An unprecedented fivefold interpenetrated lvt network containing the exceptional racemic motifs originated from nine interwoven helices†

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An unprecedented fivefold interpenetrated lvt network, containing the rare racemic motifs originated from nine interwoven helices, is reported, which represents the highest degree of interpenetration presently known for 3D nets containing only planar four-coordinate nodes.

Current interest in polymeric coordination networks is rapidly expanding for their intriguing architectures[1] and potential applications,[2] although true crystal engineering of coordination polymers (*i.e.* prediction of the solid-state structure precisely) still remains a long-term challenge for the crystal engineer. 'Network approach' or topological approach considered as an important achievement in crystal chemistry, is a powerful tool for the design and interrogation of crystal structures. To date, network topologies in coordination polymers have been discussed in several notable reviews[3] following a seminal compilation by Wells decades ago.[4] Many structural types and topological features anticipated on a pure theoretic background within crystal chemistry but unprecedented in the world of inorganic compounds and minerals, such as the 12^3 self-penetrating net[5] discussed by Wells,[4a] the 'dense' net[6] suggested by O'Keeffe,[7] and the unusual uniform 8^6 net[8] unrecognized by Wells, have been successively discovered in the area of coordination polymers, thanks to the continuous efforts of synthetic chemists. More recently, a most comprehensive analysis on the 774 three-periodic extended metal-organic frameworks (MOFs) with uninodal net topology reveals that significantly fewer MOF structures have square geometry (47, 6.1%) in contrast to the large majority of MOFs having tetrahedral geometry, octahedral or triangular geometries.[9] On the other hand, the phenomenon of interpenetration, once a rarity, is now becoming increasingly common[10] aided by the rapid growth of network-based crystal engineering, especially for the four-connected diamondoid nets with a total degree of interpenetration (hereafter termed Z) from 2 to 10.[11] However, little progress has been made with other four-connected networks based solely upon square planar nodes, for instance, tetragonal CdSO$_4$ (6^58), cubic NbO (6^48^2), quartz dual (7^59), and lvt (4^28^4), as evidenced in a recently complete investigation of all 3D interpenetrated structures contained in the Cambridge Structural Database (CSD).[11] This may be attributed, at least in part, to the fact that unlike other network topologies, such as SrSi$_2$, diamond, or primitive cubic,

these nets except CdSO$_4$ are not self-dual, namely they are not fully catenated when two dual nets are intergrown, thereby limiting their propensity to give interpenetration in crystalline frameworks.[12] As far as we know, within these species the maximum value of Z is 4 (two CdSO$_4$ networks of Classes Ia and IIIa).[13] Therefore, particularly interesting and challenging is the issue of how to construct a network containing only planar four-coordinate nodes and whether it is possible to realize the relatively high degree of interpenetration for it.

In an attempt to construct 3D networks of square planar centers, we chose a long, flexible dicarboxylate ligand, 4,4′-oxybis(benzoate) (oba), based on the following considerations: i) multidentate carboxylates are known to be essential in chelating metal ions and locking their position into M–O–C clusters.[14] The most popular is the "paddle-wheel" cluster in which a metal dimer is bridged by four dimonodentate carboxylates. It is a well-defined square motif from the perspective of the second building unit (SBU), the baricentre of which defines a planar four-coordinate node (Fig. 1). Yaghi and co-workers have successfully constructed decorated-expanded PtS networks from the assembly of square (M–paddle-wheel) and tetrahedral (organic ligand) building blocks.[14,15] Therefore, it should be possible to link such square units by the long oba bridges to give a 3D network containing planar nodes. ii) Generally, longer ligand will lead to larger voids. In a very loose and general sense it can be said that the larger the voids in a 3D net the more likely interpenetration occurs and the more number of independent nets a particular void is passed through. The oba ligand (12.1 Å), which we make use of here, is longer than those (usually 4,4′-bipyridyl, 7.1 Å) employed in previously reported network topologies containing planar centers,[16] thus presumably allow higher degree of interpenetration. Fortunately, by trial and error we have now isolated a new compound, [Cu(oba)(H$_2$O)]$_2$·0.5H$_2$O (**1**), exhibiting an unprecedented fivefold interpenetrated **lvt** topology, according to the aforementioned idea. This species has several unusual features: i) it is the highest degree of interpenetration presently known for 3D
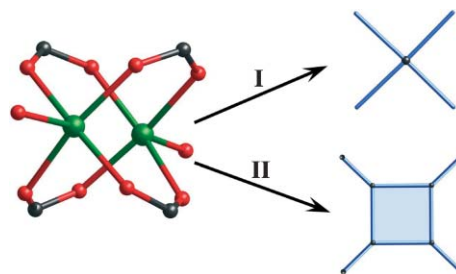
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† Electronic supplementary information (ESI) available: synthetic details and additional plots of the structures. See DOI: 10.1039/b510089e

Fig. 1 Definitions of 4- and 3-connected nodes.

nets containing only planar four-coordinate nodes, ii) the fivefold interpenetrated network incorporates the unique racemic motifs originating from nine interwoven helices, and iii) a single net can also be defined as an '*augmented **lvt***' net by replacing the vertices of the **lvt** net by squares, showing an unprecedented three-connected 4·8·20 topology.
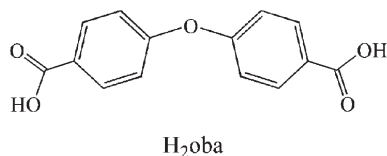
H$_2$oba

Compound **1** was obtained as blue block crystals in 45% yield by hydrothermal reaction of CuCl$_2$·2H$_2$O, H$_2$oba, triethylamine and H$_2$O at 160 °C for 5 days.†

Singe-crystal X-ray diffraction‡ reveals that **1** crystallizes in tetragonal space group $I\bar{4}$§ and exhibits a fascinating 3D polymeric architecture consisting of five equivalent interwoven nets of **lvt** topology. For a single net, the unsymmetric unit consists of two crystallographically unique copper(II) atoms, each exhibiting identical coordination environment with four equatorial carboxyl-ate oxygen atoms (Cu–O 1.9600(17)–1.9832(19) Å) and one axial aqua ligand (Cu–O 2.1460(19) and 2.1839(19) Å) (see Fig. S1 of ESI†). The two unique copper atoms are bridged by four dimonodentate carboxylates to form a paddle-wheel Cu$_2$(CO$_2$)$_4$ motif with a Cu···Cu distance of 2.6063(5) Å that is further linked to four equivalent neighbors through four oba ligands into a 3D net (Fig. S2†). If one considers the baricentres of paddle-wheel Cu$_2$(CO$_2$)$_4$ motifs to be four-connected nodes (Fig. 1, I), the single net can then be rationalized as a 3D net with planar four-coordinate vertices. Fig. 2 reveals the unusual topology displayed by this structure with short and long Schläfli symbol 4^{2}8^4 and 4.4.8$_4$.8$_4$.8$_8$.8$_8$. In spite of the same circuit symbol with PtS net, it is geometrically and topologically quite different (Fig. S3†). This topological type, initially classified by O'Keeffe as 'net #97'[7a] and subsequently described as symbol **lvt**,[7b] is uncommon among four-connected nets, occurring in only seven metal–organic frameworks (MOFs) out of 1127 refcodes (0.62%) analyzed from the CSD.[9] An interesting feature of the single net is the presence of helical subunits that are formed by V-shaped oba ligands bridging adjacent dicopper units (see Fig. 2 and Fig. S2†). This therefore provides a better insight into the intricate 3D architecture. That is, it can be considered being constructed by the assembly of these
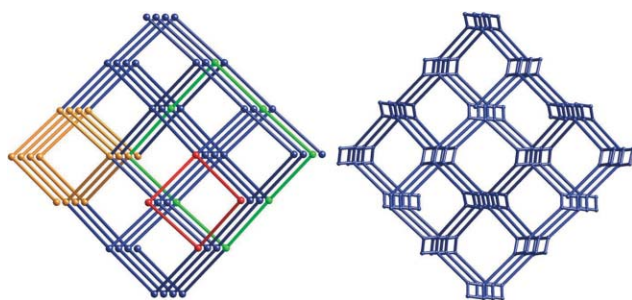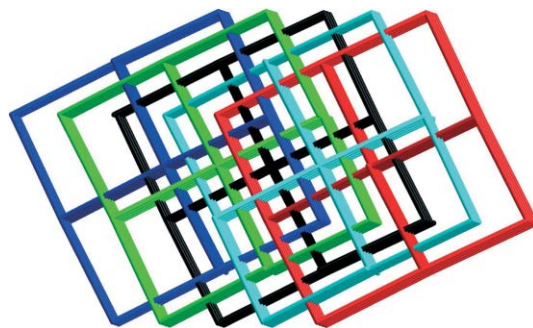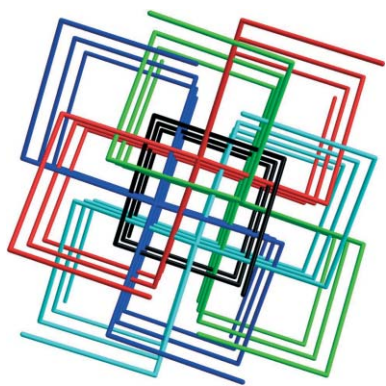
helical subunits *via* sharing four-connected nodes where each helix is connected with four adjacent ones of opposite handedness (Fig. S2†). Very intriguingly, the steric array of these helices produces two types of nanoporous channels in an independent 3D network along the crystallographic *c* axis, both of square section (*ca.* 15 × 15 Å): one is spiral encircled by helical chains, the other is simply formed by the stacking of the squares (Fig. S4†). Of equal interest is that if the Cu$_2$O$_8$C$_4$ moiety is regarded as a square SBU rather than a single point by connecting C atoms in turn (Fig. 1, II), the four-connected net of **1** can be augmented into a novel three-connected net symbolized as 4·8·20 (see Fig. 2, right), which is unprecedented though a large number of three-connected 3D nets were listed by Wells.[4]

In the present case, the longer separations between four-connected nodes (14.689(2) and 14.746(2) Å) generate two very large rhombic windows. One is planar eight-membered circuit (Fig. 2, green) with edges as long as 29.431(3) Å, the other is non-planar four-membered circuit (Fig. 2, red) with edges of 14.746(2) Å. The sizes of the two circuits in an individual net, to the best of our knowledge, are the largest in the known **lvt** nets, so that allow a much greater degree of interpenetration to occur. Fig. 3 shows a representation of the fascinating entangled array in which each given **lvt** net is interpenetrated by four other independent, identical nets in a parallel manner. Note that 4^{2}8^4 net in **1** is 'partially catenated', meaning that only the larger eight-membered rings are catenated by others, leaving four-membered rings uncatenated. Five interpenetrating eight-membered rings from separate nets are shown in Fig. S5† As a consequence, though a single net contains large channels, they are mainly filled by the other interpenetrated nets, leaving only small cavities (3.2% of the cell volume calculated by PLATON) to host the guest water molecules (Fig. S6†).

Based on the number of examples known at present, there is an apparent preference of interpenetrating four-connected nets to adopt tetrahedral geometry, while those exclusively based on planar four-coordinate nodes, are not well known. As far as we know, the value of *Z* is 2 for only two reported interpenetrating cases with **lvt** topology,[17] and up to 4 for interpenetrated **cds** networks. Therefore, the unusual fivefold interpenetration of **1** not only contains the maximum interpenetrating number presently known for such nets, but also represents the highest degree of interpenetration for four-connected networks containing planar nodes. The most fascinating structural feature of the fivefold interpenetrated network consists in the presence of the unique racemic motifs originated from nine interwoven helices. If we

Fig. 2 Schematic presentations of a single 3D net of **1**: 4-connected **lvt** net (left) and the augmented **lvt** net derived by replacing the vertices of the **lvt** net by squares (right). Highlighted are a single helix (yellow), four- and eight-membered circuits (red and green).

Fig. 3 Schematic view of the fivefold parallel interpenetration in **1**.

Fig. 4 A schematic illustration of the racemic motif originated from nine interwoven helices.

choose a helical chain from a single network, then there are eight equivalent helices appearing in pairs from four other nets interweaving it in all directions, four same handedness and four opposite. A representation of the beautifully interwoven helices is presented in Fig. 4. The sole known chiral entangled array of ninefold helixes was reported by us very recently,[18] in which nine independent homochiral helices interlock in a manner similar to that observed for a remarkable example reported by Lin and coworkers.[19]

In summary, we have prepared and characterized the first fivefold interpenetrated **lvt** net, containing only planar four-coordinate nodes by using a long flexible carboxylate ligand, whose observed unusual features make it an interesting member of four-connected networks. The current work also indicates that the chemical nature of ligands (*e.g.* size, donor properties and conformations), can be used to achieve control over the product topology.

Notes and references

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