Highly symmetric networks derived from cubane-related octametallic complexes of a new oxy-anion of carbon, C₄O₇⁻, each molecule attached to eight neighbors by 24 equivalent hydrogen bonds.

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Supporting information:

1. Preparative procedures for [(MII)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O (M = Zn, Co, Mg, Fe)

2. Powder diffraction patterns for [(MII)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O (M = Zn, Co, Mg)

1. Preparation of [(MII)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O:

[(Zn)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O

A solution of Zn(OAc)₂.6H₂O (742 mg, 3.4 mmol) and Zn(NO₃)₂.6H₂O (603 mg, 3.4 mmol) in water (100 ml) was added to a stirred solution of dihydroxyfumaric acid (500 mg, 3.4 mmol) in water (100 ml). The solution was stirred overnight. Colourless crystals separated from the solution which were filtered off, washed with water and dried at the pump (305 mg, 0.7 mmol, 21 %). Analysis calculated for Zn₈C₁₆H₅₆O₆₄ (i.e. Zn₈(C₄O₇)₄(H₂O)₁₂.24H₂O): C 10.6, H 4.0, Zn 28.8. Found: C 10.4, H 3.6, Zn 28.0.

[(Co)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O

A solution of Co(OAc)₂.4H₂O (1.7 g, 6.8 mmol) in water (100 ml) was added to a stirred solution of dihydroxyfumaric acid (500 mg, 3.4 mmol) in water (100 ml). The solution was stirred overnight. Red crystals separated from the solution which were filtered off, washed with water and dried at the pump (104 mg, 0.32 mmol, 9 %). Analysis calculated for Co₈C₁₆H₅₆O₆₄ (i.e. Co₈(C₄O₇)₄(H₂O)₁₂.24H₂O): C 10.69, H 4.1. Found: C 10.4, H 3.6, Zn 28.0.

[(Mg)₈(C₄O₇)₄(H₂O)₁₂]~24H₂O

A solution of Mg(OAc)₂.4H₂O (2.2 g, 17 mmol) in water (50 ml) was added to a stirred solution of dihydroxyfumaric acid (500 mg, 3.4 mmol) and Me₄NOH (6.8 mmol) in water (100 ml). The solution was stirred for ca. 4 hours and allowed to stand overnight. Colourless crystals separated from the solution which were filtered off, washed with water and dried at the pump (40 mg, 0.13 mmol, 3.2 %).
\[(\text{Fe})_8(\text{C}_4\text{O}_7)_4(\text{H}_2\text{O})_{12}]\sim24\text{H}_2\text{O}\]

Aqueous reaction mixtures containing \(\text{Fe}()\text{SO}_4\_2(\text{NH}_4)_2.6\text{H}_2\text{O}\), dihydroxyfumaric acid and \(\text{NaOAc}\) gave variable proportions of rhombic dodecahedral crystals of \([(\text{Fe})_8(\text{C}_4\text{O}_7)_4(\text{H}_2\text{O})_{12}]\sim24\text{H}_2\text{O}\), which in all cases was a very minor component, together with an unidentified fine precipitate.
2. X-Ray Powder Diffraction Patterns for [(M$^{II}$)$_8$(C$_4$O$_7$)$_4$(H$_2$O)$_{12}$]$\cdot$24H$_2$O:

[(Zn)$_8$(C$_4$O$_7$)$_4$(H$_2$O)$_{12}$]$\cdot$24H$_2$O

Calculated (Platon 2003):

![X-Ray Powder Diffraction Pattern](image)

Observed:
\[(\text{Mg})_8(\text{C}_4\text{O}_7)_4(\text{H}_2\text{O})_{12}]\sim 24\text{H}_2\text{O}\]

Calculated:

Observed:
\[ [(\text{Co})_8(\text{C}_4\text{O}_7)_4(\text{H}_2\text{O})_{12}] \cdot 24\text{H}_2\text{O} \]

**Calculated:**

**Observed:**