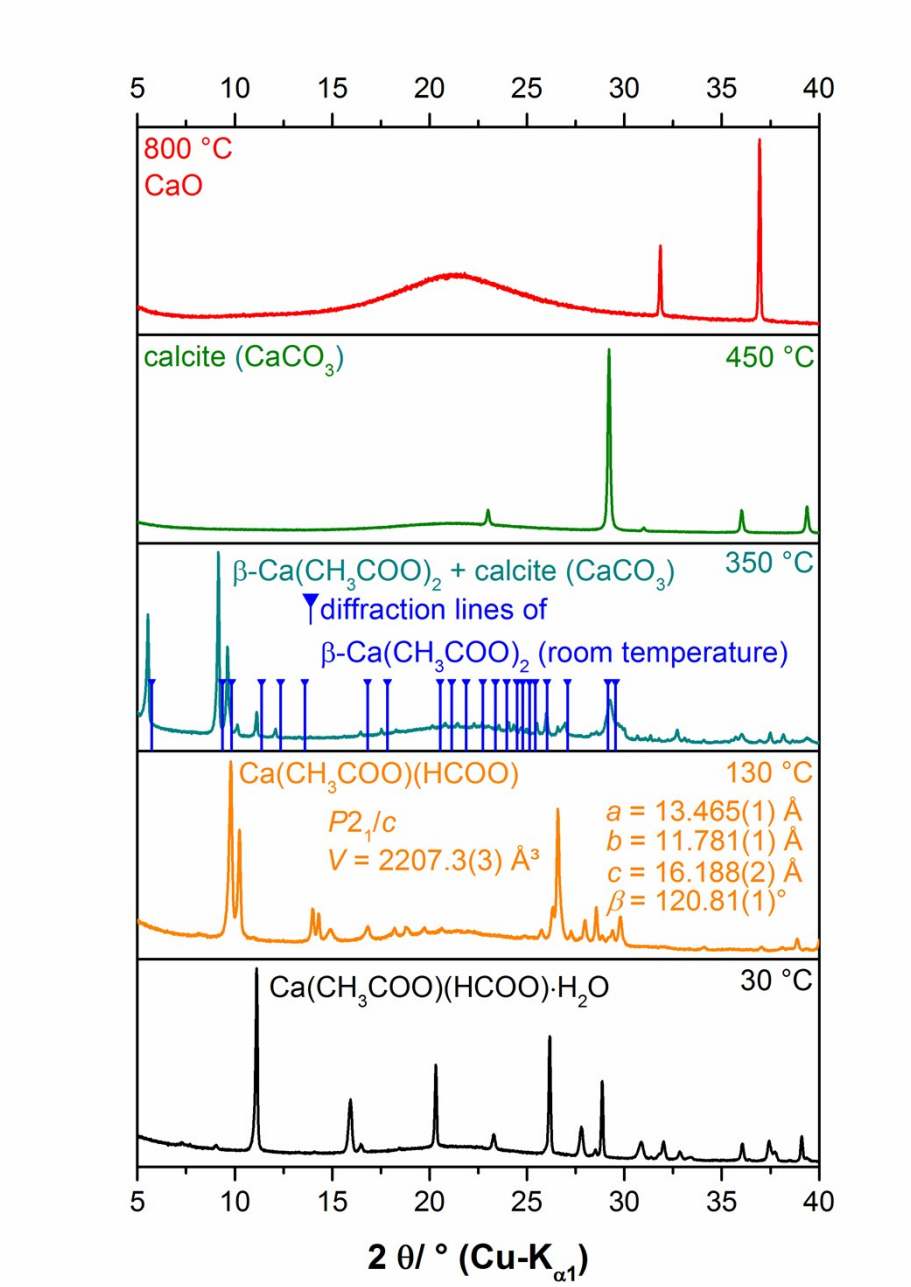

Figure S 4. Temperature dependent *in situ* XRPD patterns taken during the thermal decomposition of $Ca(CH_3COO)(HCOO)\cdot H_2O$. The cell parameters of the anhydrous phase obtained during the decomposition were obtained by LSI indexing[2] and a subsequent Pawley refinement[3]. The reference data for the identification of β-$Ca(CH_3COO)_2$ were taken from Walter-Levy and Laniepce[4] and refer to room temperature studies.

References

[1] N. H. Tennent, T. Baird, *Studies in Conservation* **1985**, *30*, 73-85.
[2] A. A. Coelho, *Journal of Applied Crystallography* **2003**, *36*, 86-95.
[3] G. S. Pawley, *J. Appl. Crystallogr.* **1981**, *14*, 357-361.
[4] L. Walter-Levy, J. Laniepce, *Compt. rend.* **1960**, *250*, 3320-3322.