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

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Additional Tables and Figures

Table S 1. Crystallographic and Rietveld refinement data of Ca(CH\textsubscript{3}COO)(HCOO)\cdot1H\textsubscript{2}O and Ca\textsubscript{3}(CH\textsubscript{3}COO)\textsubscript{4}(HCOO)\cdot4H\textsubscript{2}O at ambient conditions.

| Property                                      | Ca(CH\textsubscript{3}COO)(HCOO)\cdot1H\textsubscript{2}O | Ca\textsubscript{3}(CH\textsubscript{3}COO)\textsubscript{4}(HCOO)\cdot4H\textsubscript{2}O |
|----------------------------------------------|-----------------------------------------------------------|----------------------------------------------------------------------------------------|
| molecular formula                             | Ca(CH\textsubscript{3}COO)(HCOO)\cdot1H\textsubscript{2}O | Ca\textsubscript{3}(CH\textsubscript{3}COO)\textsubscript{4}(HCOO)\cdot4H\textsubscript{2}O |
| sum formula                                   | C\textsubscript{7}H\textsubscript{6}CaO\textsubscript{5}  | C\textsubscript{10}H\textsubscript{22}Ca\textsubscript{3}O\textsubscript{16}            |
| molecular weight (g/mol)                      | 162.15                                                   | 518.49                                                                                 |
| space group                                   | \textit{P}2\textsubscript{1}/c (14)                     | \textit{P}4\textsubscript{1}2\textsubscript{1}2\textsubscript{1} (92)                   |
| \(Z\)                                        | 4                                                        | 4                                                                                      |
| \(a /\text{Å}\)                               | 9.2729(1)                                                | 6.8655(1)                                                                              |
| \(b /\text{Å}\)                               | 6.8002(1)                                                | 6.8655(1)                                                                              |
| \(c /\text{Å}\)                               | 11.2219(2)                                               | 45.5454(6)                                                                             |
| \(\alpha /^\circ\)                            | 90                                                       | 90                                                                                     |
| \(\beta /^\circ\)                             | 121.232(1)                                               | 90                                                                                     |
| \(\gamma /^\circ\)                            | 90                                                       | 90                                                                                     |
| \(V /\text{Å}^3\)                             | 605.08(1)                                                | 2144.77(4)                                                                             |
| \(\rho_{\text{calc}} /\text{g} \cdot \text{cm}^{-3}\) | 1.78                                                     | 1.61                                                                                   |
| Wavelength / \(\text{Å}\)                     | 1.5406                                                   | 1.5406                                                                                 |
| \(R-p /\% \)\textsuperscript{*}               | 1.24                                                     | 4.74                                                                                   |
| \(R-wp /\% \)\textsuperscript{*}              | 1.58                                                     | 6.34                                                                                   |
| \(R-F^2 /\% \)\textsuperscript{*}             | 0.85                                                     | 3.39                                                                                   |
| starting angle (\(^{\circ} 2\theta\))        | 10                                                       | 5                                                                                      |
| final angle (\(^{\circ} 2\theta\))           | 110                                                      | 105                                                                                    |
| step width (\(^{\circ} 2\theta\))            | 0.01                                                     | 0.01                                                                                   |
| time/scan (h)                                 | 20                                                       | 20                                                                                     |
| no. of variables                              | 68                                                       | 62                                                                                     |

\textsuperscript{*} \(R-p, R-wp, \text{and } R-F^2\) as defined in TOPAS (Bruker AXS)
Table S 2. Atomic coordinates of Ca(CH$_3$COO)(HCOO)$_2$·H$_2$O and Ca$_3$(CH$_3$COO)$_4$(HCOO)$_2$·4H$_2$O at ambient conditions.

| Atom     | Wyck. | Site | S.O.F. | x/a  | y/b  | z/c  | B /Å$^2$ |
|----------|-------|------|--------|------|------|------|----------|
| 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)* |

Table S 3. Selected bond lengths and angles of Ca(CH$_3$COO)(HCOO)$_2$·H$_2$O and Ca$_3$(CH$_3$COO)$_4$(HCOO)$_2$·4H$_2$O at ambient conditions.

| Atoms        | Distance | Atoms        | Distance | Atoms        | Angle   |
|--------------|----------|--------------|----------|--------------|---------|
| 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(2a) | 125(1)* |
| Ca(1)-O(2a)  | 2.53(1) Å | Ca(1)-O(2b)  | 2.30(2) Å |                   |         |
|              | 2.60(3) Å |              | 2.56(5) Å |                   |         |

| Atoms        | Distance | Atoms        | Distance | Atoms        | Angle   |
|--------------|----------|--------------|----------|--------------|---------|
| Ca(1)-O(1a)  | 2.57(1) Å | Ca(2)-O(1)   | 2.34(1) Å | O(1a)-C(1a)-O(2a) | 125(5)* |
| Ca(1)-O(2a)  | 2.50(1) Å | Ca(2)-O(1a)  | 2.46(1) Å | O(1b)-C(1b)-O(2b) | 110(3)* |
| Ca(1)-O(1b)  | 2.50(1) Å | Ca(2)-O(2a)  | 2.35(2) Å |                   |         |
|              | 2.38(4) Å | Ca(2)-O(1b)  | 2.63(4) Å |                   |         |
|              | 2.38(4) Å | Ca(2)-O(2b)  | 2.38(2) Å |                   |         |
| Ca(1)-O(2b)  | 2.47(4) Å | Ca(2)-O(1c)  | 2.54(1) Å |                   |         |
|              | 2.47(4) Å |              |          |                   |         |
Figure S 1. Scattered X-ray intensities of (a) Ca(CH_3COO)(HCOO)·H_2O and (b) Ca_3(CH_3COO)_4(HCOO)_2·4H_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$_3$COO)(HCOO)·H$_2$O given by Tennent and Baird with the calculated diffraction pattern.

| Tennent and Baird$^{[1]}$ | This study | relative intensity |
|---------------------------|------------|--------------------|
| d/ Å                      | d/ Å       |                    |
| 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$_3$COO)(HCOO)·H$_2$O.

Figure S 3. IR (black line) and Raman spectrum (green line) of Ca$_3$(CH$_3$COO)$_4$(HCOO)$_2$·4H$_2$O.
Figure S 4. Temperature dependent in situ XRPD patterns taken during the thermal decomposition of Ca(CH$_3$COO)(HCOO)·H$_2$O. 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$_3$COO)$_2$ 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.
