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

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The identity of the metal–organic framework formed by Mn(II) and 4,4′-dicarboxy-2,2′-bipyridine (H$_2$dcbp) depends upon the predominant solvent employed in the synthesis and yields the robust network isomers {[Mn(dcbp)]·½DMF}$_n$, 1, and {[Mn(dcbp)]·2H$_2$O}$_n$, 2, which possess vastly different physical properties: 1 irretrievably binds DMF, whereas 2 reversibly binds water whilst retaining crystallinity.

Porous metal–organic frameworks (MOFs) are promising materials for such diverse applications as catalysis, gas storage, selective inclusion and separation and magnetic materials.[1,2] A current challenge is to develop molecular building blocks that will convey specific structural and functional information into a target MOF to yield truly hybrid materials.[1] In this respect we have been attracted to the use of H$_2$dcbp as it potentially has a rich coordination chemistry, which derives from both bipyridyl and carboxylate functionality, each of which possess many and varied physicochemical properties.[3,4] H$_2$dcbp's rigidity should enhance the resultant MOF's stability and its negative charge negate the need for counterions which might otherwise obstruct any voids and reduce porosity. We report herein the synthesis, structural characterisation and thermal properties of two robust MOFs incorporating dcbp: {[Mn(dcbp)]·½DMF}$_n$, 1, and {[Mn(dcbp)]·2H$_2$O}$_n$, 2, which result from the reaction of Mn(II) and H$_2$dcbp under solvothermal conditions. 1 and 2 are network isomers that possess striking differences in their physical properties *i.e.* 1 contains cavities which irretrievably enclathrate DMF molecules, whereas 2 contains channels that reversibly bind water. We believe these to be the first MOFs to show such network isomerism and striking physical disparity.[5]

The solvothermal reaction of H$_2$dcbp and MnCl$_2$ in DMF produced pale yellow plate-like crystals of 1, whereas needle-like crystals of 2 result under hydrothermal conditions.‡ Furthermore, solvent mixtures at or above 50% DMF (by volume) gave 1 while a majority of water gave 2. At no time was the co-existence of 1 and 2 noted within a given preparation. The atomic numbering scheme and atom connectivity for 1 are shown in Fig. 1.§ Distorted octahedral geometry around Mn1 is provided by five deprotonated dcbp ligands. One ligand chelates through bipyridine nitrogen
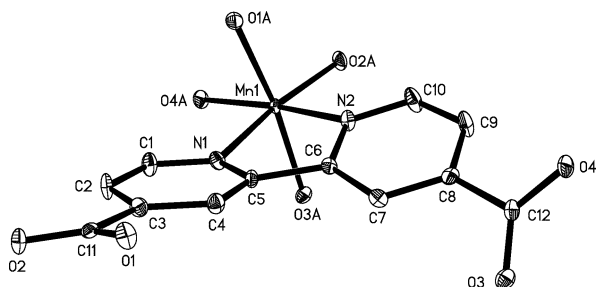
atoms, whilst the remainder coordinate *via* carboxylates from four adjacent dcbp ligands. Each dcbp coordinates to five Mn centres giving a neutral 1 : 1 polymer. The carboxylate about C11 is almost coplanar (11°) with the pyridyl moiety to which it is attached, whereas the carboxylate about C12 is more twisted (*ca.* 34°). A striking feature of this complex is the heavy distortion of the dcbp ligand. The pyridyl rings are rotated at *ca.* 21° to each other and also face 'inwards' giving the dcbp a bent appearance. Consideration of the angles across C5–C6 gives the degree of bending *i.e.* C2–C5–C6 (173.6°) and C9–C6–C5 (171.6°). This is a very strained conformation for the ligand (ESI).

The carboxylate groups join adjacent Mn centres to produce bis-carboxylato bridged chains (ESI) which run down (110) and (−110). Chains within alternate *ab* layers run parallel, but subtend an angle of *ca.* 66° to those in adjacent layers, and cross-link through dcbp to generate a 3D network, Fig. 2. The Schläfli notation for the network[6] is: (4.6^2)(4^2.6)(4^3.6^6.8^6). The network is elaborately perforated with channels along *a*, *b*, and *c* which measure[7] *ca.* 0.34 × 0.45, 0.25 × 0.70, and 0.32 × 0.63 nm, respectively. The channels constitute 23.3% of the crystal volume[8] and naturally contain larger voids at their points of intersection, which are occupied by DMF guests disordered over two positions. TGA of 1 showed that it is exceptionally robust and stable to guest loss up to 410 °C, after which decomposition begins (ESI). MOF guest loss typically precedes host decomposition,[1b] however it appears that DMF is too large to fit through the apertures of the pores and is therefore irreversibly enclathrated within the host network.

A crystal structure analysis revealed 2 to be the same compound as that reported recently by Schareina *et al.*[9] Our lower temperature refinement§ is included here for comparison with 1 and 2a. Apart from small differences in the distortion from octahedral symmetry, the coordination sphere about Mn in 2 is identical to that found in 1 (ESI). However, the dcbp ligand is less distorted as exemplified by the 176.4° angle across the central C1–C1a bond (*i.e.* C4–C1–
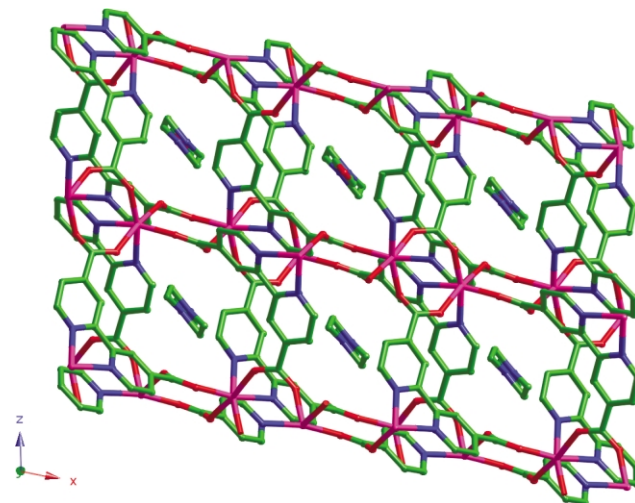

Fig. 1 Molecular structure and atomic numbering scheme for 1. Thermal ellipsoids drawn to 50% probability level. Hydrogen atoms and DMF omitted for clarity. Note the degree of bending around C5–C6.

Fig. 2 The 3D network of 1 showing the disordered DMF molecules within the *ca.* 0.25 × 0.70 nm channel. (Hydrogens omitted)

† Electronic Supplementary Information (ESI) available: figures and experimental data. See http://www.rsc.org/suppdata/cc/b3/b315483a/

C1a). Symmetry dictates that this distortion buckles the ligand as opposed to bending it, as was observed in **1**. The carboxylate group, which is rotated by *ca*. 42° to the pyridyl ring (*cf*. 11° and 34° in **1**), bridges adjacent Mn centres and forms chains that cross-link through dcbp to give a 3D network, Fig. 3. Although the components, and essentially the coordination spheres, of the networks in **1** and **2** are identical their topology is different. The Schläfli notation for the network[6] in **2** is: $(4^2.6)(4^4.6^2.8^8.10^1)$. In contrast to **1**, all carboxylate chains in **2** run parallel to each other and down the crystallographic *c*-axis (ESI). The network is not as heavily perforated as **1** with only two directions containing channels of appreciable dimension[7] that measure *ca*. 0.38 × 0.68 nm (down *c*-axis) and 0.23 × 0.57 nm (down 101). The water molecules reside in the former channels, with each disordered over two close positions, and hydrogen bond to each other giving chains extending along the *c*-axis. They also hydrogen bond to the carboxylate groups. The channels in **2** constitute 18.2% of the crystal volume.[8] TGA showed that the water molecules are rather weakly bound and vacate the pores before 65 °C with the network remaining intact up to 410 °C (ESI).

1 and **2** display essentially the same network decomposition temperature (*i.e.* independent of topology). Notably, **1** and **2** retain single crystallinity even after extreme thermal treatment. Indeed, when a single crystal of **2** was heated to 70 °C on the diffractometer and a new data set collected, the structure of the 'guest-free' host [Mn(dcbp)]$_\infty$, **2a**, was revealed.§ Thus, **2** is a new member of only a handful of examples of molecular materials to be characterised by single crystal X-ray diffraction in both the presence and absence of guests.[1,10] The cell parameters of **2a** *cf*. **2** (153K) vary slightly but significantly: *a* and *b* lengthen by 1.9 and 0.4%, *c* contracts by 2.6%, *β* increases by 2.7%, and *U* decreases by 5.1%. These changes are accompanied by a decrease in the torsion angles between pyridyl rings (*ca*. 18° *cf*. 22° in **2**) and between the carboxylate group and the pyridyl ring (*ca*. 35° *cf*. 42° in **2**). Nevertheless, **2a** retains its porous nature, which now accounts for 17.0% of the cell volume.[8] Furthermore, when crystals of **2a** were exposed to air on cooling, **2** was regenerated showing the reversibility of the desorption–adsorption process. We are currently investigating whether the porous network of **2a** adsorbs guests other than water.

In conclusion, we have shown that the identity and physical properties of the network generated during the solvothermal reaction of MnCl$_2$ and H$_2$dcbp is solvent dependent. The solvent molecules provide a template around which the network 'building blocks' assemble. As DMF and H$_2$O possess different steric profiles the resultant networks also differ and the predominant solvent within a mixture dictates which network forms. This finding is significant as it augurs well for the generation of dissimilar but related families of MOFs from dcbp and metal combinations by simply changing the solvent used during synthe-
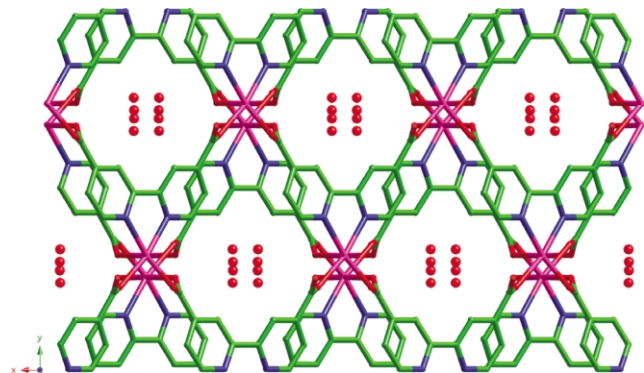
sis. Furthermore, we have shown that whilst network topology differs in this case, thermal stability does not, verifying that host integrity is independent of the nature of the guest. Current studies extend this work to include the use of additional metal ions and solvents and results from this research will be reported in due course.

Notes and references

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Fig. 3 The 3D network of **2** showing the disordered H$_2$O molecules within the *ca*. 0.38 × 0.68 nm channel. Note how all carboxylate chains run parallel to each other along the *c*-axis. (Hydrogen atoms omitted)