Electronic Supplementary Information

Calcium Cyclic Carboxylates as Structural Models for Calcium Carbonate Scale Inhibitors

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Materials

All reagents were purchased commercially and used without further purification.
The PXRD, IR and TGA data for Crystals 2-4

The following figures are drawn by software Plot2.

Figure S1. The XRPD patterns plot in a 2θ range of 5° to 50° for new complexes obtained from (a) reactions of Ca(OH)$_2$ with 1,2,3,4-cyclopentanetetracarboxylic acid (CPTCA, a mix of trans- and cis-), in 1:1 ratio, resulted in the crystallisation of Ca(H$_2$O)$_8$[Ca(C$_9$H$_8$O$_8$)$_2$(H$_2$O)$_4$] (3), and [Ca(C$_9$H$_8$O$_8$)$_2$(H$_2$O)$_4$] (4); (b) after four months later, this mixture transformed into a mix of [Ca(µ-C$_9$H$_8$O$_8$)(H$_2$O)$_4$)$_n$ (1)$^2$ and 4. Experimental pattern and simulated pattern are shown in green, red and black, respectively.
Figure S2. PXRD pattern plot in the 2θ range of 5° to 50° shows the bulk sample of compound [Ca(H₂O)₈][Ca(C₉H₈O₈)(H₂O)]·2H₂O (2) transforms into compound [Ca(µ-C₉H₈O₈)(H₂O)] (1) upon drying up. Experimental pattern and simulated pattern are shown in green and red, respectively.

Figure S3. PXRD pattern plot in the 2θ range of 5° to 50° for compound Ca(C₉H₈O₈)(H₂O) (4). Experimental pattern and simulated pattern are shown in green and red, respectively; the pattern in black is the original material CPTCA (a mix of cis- and trans-). The peak positions correspond well with the results simulated from the single crystal data of compound (4). The unmatched peaks belong to CPTCA, which may belong to the unreacted trans-CPTCA.
Figure S4. IR spectra for complex \([\text{Ca(C}_9\text{H}_9\text{O}_8]_2(\text{H}_2\text{O})_4\) in the range 4,000 to 400 cm\(^{-1}\).

Figure S5. TGA with MS for compound 4. An obvious water loss is observed from 88 °C to 168 °C, followed by ligand decompostion of water, CO and CO\(_2\). The water content is calculated from the first peaks, as the second water peak is correlated with ligand decomposition. Green line for N\(_2\) and CO. Blue curve and arctic curves are for water and CO\(_2\), respectively. The red curve is for thermal curve and derivative curve, respectively.
The PXRD, IR and TGA data for Crystals 5-7

Figure S6. XRPD patterns plot in the 2θ range of 5° to 50° for compound \([\text{Ca}_3(\text{C}_9\text{H}_9\text{O}_6)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}\) (5). The peak positions of the experimental pattern correspond well with simulated from the single crystal data of 5, indicating the purity of the synthesised sample. The experimental pattern and simulated patterns of 5 are shown in green and red, respectively.

Figure S7. IR spectra for complex \([\text{Ca}_3(\text{C}_9\text{H}_9\text{O}_6)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}\) (5) in the range 4,000 to 400 cm\(^{-1}\).
Figure S8. TGA with MS for compound 5. Green line for N\textsubscript{2} and CO. Blue curve and arctic curves are for water and CO\textsubscript{2}, respectively. The red curve is for thermal curve and derivative curve, respectively. The water content is calculated from the first broad peaks from 36 °C to 340 °C. The water peak from 375 °C to 450 °C is correlated with ligand decomposition where water, CO and CO\textsubscript{2} were released.

Figure S9. XRPD patterns plot in the 2θ range of 5° to 50° for a mix of 5 and 6 grown in the media of ethanol. The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.
Figure S10. XRPD patterns plot in the 2θ range of 5° to 50° for \([\text{Ca(C}_9\text{H}_{10}\text{O}_6)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O} \) (6). The peak positions of the experimental pattern correspond well with simulated from the single crystal data that collected at 290 K that with half a lattice water less. The variable temperature study shows that compound 6 can easily transform into 7 after 290 K. The experimental pattern and simulated pattern are shown in green, red and black, respectively.

Figure S11. IR spectra for complex and \([\text{Ca(C}_9\text{H}_{10}\text{O}_6)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O} \) (6) in the range 4,000 to 400 cm\(^{-1}\).
Figure S12. TGA with MS for compound 6. Green line for N₂ and CO. Blue curve and arctic curves are for water and CO₂, respectively. Red and dashed purple line are for thermal curve and derivative curve, respectively. The water content is calculated from the first derivative peak from 30 °C to 247 °C. The water peak after is correlated with ligand decomposition where water, CO and CO₂ were released. The sudden drop of CO&N₂ (in green) is due to the shake of machine.

The PXRD, IR and TGA data for Crystals 8-10

Figure S13. XRPD patterns plot in the 2θ range of 5° to 50° show the presence of compounds [Ca₂(C₁₀H₆O₈)(H₂O)₇]·2H₂O (8) and [Ca(C₁₀H₆O₈)(H₂O)₆]·H₂O (9). The peak positions of the experimental pattern correspond well with simulated from the single crystal data of 8 and 9, indicating a mix of 8 and 9 with 8 as the majority phase formed in the bulk sample. The experimental pattern and simulated patterns of 8 and 9 are shown in green, red and black, respectively.
Figure S14. XRPD patterns plot in the 2θ range of 5° to 50° for compound [Ca\textsubscript{2}(C\textsubscript{10}H\textsubscript{8}O\textsubscript{8})(H\textsubscript{2}O)\textsubscript{7}]\cdot2H\textsubscript{2}O (8). The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.

Figure S15. IR spectra for complex [Ca\textsubscript{2}(C\textsubscript{10}H\textsubscript{8}O\textsubscript{8})(H\textsubscript{2}O)\textsubscript{7}]\cdot2H\textsubscript{2}O (8) in the range 4,000 to 400 cm\textsuperscript{-1}. 
Figure S16. TGA with MS for compound 8. The thermal curve is shown in red; green line for N₂ and CO; blue curve and arctic curves are for water and CO₂, respectively; The difference in percentage may be due to the loss of free water. The water loss is observed from 38 °C to 252 °C. The structure seems to be stable even after 400 °C.

Figure S17. IR spectra for complex [Ca(C₁₀H₁₀O₈)(H₂O)₆]·H₂O (98) in the range 4,000 to 400 cm⁻¹.
Figure S18. TGA with MS for compound 9. Green line for N\textsubscript{2} and CO. Blue curve and arctic curves are for water and CO\textsubscript{2}, respectively. The red curve is for thermal curve and derivative curve, respectively. An obvious water loss is observed from the 30 °C to 206 °C. The CO and CO\textsubscript{2} from structure starts to combust from 350 °C.

Figure S19. Low precision crystal structure of [Ca(C\textsubscript{10}H\textsubscript{12}O\textsubscript{8})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}]\textsubscript{n} (10). Crystal data for [Ca(C\textsubscript{10}H\textsubscript{12}O\textsubscript{8})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}]\textsubscript{n}: M = 630.52, colorless, 0.31 × 0.22 × 0.03 mm\textsuperscript{3}, monoclinic P2\textsubscript{1}c, a = 23.544(5) Å, b = 16.359(3) Å, c = 13.049(3) Å, α = 90.00\textdegree, β = 90.05(3)\textdegree, γ = 90.00\textdegree, V = 5025.9(17) Å\textsuperscript{3}, Z = 8, D\textsubscript{c} = 1.667 g/cm\textsuperscript{3}, F\textsubscript{M00} = 2640.0, Mo K\textalpha radiation, i = 0.71073 Å, T = 120 K, 2θ\textsubscript{max} = 54.0\textdegree, 46548 reflections collected, 10883 unique (R\textsubscript{int} = 0.1089, R\textsubscript{sigma} = 0.0910). Final GOF = 1.061, R\textsubscript{1} = 0.0915, wR\textsubscript{2} = 0.2595, R indices based on 10883 reflections with I \textgeq 2σ(I) (refinement on F\textsuperscript{2}), 358 parameters, 12 restraints, Max/min residual electron density 1.63/-0.83 Å\textsuperscript{3}. Lp and absorption corrections applied, μ = 0.348 mm\textsuperscript{-1}. 

![Crystal structure diagram](image-url)
Figure S20. XRPD patterns plot in the 2θ range of 5° to 50° for compound [Ca(C₉H₈Os)₃(H₂O)₁₂]ₙ (10). The broadening of peaks show the poor crystallinity of the synthesised samples, however, the essential peak positions of the experimental pattern correspond well with simulated pattern from the single crystal, indicating the reasonable unit cell parameter we get. The experimental pattern and simulated pattern are shown in green and red, respectively.

Figure S21. IR spectra for compound [Ca(C₉H₈Os)₃(H₂O)₁₂]ₙ (10) in the range 4,000 to 400 cm⁻¹. The absorption peaks around 3500 cm⁻¹ indicates the stretching vibration of OH⁻ from water as we observed in other hydrated synthesised materials. Peaks at 1200-1700 cm⁻¹ belongs to the CH₂ bending and the C-O stretching indicates the presence of carboxylate group.
Figure S22. TGA with MS for compound [Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n (10). Green line for N\textsubscript{2} and CO. Blue curve and arctic curves are for water and CO\textsubscript{2}, respectively. Red and purple line are for thermal curve and derivative curve, respectively. The water content is calculated from the first derivative peak from 78 \degree C to 178 \degree C. The water peak after is correlated with ligand decomposition where water, CO and CO\textsubscript{2} were released.

The PXRD, IR and TGA data for Crystal 13

Figure S23. PXRD patterns plot in the 2\theta range of 5\degree to 50\degree for compound Ca(C_{10}H_{15}O_4)(H_2O)_2]_n (13). The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.
Figure S24. IR spectra for complex Ca(C_{10}H_{15}O_{4})(H_{2}O)_{2}n (13) in the range 4,000 to 400 cm^{-1}.

Figure S25. TGA with MS for compound Ca(C_{10}H_{15}O_{4})(H_{2}O)_{2}n (13). The amount of the coordinated water is calculated from the first derivative water peak from 71 °C to 140 °C, followed by the ligand decomposition of water, CO and CO_{2}. Green line for N_{2} and CO. Blue curve and arctic curves are for water and CO_{2}, respectively. Red and dashed purple line are for thermal curve and derivative curve, respectively.

References: