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Pentagonal helices in a periodic metal-organic framework. Crystals as computers for discovering structures of minimal transitivity.

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The structure of a recently-published metal-organic framework is deconstructed into its underlying net which is found to be of exceptional complexity. It is shown that this is because of local pentagonal symmetry and the structure is in fact the simplest possible (minimal transitivity) given that local symmetry.

In this communication we analyze the underlying net of a recently-published[1] metal-organic framework (MOF). The indium carboxylate material is made up of rods of metal-oxygen polyhedra sharing opposite corners linked by ditopic linkers – a common structural scheme in MOFs. A simple topological description of such structures is obtained by examining the pattern of points of extension and how they are linked.[2] Points of extension are points on links at the interface between the organic and inorganic components – in the case of carboxylate MOFs the carboxylate carbon atoms. Most of the examples adduced earlier had topologies described by uninodal (vertex-transitive) nets.[2] This is accord with the *minimal transitivity* principle which states that the number of independent vertices and edges of the net (vertex and edge transitivity) should be as small as possible.[3] Thus for nets of linked ladders (ribbons of quadrangles sharing opposite edges) there must be two kinds of edge on the ladder and at least one more linking the ladders, so the minimum number of edges is three and the minimal transitivity of the net is 1 3 as commonly found.[2,4] The MOF in question has a similarly-obtained underlying net, now containing ribbons of triangles sharing edges, with 10 vertices and 25 edges (transitivity 10 25) – unprecedented complexity for this sort of MOF. In this communication we show that this complex structure is indeed a minimum transitivity net that can accommodate the unusual conformation of the rod.

First we explain the minimal transitivity principle. For simplicity we restrict the discussion to crystallographic (periodic) embeddings of the nets of structures in which nodes (vertices of the abstract net) are joined by links (edges). If there are one or two kinds of node (nodes related by symmetry are the same kind) there must be at least one kind of link and the minimal transitivity is 1 1 or 2 1. Likewise with three kinds of node (say A, B and C) there must be at least two kinds of link (say A-B and A-C) and the minimal transitivity is 3 2.[3] But consider now a uninodal net with five coordination. There is no crystallographic operation of order five, so there must be at least two kinds of link and the minimal transitivity is now 1 2. As we have seen above, the nets of linked ladders have minimum transitivity 1 3. For helical ribbons of triangles there must be now three kinds of link on the ribbon so the minimal transitivity of a net constructed by linking such ribbons is 1 4. We now adduce an example of a MOF with such an underlying net.

In the structure of another recently-reported[5] Cd MOF there are rods of CdN_4O_2 octahedra linked by sharing opposite corners. These rod are linked in turn into a 3-dimensional network by the ditopic linker 4,4'-bipyrazolyl. In Fig. 1 we show a rod of the structure with a carbon atom of the pyrazolyl ring identified as point of extension. As can be seen from the figure, the pattern of points of extension forms a triangulated ribbon shaped into a hexagonal helix. These helices are then linked into the minimal transitivity net with RCSR symbol[6] **wjp** (Fig. 1), which indeed has transitivity 1 4. We note in passing that, as far as we know, there are only two minimal-transitivity nets for linking such hexagonal ribbons – the other having RCSR symbol **fna**.

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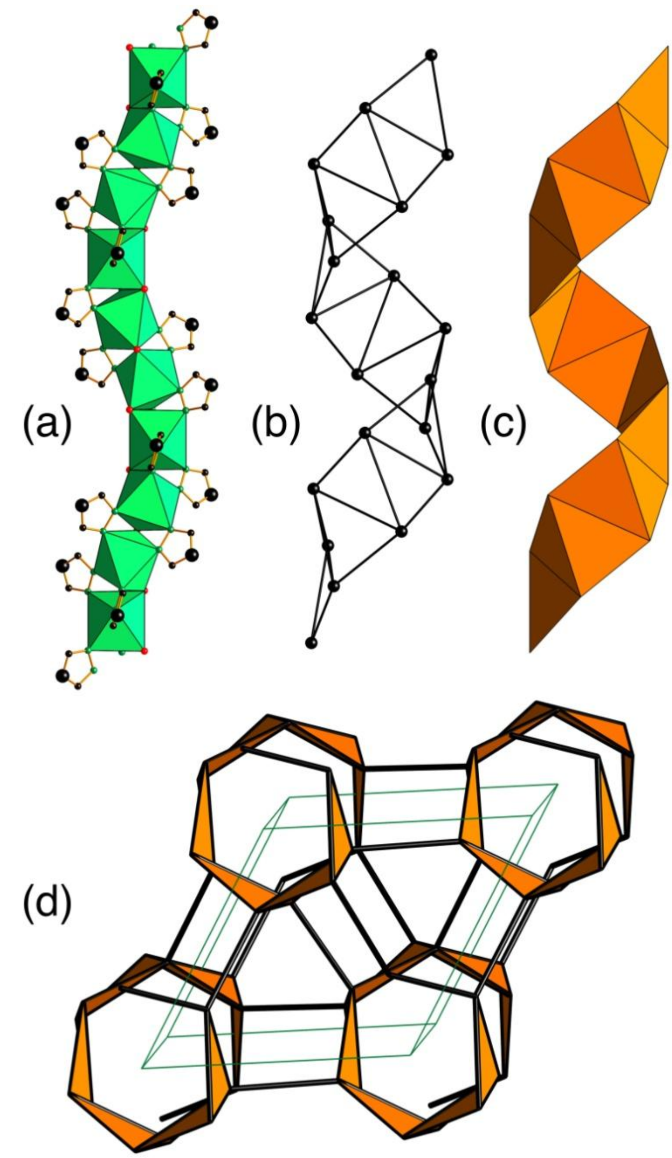

Fig. 1 (a) The rod of CdN_4O_2 octahedra in the MOF of Pettinari *et al.*[5] O red, N green, C black with points of extension as large spheres. (b) The pattern of points of extension. (c) The same as a helical ribbon. (d) The underlying net, **wjp**, of the structure, showing the hexagonal helical ribbons.

We turn now to the structure of the MOF with high-transitivity (10 25) net. The clue to understanding is provided by the observation[1] that the rod (Fig. 2) has local five-fold screw symmetry which is, of course, incompatible with periodicity. As can be seen from the figure the pattern of points of extension along the rod is a pentagonal triangulated ribbon. The net (Fig. 3) of the linked pentagonal ribbons has transitivity 10 25 and we show that that is indeed minimal transitivity.

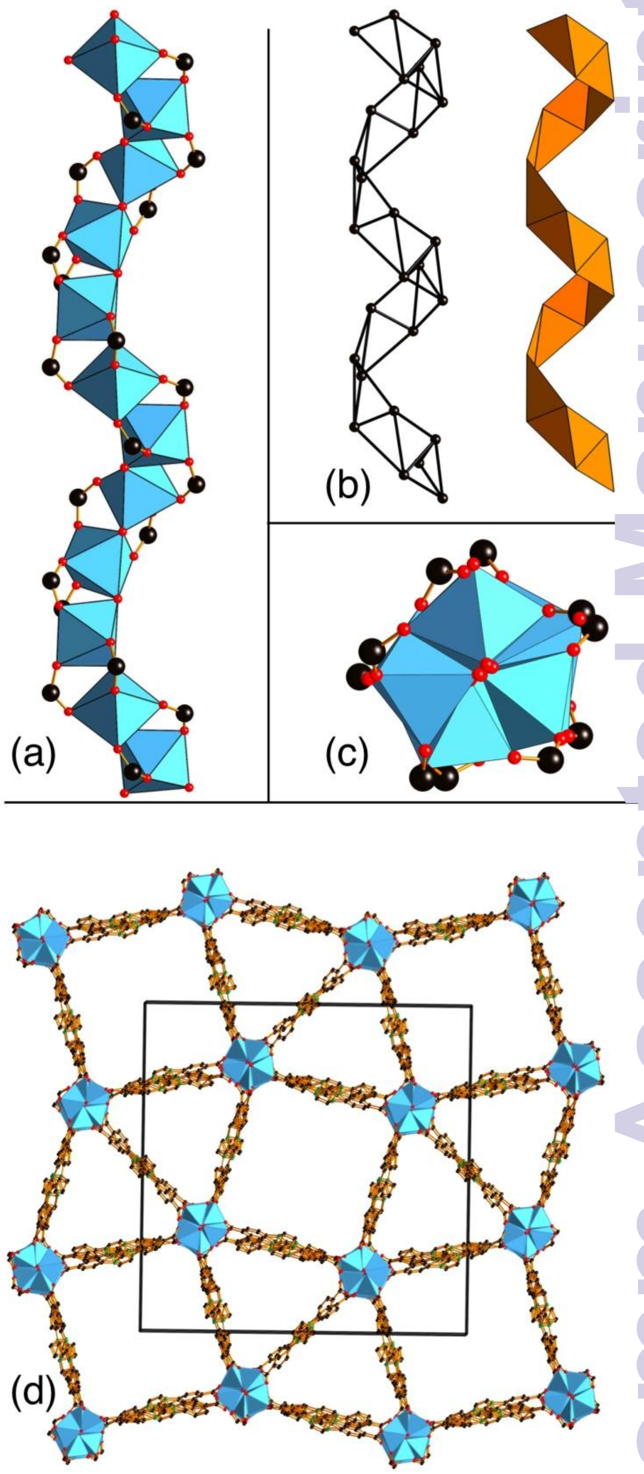

Fig. 2 The structure of the MOF of Song *et al.*[1] (a) The rod of InO_6 octahedra. O red, caboxylate C (points of extension) large black spheres. (b) The pattern of points of extension in (a) showing the helical ribbon. (c) The rod in (a) projected along the rod axis showing the 5-fold symmetry. (d) A projection of the MOF structure (viewed down the **a** axis). The rods of InO_6 octahedra are joined by essentially linear cationic ditopic carboxylate linkers 1,3-bis(carboxyphenyl)imidazolium.

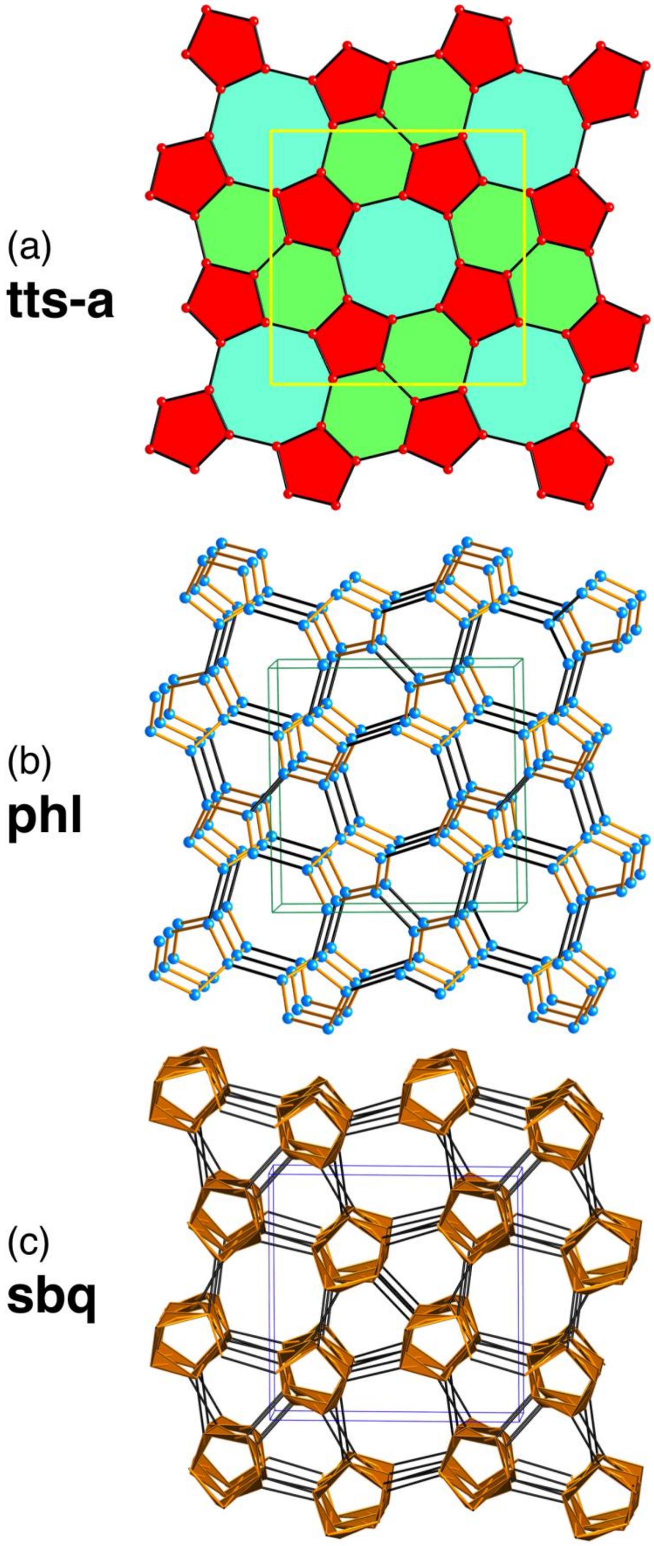

Fig. 3 (a) The augmented version of the 2-periodic 3^2.4.3.4 net (**tts**) showing linked pentagons (red). (b) The 3-periodic, 3-coordinated net **phl** with pentagonal helices (yellow links). (c) The 5-coordinated net **sbq** with pentagonal ribbons (yellow).

First we consider a simpler net. Shrinking the ribbon width to zero, so that pairs of vertices linked by an edge parallel to the rod axis merge, gives a simple pentagonal helix and linking those into a three-periodic, 3-coordinated net gives a net (**phl**) with transitivity 5 8. This is minimal transitivity as we now show. First it is noted that there can be no five-fold symmetry operation in a periodic structure so the five vertices in the repeat unit cannot be related by symmetry. As a result there must be 5 vertices and 5 edges unrelated by symmetry on the helix. It remains to link these helices with pentagonal cross-section into a three-period structure by links normal to the helix axis. It is well known that there are just three uninodal 2-periodic nets with 5-coordinated vertices. These have vertex symbols (RCSR symbols in parentheses) 3^2.4.3.4 (**tts**), 3^3.4 (**cem**) and 3^4.6 (**fsz**). The augmented versions of these, in which each vertex is replaced by a pentagon, are thus the only ways of linking one kind of pentagon into a 2-periodic layer. The most-symmetrical one, **tts-a** (Fig. 3), requires three links between pentagons, so to make the 3-periodic net of linked pentagonal helices at least three more links are required. We note that three links are also the minimum required for links between five vertices – they must be of the type 1-2, 3-4, 5-5. Accordingly the minimum transitivity is 5 8. We have no guarantee that this can be achieved, but in an actual net (**phl**, Fig. 3), indeed it can. Analysis by Systre[7] shows that the net has intrinsic symmetry $P2_1/n$ and the projected pattern of linked helices is that of **tts-a**.

Analysis of the transitivity of the net of the crystal structure under discussion proceeds similarly. There are now ten 4-coordinated vertices in the repeat unit of the ribbon. Again the absence of a five-fold symmetry means that in a periodic structure there will be ten vertices and twenty edges unrelated by symmetry on the ribbon. With ten vertices there must be at least five additional links (of the sort 1-2, 3-4, 5-6, 7-8, 9-10) between the helices, so at least 25 kinds of edge, and the transitivity of the 3-periodic, 5-coordinated net must be at least 10 25. Again we emphasize that all we have shown is that if the net exists it must have transitivity at least that large. Remarkably, the crystal finds a minimal-transitivity net (**sbq**, Fig. 3), again with symmetry $P2_1/n$ as determined by Systre. This is also the symmetry of the real crystal structure.

As previously noted,[1] the pattern of rod axes in the crystal structure (Fig. 2) is 3^2.4.3.4 (**tts**), unique to rod MOFs so far described. The above analysis explains why that comes about.

The remaining challenge is to learn why the rod has pentagonal symmetry in the first place. That knowledge might eventually lead to synthesis of exotica such as quasicrystalline MOFs.

The enumeration of nets of a certain kind is an active area of research because of their importance to designed synthesis of materials.[8] The particular problem of finding *a priori* a minimal-transitivity net containing pentagonal helical triangulated ribbons, or indeed any pentagonal motif, is daunting – certainly beyond our capabilities. There are reasons to believe that the crystal, acting as an analogue computer, has found the simplest and most symmetrical solution possible – and one that indeed satisfies the minimal transitivity principle.

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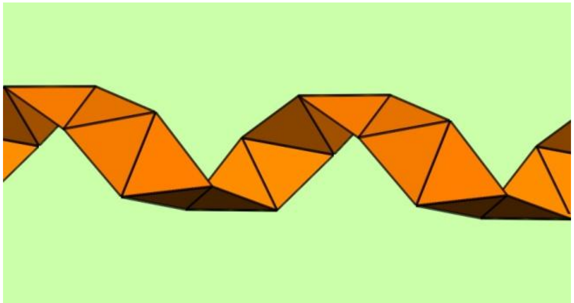

A net of exceptional complexity is found in the structure of a metal-organic framework with pentagonal structure-building units.