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Metal–organic frameworks constructed from pentagonal antiprismatic and cuboctahedral secondary building units

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Two crystalline metal–organic frameworks formulated as $Zn_6(NDC)_5(OH)_2(DMF)_2·4DMF$, MOF-48, and Zn_7(*m*-BDC)$_6(OH)_4(H_2O)_2·6DMF·4H_2O$, MOF-49, (NDC = 1,4-naphthalenedicarboxylate; *m*-BDC = 1,3-benzenedicarboxylate) have been synthesized and fully characterized by single crystal X-ray diffraction studies, which reveal that the frameworks are constructed from pentagonal antiprismatic (MOF-48) and cuboctahedral (MOF-49) secondary building units respectively, however, both are reticulated into 3-D structures having the B network of CaB_6.

In the chemistry of metal–organic frameworks (MOFs), especially where metal ions have been joined by polytopic carboxylate links, M–O–C clusters generally result in which the carboxylate C atoms define the shape of what is referred to as a secondary building unit (SBU).[1–4] Such entities have been recognized and used as tools for simplifying complex structures,[5] and in cases where reaction conditions can be directed to give specific SBU geometries; they have the potential to allow for the assembly of MOFs by design.[6–8] Furthermore, the size of SBU constructs is directly related to achieving optimal porosity and rigidity of MOFs including the design of periodic arrays of open metal sites within their voids.[6–10] With the long-term goal of understanding the factors affecting the composition, topology, shape and size of SBUs, we have begun to explore synthetic routes that may lead to new SBUs. Here we report two 3-D metal carboxylate frameworks prepared by linking Zn(II) with 1,4-naphthalenedicarboxylate (NDC), and *m*-benzenedicarboxylate (*m*-BDC) to give MOF-48 and MOF-49, respectively. We find that these MOFs are constructed from pentagonal antiprismatic and cuboctahedral SBUs; however, both form 6-connected CaB_6 type networks rather than 10- and 12-connected networks that one might expect to find based on the geometry of their respective SBUs. We show that pairwise connections between SBUs in MOF-48 and 49 provide the means for these frameworks to adopt networks of lower connectivity.

Vapour diffusion from a mixture of H_2O_2 (0.40 mL, 40% in water) and chlorobenzene–triethylamine (20 mL/1 mL) into a clear solution of *N,N′*-dimethylformamide (DMF)/chlorobenzene (5 mL/5 mL) containing $Zn(NO_3)_2·6H_2O$ (0.029 g, 0.097 mmol) and NDC acid (0.015 g, 0.069 mmol) gives, after 7 d, cube-like crystals of MOF-48 in 33% yield (based on NDC acid). MOF-49 was prepared by dissolving $ZnCl_2$ (0.060 g, 0.44 mmol) and *m*-BDC acid (0.040 g, 0.261 mmol), in that order, in DMF (5 mL). This solution was subjected to dropwise addition of a mixture of 0.6 M aqueous methylamine–acetonitrile (2 mL/5 mL). The resulting clear solution was left undisturbed for three days at room temperature to give hexagonal shape crystals in 27% yield (based on *m*-BDC acid). MOF-48 and 49 were formulated and characterized by elemental microanalysis† and X-ray single crystal diffraction studies.‡

MOF-48, $Zn_6(NDC)_5(OH)_2(DMF)_2·4DMF$, is constructed from hexameric units composed of four tetrahedral and two octahedral Zn(II) centres, where a total of ten NDC links doubly bridge the zinc atoms in a dimonodentate fashion (Fig. 1a). Each cluster has an inversion centre, which relates two zinc trimer units in which the zinc centres are further joined by a triply bridging μ_3–OH group. One terminal DMF ligand is bound to each of the octahedral zinc centres. The assignment of μ_3-OH was based on the near tetrahedral angles around the central O (110.8(6), 114.0(4), 114.0(4)°), which are in the range of those found in molecular complexes.[11]

It is useful to connect the points-of-extension (the carboxylate C atoms) in the hexameric units, a process that leads to SBUs having pentagonal antiprismatic geometry (Fig. 1b). Each SBU is connected to six other SBUs to give a 3-D framework having 6.2 Å diameter[12] 1-D channels where four DMF guests per formula unit reside (Fig. 1c). It is important to note that in addition to two single NDC connections along [001] between SBUs, there are eight pairwise connections (Fig. 1c). Here each pair of NDC links connecting two SBUs can be considered topologically as a single ditopic link, in essence a doubly reinforced link. Since each SBU acts as a six connector, the structure of MOF-48 has the topology of a decorated B network of CaB_6.[13]

The crystal structure of MOF-49, Zn_7(*m*-BDC)$_6(OH)_4(H_2O)_2·6DMF·4H_2O$, is constructed from a unit composed of four tetrahedral and three octahedral Zn(II) centres in which two identical units, each composed of two tetrahedra and one octahedron, are joined together by an octahedron (Fig. 2a). Within each such unit, the carboxylates of four *m*-BDC links bridge the zinc centres in a dimonodentate fashion, and an additional two links bind as monodentate to the tetrahedral zinc

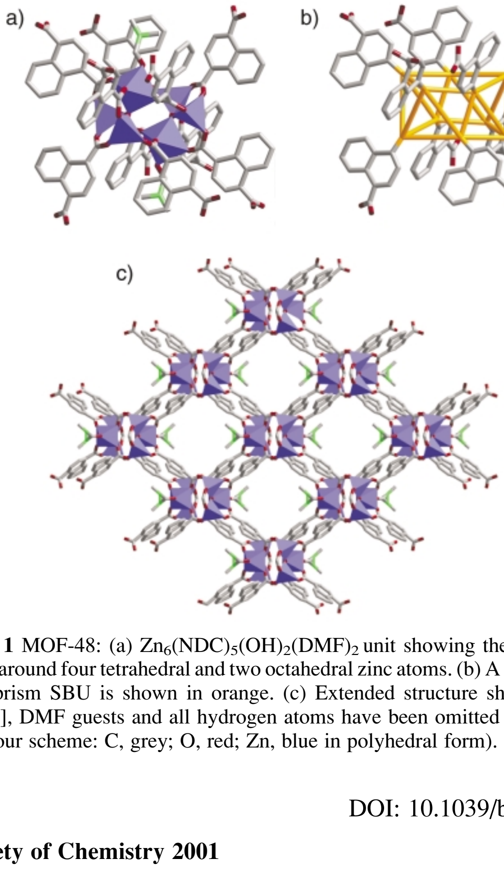

Fig. 1 MOF-48: (a) $Zn_6(NDC)_5(OH)_2(DMF)_2$ unit showing the coordination around four tetrahedral and two octahedral zinc atoms. (b) A pentagonal antiprism SBU is shown in orange. (c) Extended structure shown along [001], DMF guests and all hydrogen atoms have been omitted for clarity. (colour scheme: C, grey; O, red; Zn, blue in polyhedral form).

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centres. Each unit also contains two μ_3-OH groups (their identity was confirmed as in MOF-48) and only one terminal water ligand bound to each octahedral centre.

In the crystal structure of MOF-49, a total of twelve carboxylates per formula unit in which carboxylate C atoms are found to lie on the vertices of a large, distorted cuboctahedral SBU (Fig. 2b). Here each SBU is bridged to six others *exclusively* through pairwise connections resulting in an extended framework having a topology similar to MOF-48, in that it is also related to the B network of CaB_6. MOF-49 contains a 3-D porous system with 3.5–5.5 Å diameter voids, where six DMF and four water molecules per formula unit reside as guests.

It is instructive to note that although the SBUs observed in MOF-48 and -49 have overall geometries generally associated with higher coordination (10 and 12), their large size combined with the short link do not allow for high coordination of the SBU in the solid state, as that would be sterically disfavoured. Instead the SBUs are reticulated into frameworks having six-coordination around each SBU; this made possible by the pairwise binding of links. Another factor that may be operating here was revealed upon close examination of distances between benzene rings of pair members: distances in the ranges 3.246–3.634 Å (MOF-48) and 3.315–3.725 Å (MOF-49) were found—values that indicate strong π–π intermolecular forces, and point to the possibility of their relevance in achieving lower coordination SBUs. It will be necessary to use *branched* links in order to attain SBUs with higher coordination as recently demonstrated for seven coordinated SBUs in MODF-1.[14]

Calculations of the space occupied by guests in MOF-48 and -49 indicate that it represents 50% of the crystal volume. The mobility of guests within their frameworks was assessed by thermal gravimetric studies: Here, 8.711 mg (MOF-48) and 17.23 mg (MOF-49) were heated over a range of 30–400 and 30–650 °C, respectively. For MOF-48, 25.8% weight loss was observed in the range 50–380 °C, which is equivalent to the loss of six DMF molecules per formula unit (calc.: 22.6%) representing four DMF guests and two DMF ligands. While for MOF-49, 16.95% weight loss was observed in the range 30–140 °C, which is equivalent to the loss of 3.5 DMF guests and four water guests per formula unit (calc.: 17.34%) representing the 3.5 DMF guest molecules and four water guest molecules found in the air-dried samples subjected to elemental microanalysis.† Experimentation is currently underway to examine whether the evacuated forms of MOF-48 and -49 can maintain their porosity in the absence of guests.

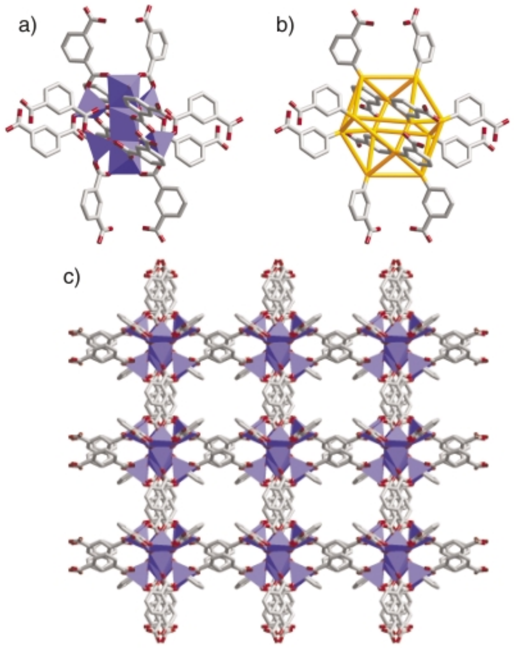

Fig. 2 MOF-49: (a) $Zn_7(m\text{-BDC})_6(OH)_4(H_2O)_2$ unit showing the coordination around four tetrahedral and three octahedral zinc atoms. (b) A cuboctahedron SBU is shown in orange. (c) Extended structure along [001], DMF and water guests and all hydrogen atoms have been omitted for clarity (same colour scheme and drawing conditions as in Fig. 1).

This study has prompted us to focus on examining the role of intermolecular forces and the geometry of the link on the symmetry, size and coordination number of SBUs, aspects central to design of MOFs.

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Notes and references

† Elemental microanalysis: MOF-48. Calc. for $Zn_6(C_{12}H_6O_4)_5(OH)_2$-$(DMF)_2 \cdot 4DMF$: C, 48.40; H, 3.85; N, 4.34. Found: C, 48.52; H, 3.74; N, 4.46%. MOF-49. Calc. for $Zn_7(m\text{-BDC})_6(OH)_4(H_2O)_2 \cdot 3.5DMF \cdot 4H_2O$: C, 32.40; H, 3.70; N, 2.62. Found: C, 32.65; H, 3.72; N, 2.63%.

‡ *Crystallographic data*: MOF-48: $Zn_6(C_{12}H_6O_4)_5(OH)_2(DMF)_2 \cdot 4DMF$, M = 1935.65, monoclinic, space group $C2/m$, a = 19.5043(16), b = 16.4817(14), c = 14.6396(12) Å, β = 95.902(2)°, U = 4681.2(7) Å^3, Z = 2, μ(Mo-Kα) = 1.586 mm^{-1}, D_c = 1.373 g cm^{-3}, T = 173(2) K $R1$ ($I > 2\sigma(I)$) = 0.0939 and $wR2$ (all data) = 0.2546.

MOF-49: $Zn_7(m\text{-BDC})_6(OH)_4(H_2O)_2 \cdot 6DMF \cdot 4H_2O$, M = 2013.43, monoclinic, space group $P2/c$, a = 13.509(2) Å, b = 11.9838(19, c = 27.039(4) Å, β = 93.459(3)°, U = 4369.4(12) Å^3, Z = 2, μ(Mo-Kα) = 1.977 mm^{-1}, D_c = 1.530 g cm^{-3}, T = 153(2) K, $R1$ ($I > 2\sigma(I)$) = 0.0983, $wR2$ (all data) = 0.2720.

CCDC reference numbers 171766 and 171767.

See http://www.rsc.org/suppdata/cc/b1/b108684g/ for crystallographic data in CIF or other electronic format.

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