Solvent templated synthesis of metal-organic frameworks: structural characterisation and properties of the 3D network isomers 
\{[Mn(dcbp)]·½DMF\}_n \text{ and } \{[Mn(dcbp)]·2H}_2\text{O}\}_n

Eithne Tynan, Paul Jensen, Paul E. Kruger* and Anthea C. Lees
Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland.
E-mail: Paul.Kruger@tcd.ie

Electronic Supplementary Information

Contents:

Synthesis of 1 and 2

Figure ESI 1: Molecular structure and atomic numbering scheme for 2 and 2a and schematic diagram showing the distortion of the dcbp ligand in 1, 2 and 2a.

Figure ESI 2: bis-Carboxylato chains found in 1 and 2.

Figure ESI 3: Packing diagrams showing how the 3D networks in 1 and 2 differ.

Figure ESI 4: Packing diagrams of 1 showing the nature of the 3D network and additional views of its porous structure.

Figure ESI 5: Packing diagrams of 2 and 2a showing the nature of the 3D network and additional views of their porous structures.

Figure ESI 6: TGA traces for 1 and 2.
Synthesis of \([\text{Mn}(4,4'-\text{dcbp}) \cdot \frac{1}{2} \text{DMF}]_n\) (1).

\(\text{MnCl}_2 \cdot 4\text{H}_2\text{O} (56 \text{ mg}, 0.285 \text{ mmol})\) and \(4,4'-\text{H}_2\text{dcbp} (140 \text{ mg}, 0.57 \text{ mmol})\) were placed in a 23ml Teflon\textsuperscript{®}-lined digestion bomb with 2ml H\(_2\)O and 2ml DMF. The bomb was sealed, placed in an oven and heated to 200 °C for 16 hrs and then very slowly cooled to room temperature (3 °C/hr). Yellow plates, suitable for a single crystal diffraction study, were obtained directly in 80% yield.

The crystals are air stable and insoluble in water and common organic solvents.

IR (KBr): 1673(s), 1600(vs), 1558(s), 1427(m), 1397(s, sh), 1380(vs), 1289(w), 1256(w), 1233(w), 1141(w), 1089(w), 1011(w), 925(w), 905(w), 883(w), 786(m), 687(s), 571(w), 538(w), 501(w) cm\(^{-1}\).

\(\mu_B (300 \text{ K}) = 5.80 \text{ B.M.}\)

Found: C 48.24; H 2.64; N 10.29%. Required for \(\text{Mn}_2\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}_9\): C 48.59, H 2.87, N 10.49.

Synthesis of \([\text{Mn}(4,4'-\text{dcbp}) \cdot 2\text{H}_2\text{O}]_n\) (2).

\(\text{MnCl}_2 \cdot 4\text{H}_2\text{O} (56 \text{ mg}, 0.285 \text{ mmol})\) and \(4,4'-\text{H}_2\text{dcbp} (140 \text{ mg}, 0.57 \text{ mmol})\) were placed in a 23ml Teflon\textsuperscript{®}-lined digestion bomb with 4ml H\(_2\)O. The bomb was sealed, placed in an oven and heated to 200 °C for 16 hrs and then very slowly cooled to room temperature (3 °C/hr). Pale yellow needles were obtained in 74% yield.

The yellow crystals are air stable and insoluble in common organic solvents.

IR (KBr): 3550(m, br), 3391 (w, br), 3230(w, br), 1600(vs), 1550(s), 1427(s, sh), 1408 (s, sh), 1383(vs), 1334(m, sh), 1296(w), 1228(w), 1151(w), 1113(w), 1010(w), 916(w), 863 (w), 791 (m), 690(vs), 597(w), 437(w) cm\(^{-1}\).

Found: C 42.94, H 1.68, N 8.27%. Required for \(\text{MnC}_{12}\text{H}_{10}\text{N}_2\text{O}_6\): C 43.26, H 3.03, N 8.41%.

\(\mu_B (300 \text{ K}) = 5.70 \text{ B.M.}\)
Molecular structure and atomic numbering scheme for 2 (left) and 2a (right). Thermal ellipsoids are drawn to 50% probability level. Hydrogen atoms (and water for 2) omitted for clarity. (N.B., data were collected at 153 K for 2 and 343 K for 2a.)

Note how the dcbp ligand is only slightly distorted across the central C1–C1a bond in 2 and 2a [i.e. buckling across C4–C1–C1a, 176.4° (2) and 176.8° (2a)] compared with 1, which is bent across C5–C6 [i.e. C2–C5–C6 (173.6°) and C9–C6–C5 (171.6°)]. See below for a schematic illustration of this difference.
Figure ESI 2:

*bi*-Carboxylato bridged manganese chains in (a) 1 and (b) 2. The black carbons are oriented in the same direction in the two chains, whereas the green carbons in 1 are pointing in a different direction to those in 2, thus resulting in a different orientation for the 4,4'-dcbp ligands and hence different linking of the chains in the two structures.
Figure ESI 3:

Packing diagrams of the networks in 1 (left, viewed down -110) and 2 (right, viewed down the b-axis) showing the relationship between the bis-carboxylato chains and demonstrating how the networks differ. Note how in 1 the chains run down (110) and (-110) and subtend an angle of ca. 66° to each other, whereas in 2 they run parallel with each other and along the c-axis. (see ESI Fig 4 and 5 for further packing diagrams).
**Figure ESI 4:** Packing diagrams of 1 viewed down: $a$, $c$, and 110, respectively.
Figure ESI 5: Packing diagrams of 2 (top) and 2a (bottom) viewed down: a, and 101, respectively. Note the change in the torsion angles between the pyridyl rings on going from 2 to 2a.
**Figure ESI 6:** TGA traces for 1 and 2 (heating rate *ca.* 10°C/min).