An unprecedented eight-connected self-penetrating network based on pentanuclear zinc cluster building blocks†

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The first eight-connected self-penetrating metal–organic framework, based on pentanuclear zinc cluster building blocks, defines a new self-penetrating topology for eight-connected networks and represents the highest connected topology presently known for self-penetrating systems.

The interest in entangled systems is rapidly increasing, not only for their potential applications as functional materials,[1] but also because of their aesthetic and often complicated architectures and topologies.[2] It is well-known that catenanes, rotaxanes and molecular knots occupy an important place in the area of molecular entanglement.[3] Interpenetrating networks can be described as polymeric equivalents of catenanes and rotaxanes. Once rare, these are now becoming increasingly common, aided by the rapid growth of network-based crystal engineering,[4] and many beautiful structures have been constructed and discussed comprehensively in reviews.[5] More recently, a complete analysis of all 3D-interpenetrated metal–organic framework structures contained in the Cambridge Structural Database, with a rationalization and classification of the topology of their interpenetration, has been undertaken.[6] However, the study of self-penetrating (self-entangled or polyknotting) networks, considered as extended equivalents of molecular knots, is still in its infancy. This is in contrast to the extensively-studied interpenetrating networks, as evident from a recent review by Ciani and co-workers.[7] These structures are single nets, having the peculiarity that the smallest topological rings are catenated by other rings belonging to the same net. Until now, no actual eight-connected self-penetrating net has been observed in metal–organic frameworks (MOFs), implying a challenging issue in coordination chemistry.

Of concurrent interest has been the construction of highly connected coordination frameworks.[8] This has been a formidable task in crystal engineering due to the limited coordination numbers of metal centers and the steric hindrance issues of most commonly-used organic ligands. Recently, the utilization of polynuclear metal clusters as building blocks to construct highly connected frameworks has proved to be a feasible route to them; their large surface areas (sometimes even nanoscale) meaning they can more readily accommodate the steric demands of organic linkers. On the other hand, the introduction of metal clusters into MOFs may lead to new functional solid-state materials that possess fascinating structures[9] and special properties.[10,11] A few uninodal six-connected network structures obtained through this approach have been reported;[10,12] for example, the exceptionally stable and highly porous 3D MOFs reported by Yaghi's group[10,12a] and the porous, highly interpenetrating MOFs reported by Lin and co-workers,[12d] which use tetrameric zinc clusters as six-connected nodes. Furthermore, two isomorphous structures with eight-connected nets have also been reported, based on metal–carboxylate trimeric cluster nodes.[13] These structures contain 2D (3,6) nets, bridged by axial links into two interpenetrating 3D nets. However, in a very loose and general sense, it can be said that the higher the nuclearity of a metal cluster, the more likely that a highly connected net is obtained. Thus, this strategy provides a promising pathway towards the generation of MOFs with highly connected nodes.

One common approach to the synthesis of high-nuclearity clusters is to control the hydrolysis of metal salts with the aid of carboxylate ligands.[14] In this communication, we chose 1,4-benzenedicarboxylic acid (H_2bdc) as the carboxylate-containing ligand because the carboxylate group may induce core aggregation, and it should be feasible to link discrete clusters into an extended network *via* its linear bridging ability. Herein, we report an unprecedented eight-connected network utilizing pentanuclear zinc clusters as eight-connected nodes and linear dicarboxylates as linkers. Remarkably, this net defines a new self-penetrating topology for eight-connected networks, thereby filling a lacuna for the entanglement of more highly connected coordination nets. In addition, the isolation of the species $[Zn_5(\mu_3\text{-}OH)_2(bdc)_4(phen)_2]$ (**1**) (phen = 1,10-phenanthroline) shows that polynuclear metal clusters have the ability to afford enough coordination space to construct highly connected frameworks, even in the presence of chelating ligands.

Compound **1** was prepared by hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$, H_2bdc, phen and H_2O at 140 °C for 5 days.‡ Single crystal X-ray analysis§ shows that the structure of **1** contains pentanuclear zinc clusters, in which each μ_3-OH interlinks three crystallographically unique Zn atoms, with non-bonding Zn···Zn distances of 3.276(4)–3.416(4) Å. The three independent Zn atoms represented herein, exhibit three different coordination geometries, as depicted in Fig. 1. Another pentanuclear zinc cluster having three types of Zn environment has also been observed,[15] but in which all the Zn atoms are 4-coordinate. The Zn(2) atom lies at a center of symmetry and coordinates to two μ_3-OH moieties (Zn–O 2.060(2) Å) and four carboxylate oxygen atoms (Zn–O 2.031(2)–2.292(2) Å) from four different bdc ligands giving a distorted

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† Electronic Supplementary Information (ESI) available: Details of the synthesis, additional figures, and luminescent spectra of **1**. See http://dx.doi.org/10.1039/b506398a

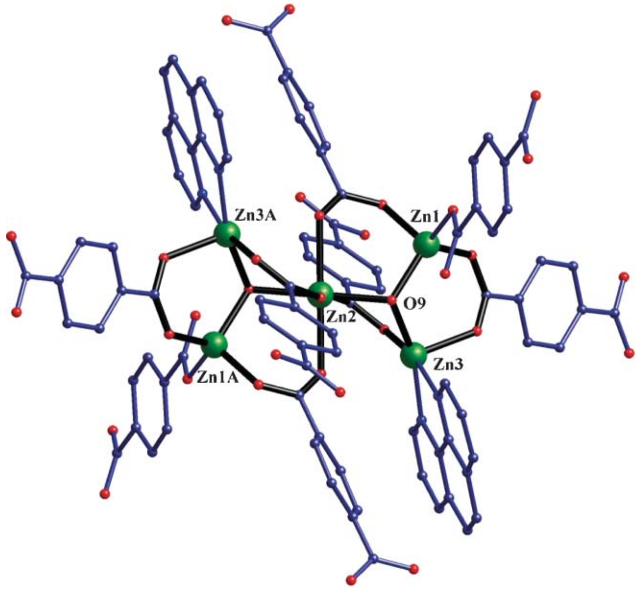

Fig. 1 The pentanuclear zinc building unit of **1**.

octahedral geometry. The Zn(1) atom is coordinated by three carboxylate oxygen atoms (Zn–O 1.948(2)–1.962(2) Å) from three bdc ligands and a μ_3-OH atom (Zn–O 1.980(2) Å) to complete a distorted tetrahedral environment, whereas Zn(3) exists in an approximately tetragonal-pyramidal geometry, being ligated by two nitrogen atoms (Zn–N 2.107(3)–2.124(3) Å) from a chelating phen ligand, two carboxylate oxygen atoms (Zn–O 2.046(3) and 2.058(2) Å), two bdc ligands and a μ_3-OH atom (Zn–O 2.005(2) Å). Thus, this unique pentanuclear zinc cluster includes all the common coordination numbers of the Zn^{II} ion. Moreover, two coordination modes for the bdc ligands have been found; one is bis(bidentate) and the other bis(monodentate) (Scheme S1†). As such, each pentanuclear metal cluster is surrounded by ten organic ligands—eight bridging bdc and two chelating phen. This, therefore, defines an eight-connected node. Each pentazinc core is further linked to eight nearest-neighbors, with distances of 11.237(3)–15.885(4) Å, through eight bdc ligands (Fig. 2), thus resulting in a unique 3D uninodal eight-connected framework of $4^{24}.5.6^{3}$ topology.

Notably, the structure of **1** is completely different from that of the familiar body centred cubic lattice (**bcu**, sometimes called the CsCl net).[2e,f] As shown in Fig. 3, the parallel (4,4) nets (yellow) of both **bcu** and **1** are cross-linked by zigzag chains, however, the detailed connection modes are different. In **bcu**, the green zigzag chain in the inter-layer region bridges across the diagonal of a single window in the (4,4) net (Fig. 3, left). In **1** however, it bridges across the diagonal of two neighboring windows (Fig. 3, right). Such an unusual linkage mode is also distinct from a previously-known non-**bcu** eight-connected net,[8b] in which the zigzag chains bridge the edges of one (4,4) net and the diagonal of the next. As a result of the unusual bridging of parallel layers, catenations of the four-membered shortest circuits by other four-membered shortest circuits are observed in the inter-layer connections (two rings shaded blue and green in Fig. 3, right). Therefore, the resulting array is a single eight-connected self-penetrating network (Fig. 4, left). The maximum symmetry net for this topology (with links equal to 1) is trigonal *R*-3*m* (*a* = 1.291, *c* = 1.000) with the vertex at 0,0,0.

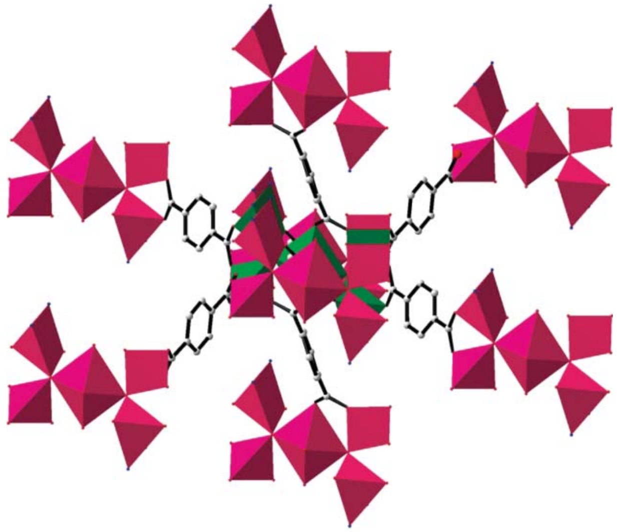

Fig. 2 View of the linkages of a pentazinc core (green) with eight adjacent cores (red).

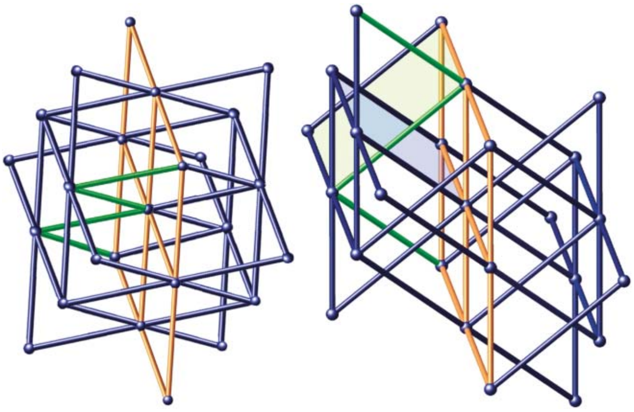

Fig. 3 Schematic representations of the topologies observed in the **bcu** network (left) and **1** (right), highlighting the essential differences between them.

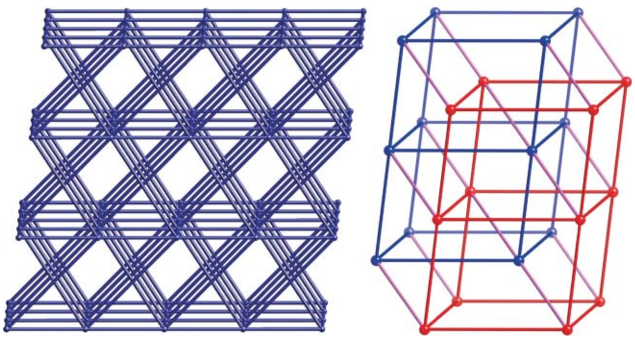

Fig. 4 The eight-connected self-penetrating net (left), and its relationship to two cross-linked interpenetrating **pcu** nets (right).

To our knowledge, of the previously-reported eight-connected coordination polymers,[8,13] none of them display self-penetration. Consequently, this represents the first and only example of self-penetration occurring in such a highly connected coordination polymer network and this net also represents the highest connected topology of any known entangled species. To the best of our knowledge, only one self-penetrating structure, assembled purely from organic molecules, has been reported to contain nodes with connectivity higher than six.[16] In this structure, however, the eight-connected networks are constructed by weak iodo···nitro interactions. The topology may be described in terms of (4,4) sheets, displaying threefold 2D→2D parallel interpenetration, and diamondoid nets intersecting through shared nodes. The topology is significantly different to the structure of the coordination polymer described here.

Further insight into the nature of this intricate architecture can be obtained by considering the net constructed from two interpenetrating primitive cubic nets (**pcu** or α-Po), which are cross-linked by two extra connections from each node along the cube diagonals (Fig. 4, right).

In summary, we have prepared and characterized the first eight-connected self-penetrating coordination net, in which pentanuclear zinc clusters act as eight-connected nodes. The successful isolation of this species not only provides an intriguing example of chemical topology, but also confirms the significant potential of constructing new highly connected frameworks using polynuclear metal clusters as building blocks. Appropriate choices of metal clusters as well as spatial linkers will lead to the discovery of a large variety of new topological structures and types in the near future.

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Notes and references

‡ Synthesis of **1**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (149 mg, 0.5 mmol), H_2bdc (66 mg, 0.4 mmol), phen (40 mg, 0.2 mmol) and water (10 mL) in a 23 mL Teflon reactor under autogenous pressure was heated at 140 °C for 5 d and then cooled to room temperature at a rate of 10 °C h^{-1}. Colorless crystals of **1** were obtained (yield: 50 mg, 36% based on Zn). Found: C, 48.93; H, 2.32; N, 4.15. $C_{56}H_{34}Zn_5N_4O_{18}$ requires: C, 48.82; H, 2.49; N, 4.07%

§ Crystal data for **1**: $C_{56}H_{34}N_4O_{18}Zn_5$, M = 1377.72, triclinic, space group P-1, a = 11.225(2), b = 11.237(2), c = 12.435(3) Å, α = 95.87(3), β = 103.14(3), γ = 118.47(3)°, V = 1301.4(4) Å^3, Z = 1, D_c = 1.758 g cm^{-3}, $F(000)$ = 692, μ = 2.354 mm^{-1}, 12847 reflections measured, 5895 unique (R_{int} = 0.0354), final R_1 = 0.0397, wR_2 = 0.0889, S = 1.020 for all data. The data were collected at 298(2) K on a Rigaku R-AXIS RAPID IP diffractometer with Mo–Kα monochromated radiation (λ = 0.71073Å). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program. CCDC 267795. See http://dx.doi.org/10.1039/b506398a for crystallographic files in CIF or other electronic format.

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