Twelve-connected porous metal–organic frameworks with high H_2 adsorption†

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The twelve-connected metal–organic frameworks {[$Ni_3(OH)(L)_3$]·*n*(solv)}$_\infty$ 1 and {[$Fe_3(O)(L)_3$]·*n*(solv)}$_\infty$ 2 [LH_2 = pyridine-3,5-bis(phenyl-4-carboxylic acid)] have been prepared and characterised: these materials can be desolvated to form porous materials that show adsorption of H_2 up to 4.15 wt% at 77 K.

Metal–organic co-ordination framework materials have attracted much attention in recent years due to their inherent design flexibility,[1] and their potential to form stable, highly-porous scaffolds,[2,3] which can be used for gas storage[4] and for the adsorption of volatile organic compounds.[5] In particular, frameworks constructed from metal–carboxylate interactions can exhibit high thermal stability and permanent porosity upon desolvation.[2–5] Trinuclear clusters of the type $[M_3(\mu_3\text{-O})(O_2CR)_6(X)_3]^{n-}$ (M = Cr, Fe) have been reported as building blocks for metal–organic framework construction;[6] however, in most of these reported cases, the metal ions bind to a terminal solvent molecule (X), typically water or pyridine. We reasoned that angular pyridyldicarboxylate ligands[7] would template the formation of trinuclear clusters in a divergent synthesis in which the ligand building block would act not only as a bridging carboxylate, but would also involve the terminal pyridyl N-donor to replace X in the trinuclear fragment $[M_3(\mu_3\text{-O})(O_2CR)_6(X)_3]^{n-}$ and afford extended and highly-connected frameworks. We are especially interested in developing frameworks of high connectivity[8] that might show enhanced stability and stable porosity for reversible gas adsorption. We report herein the use of the angular ligand pyridine-3,5-bis(phenyl-4-carboxylic acid) (LH_2) in the construction of two isomorphous 12-connected 3D porous frameworks, which can be desolvated to afford porous materials that can adsorb H_2.

Reaction of $Ni(NO_3)_2·6H_2O$ or $Fe(NO_3)_3·9H_2O$ with LH_2 in dmf afforded the two compounds {[$Ni_3(OH)(L)_3$]·*n*(solv)}$_\infty$ **1** and {[$Fe_3(O)(L)_3$]*n*(solv)}$_\infty$ **2**, respectively. The structure of **1**‡ is based around the trinuclear cluster node [$Ni_3(OH)(O_2CR)_6$] (Fig. 1) extended by the branched organic spacer L^{2-} *via* carboxylate bridging and, as predicted, N-binding to each Ni centre (Fig. 2(a)). The trinuclear cluster is held together by a central bridging hydroxo ligand, Ni–O 1.9824(4) Å, and each pair of Ni centres is bridged by two carboxylate groups from separate ligands above and below the $Ni_3(OH)$ plane (Fig. 1). When the pyridine nitrogen is included, the local stereochemistry at each Ni centre can be viewed as octahedral. Each trinuclear cluster [$Ni_3(OH)(O_2CR)_6$] acts as a node and is linked to six nearby cluster nodes (green spheres in Fig. 2(b)) to form an α-Po lattice (Fig. 2(c)), with an internode separation of 13.4017(13)–13.402(2) Å. This array affords pores of some 10 Å diameter as calculated by PLATON[9] and these are filled with solvent molecules. In addition, the L^{2-} bridges extend to six further cluster nodes (red spheres in Fig. 2(b)) at a distance of 18.848(2) Å to give an overall 12-connected framework of $3^{18}4^{42}5^{6}$ topology (Fig. 2(b)). The 12-membered polyhedron defined by the six close and six further distant nodes is a highly distorted cube-octahedron in which the two triangles above and below the central hexagon are displaced in opposite directions. Alternatively, this polygon can also be viewed as an octahedron capped by two triangular units (see ESI†). Twelve-connected metal–organic frameworks are very rare and the two reported examples are based on a more regular cube-octahedral structural matrix.[10] The topology of **1** can be described in an alternative manner in which the cluster node [$Ni_3(OH)(O_2CR)_6$] links to ligand nodes. In this analysis, the cluster node forms a highly novel 9-connected tricapped trigonal prismatic polyhedron of $4^{6}6^{21}8^{9}$ topology (see ESI†), with the 3-connected ligand nodes having $4^{2}6$ connectivity.

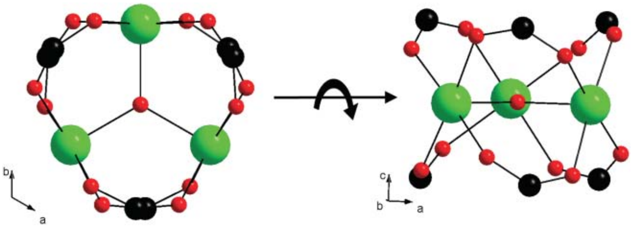

Fig. 1 View of [$Ni_3(OH)(O_2CR)_6$] cluster along *c* axis (left) and *b* axis (right).

Compound **2** was obtained by the same procedure as above but substituting $Fe(NO_3)_3·9H_2O$ for $Ni(NO_3)_2·6H_2O$. The framework structure of **2**‡ is isomorphous to that of **1** except that the trinuclear cluster node in **2** comprises a [$Fe_3(O)(O_2CR)_6$] moiety rather than [$Ni_3(OH)(O_2CR)_6$] as in **1**. Thus, in both **1** and **2** the central oxygen lies on a site of crystallographic 32 (D_3) symmetry with the metal centres occupying two-fold sites. There are a considerable number of analogous mixed-valence Fe_3O cluster complexes reported in the literature,[11] but fewer related Ni-based

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† Electronic supplementary information (ESI) available: Experimental details and characterization of ligands and complexes, single-crystal X-ray structure analyses, PXRD and TGA data, details of bond valence sum (BVS) analyses, N_2 isotherms for **1** and **2**, and magnetochemical analysis on **1**. See DOI: 10.1039/b614254k

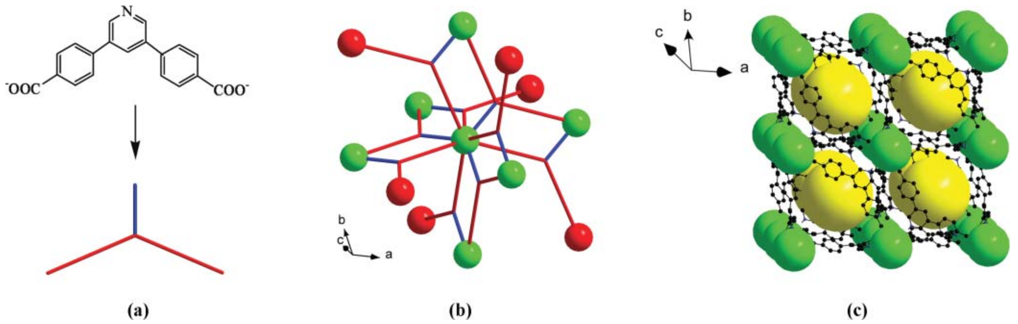

Fig. 2 (a) Schematic representation of the tri-branched ligand L^{2-}; (b) 12-connectivity about the $[Ni_3(OH)(O_2CR)_6]$ cluster node (shown as green and red spheres) and (c) pores in **1** shown as yellow spheres.

systems.[12] Significantly, a literature search using CCDC ConQuest version 1.8 confirms that the majority of Ni_3 cores are based around μ_3-OH bridging (119 hits) as in **1** with only 2 hits[13] for complexes showing a planar Ni_3O unit. No hits were observed for μ_3-O bridging to Ni_3 cores. Thus, the assignments of μ_3-OH and μ_3-O moieties in **1** and **2**, respectively, are based upon literature precedents and upon bond valence sum analyses (see ESI†).[14] Although the latter approach is not definitive, these structural assignments do not affect the subsequent discussion of the porosity of the desolvated materials. The assignment for **1** as incorporating a μ_3-OH moiety is further supported by magnetochemical measurements confirming the formation of formal Ni(II)Ni(II)Ni(III) mixed-valence centres (see ESI†).

Thermal gravimetric analyses show one main weight loss of 38% for **1** and 31% for **2** between 20 and 250 °C. A plateau is reached above 250 °C before the structure decomposes at 350 °C. To determine the stability of the framework after removal of solvent, both *in situ* variable-temperature powder X-ray diffraction (PXRD) measurements under vacuum and single-crystal X-ray data of **1** following *in situ* heat treatment of the crystal were carried out. *In situ* PXRD measurements were taken every 10 °C from 30 to 120 °C with the sample heated at 2 °C min^{-1}. The temperature was held for 1 h at each setting point before measuring the X-ray diffraction pattern. All experimental PXRD data match the calculated X-ray pattern derived from the single crystal structures very well, and thus confirm high thermal stability of the framework under vacuum. Even after 20 h at 100 °C under vacuum, the PXRD pattern for the frameworks **1** and **2** as defined by the single-crystal structure analyses can be clearly identified. Moreover, single-crystal X-ray diffraction data for **1** also confirm the stability of the framework structure on heating and desolvation. Thus, a single crystal of **1** was taken directly from the crystallisation solvent and mounted in a dry N_2 flow at −123 °C and a data set collected for the fresh sample. The crystal was then heated *in situ* to 50 °C at a rate of 2 °C/min, and held at this temperature for 1 h. The crystal was then cooled to −123 °C and a full data set collected. The procedure was repeated with heating to 100, 150, 200, and 227 °C with the crystal held in a dry N_2 gas flow at all times. The framework, as described above, is clearly conserved at all points in this treatment, reinforcing the PXRD results and confirming the thermal stability of this framework. Only very small crystals were obtained for compound **2** and a single-crystal X-ray diffraction study has been carried out on the fresh sample only; however, *in situ* PXRD results confirm high thermal stability for this framework as well.

The N_2 adsorption of desolvated **1** and **2** at 77 K each shows a reversible type-I isotherm characteristic of microporous material. The BET surface areas for **1** and **2** were calculated to be 1553 and 1200 m^2 g^{-1}, respectively. Sorption data for desolvated **1** and **2** are listed in Table 1. D_2 and H_2 sorption were measured to 1 bar for both samples and the molar ratio of adsorbed D_2 or H_2 (Fig. 3) is within the anticipated range of 1.0–1.1.[15] This consistency between H_2 and D_2 sorption results for both compounds confirms the accuracy of the recorded data for H_2 adsorption and the absence of any significant uptake of impurities. In addition, all H_2 adsorption results were corrected for buoyancy effects. At 1 bar, the wt% adsorption of H_2 is 1.99% for **1** and 1.60% for **2** at 77 K. At 20 bar (Fig. 4) this reaches a maximum at 4.15 and 3.05% for **1** and **2**, respectively, corresponding to 23.7 and 17.3 H_2 molecules per formula unit for **1** and **2**, respectively.

In summary, through the use of a designed angular ligand with two different donors in a 2 : 1 carboxylate : amine ratio, two isomorphous 12-connected metal–organic framework materials have been successfully synthesized and characterised. These

Table 1 Sorption data for compound **1** and **2** at 77 K

Material	N_2/ mg g^{-1}	A_{surf}[a]/ m^2 g^{-1}	H_2 (D_2) wt% uptake at 1 bar	No. of H_2 molecules per formula unit[b] at 1 bar (20 bar)	H_2 wt% adsorption at 20 bar
1	547	1553	1.99 (4.47)	11.4 (23.7)	4.15
2	425	1200	1.60 (3.46)	9.1 (17.3)	3.05

[a] BET surface area calculated assuming a monolayer coverage of close-packed N_2 with a cross-sectional area of 16.2 Å^2 molecule^{-1}. [b] Formula unit is $[Ni_3(OH)(L)_3]$ for **1** and $[Fe_3(O)(L)_3]$ for **2**.

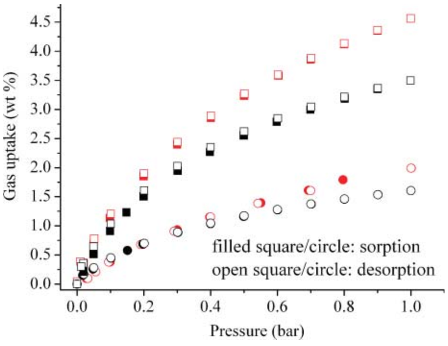

Fig. 3 H_2 (circles) and D_2 (squares) isotherms for **1** (red) and **2** (black) at 77 K.

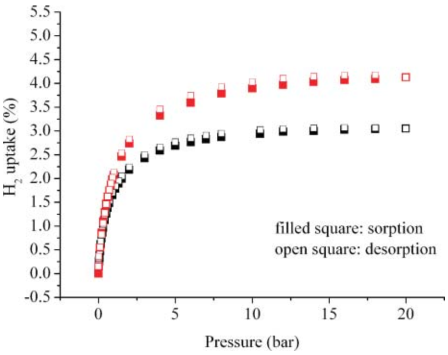

Fig. 4 H_2 sorption isotherm up to 20 bar for **1** (red) and **2** (black) at 77 K.

frameworks exhibit extremely high thermal stability under vacuum. H_2 adsorption measurements at 1 bar and up to 20 bar, coupled to D_2 adsorption at 1 bar, confirm high H_2 adsorption in these materials with excellent reversibility. The adsorption at 20 bar is among the highest capacities thus far reported for metal–organic frameworks.[16]

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Notes and references

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