Nets, tiles, and metal-organic frameworks

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Nets, tiles, and metal-organic frameworks

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An account is given of the basic nets that are important in the description and design of metal-organic framework (MOF) structures. These are generally of *minimal transitivity*, a concept which is explained. Derived nets are defined and the advantages of using derived nets to describe the topology of MOF frameworks with multiple branch points are emphasized. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4901292]

Possibly, the most significant development in materials chemistry in recent years has been the synthesis and characterization of metal-organic frameworks (MOFs).[1] The subject is a unique combination of inorganic and organic chemistry that calls for the synthetic skills of both those disciplines. The lure for many are the actual and potential applications in gas storage, separations, catalysis, etc. For the lover of chemistry, the appeal is also the extraordinary cornucopia of beautiful and unprecedented structures (atomic arrangements) that have emerged and the remarkable success that has been achieved by producing materials with targeted structures by design. This has brought about a paradigm shift in the way we think about crystal structures: from point sets to *connected* point sets, i.e., *graphs*. The challenge is to describe these last structures and to evaluate the possibilities.

MOFs have two components known as secondary building units (SBUs): metal-containing "inorganic" clusters and organic linkers. The metal SBU may be a finite cluster generally with either a polygonal or a polyhedral shape (Figure 1) or infinite as, for example, a 1-periodic rod of linked metal-oxygen octahedra. This article is concerned only with the structures of MOFs with finite SBUs. The shapes of the metal SBUs are defined by *points of extension*, in the examples shown in the figure carboxylate carbon atoms, where the SBUs are joined to the organic component. The linker, commonly a carboxylate, may be ditopic, polytopic with just one branch point, or polytopic with multiple branch points as shown in Figure 2. Figures 1 and 2 show also how the SBUs are abstracted as nodes and links forming geometric shapes. The art and science of linking these shapes into desired frameworks with targeted pore geometry and chemistry is what we have called *reticular chemistry*.[2] Our approach to analyzing (*deconstructing*) structures into basic topologies has been reviewed recently with many examples of MOF structures given.[3,4] Here, I review what we know about what the principal possible topologies are.

First some informal definitions are necessary. A crystal structure is abstracted as a *net* which is a special kind of graph.[5] A graph is an abstraction free of geometry. However, we want to discuss *embeddings* in which coordinates are assigned to vertices. To make clear we are talking about an embedding, we then refer to vertices as *nodes* and edges as *links*. This is important, for example, when we want to talk about the length of a link, as an edge of an abstract graph does not have a length.

A special kind of embedding is one in which each node has coordinates that are the average of those of its neighbors—so-called *barycentric* coordinates. An important result is that if all nodes then have unique coordinates, the combinatorial "symmetry" (more accurately *automorphism group*) of the graph is isomorphic to a crystallographic space group.[6,7] Such nets are called crystallographic nets, and the nets of greatest importance in chemistry are free of collisions, but nets with collisions are occasionally found.[8]
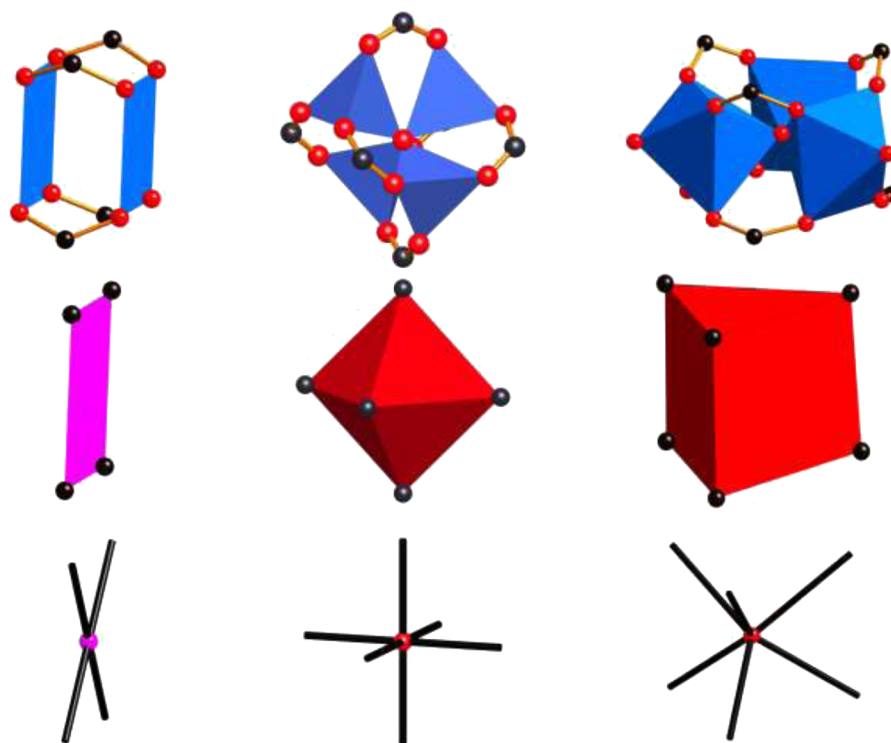
FIG. 1. Common metal SBUs in MOFs. From left, $Cu_2(-CO_2)_4$, $OZn_4(-CO_2)_6$, and $O(OH)_3Cr_3(-CO_2)_6$. Top: with metal-oxygen polyhedra linked by carboxylate (carbon black, oxygen red). Middle: the shapes enclosed by the carboxylate C atoms (points of extension). Bottom: the shape of the nodes of the net of a MOF.

For nets without collisions the computer program Systre, written by Olaf Delgado-Friedrichs, determines the intrinsic symmetry.[9] This is very important information as, in the absence of disorder, the symmetry of a crystal structure based on that net must be that symmetry or a subgroup of it. In particular if the net is chiral, the crystal structure is intrinsically chiral. Systre also determines
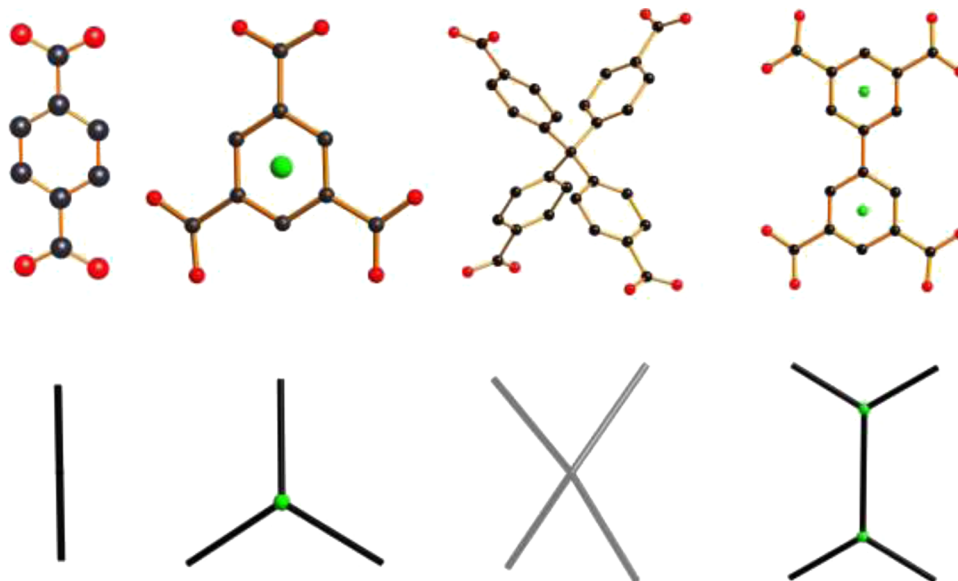

FIG. 2. Top: examples of carboxylate linkers in MOFs (carbon black, oxygen red, hydrogen not shown). Bottom: their abstraction as nodes of a net. Note that the ditopic linker is abstracted as just a link in the net and that the tetratopic linker with two branch points on the right is abstracted as two nodes of the net.

a code (a "Systre key") that is unique for a given topology so one can definitely decide whether two nets are the same or different. Thus, it has solved the notoriously difficult graph isomorphism problem (proving two graphs are the same or different). The catch is it is only done for nets without collisions—but these are just the structures of prime importance in crystal chemistry.

Periodic *sphere packings* are packings of uniform spheres. The centers of the spheres are nodes of a net and the links of the net correspond to contacts between the spheres. Such nets have embeddings in which all links are of equal length and are the shortest distances between nodes. Of special interest in chemistry are structures in which there is topologically just one kind of sphere, they have *uninodal* nets. Due to a remarkable effort over many years begun by Werner Fischer[10,11] and being continued by his associates,[12] we know almost all uninodal sphere packing nets (some monoclinic are missing). The nets of structures like diamond with C atoms as nodes and C–C bonds as links are uninodal sphere-packing nets. In tetrahedral structures such as aluminosilicates and zeolite frameworks, the tetrahedral atoms (T) are the nodes of a net and T–O–T bonds are the links of 4-coordinated nets that are invariably sphere-packing nets.

The vertices of a net are often partly characterized point symbol which is of the form $A^a.B^b\ldots$. This signifies that of all shortest cycles at each angle of a vertex a of them are A-cycles (i.e., consist of A edges), b are B-cycles, etc. For a k-c vertex $a + b + \cdots = k(k-1)/2$ (the number of angles). Point symbols and vertex symbols (not discussed here) are sometimes called *Schläfli symbols*, but that is not correct. Schläfli symbols refer specifically to regular tilings.[13]

Some of the more commonly occurring nets are given symbols and stored in the Reticular Chemistry Structure Resource (RCSR) database.[14] A RCSR symbol is generally three lower-case bold letters such as **dia** for the net of the diamond structure.

The nets we are interested in often admit a *tiling*—a division of space into generalized polyhedra we call *cages*.[15] Tiles often differ from polyhedra *sensu stricto* in that some of the vertices of the tile are only 2-c, examples are shown in Figure 3. A face of a tile is always shared between just two tiles—the tilings are *face-to-face*. A tiling is characterized by a *transitivity p q r s* which indicates that there are (topologically) p kinds of vertex, q kinds of edge, r kinds of face, and s kinds of tile. The vertices and edges of the tiling form a net of transitivity $p\ q$. If p (or q) = 1, the net is said to be *vertex-* (or *edge-*) *transitive*. A *proper* tiling is one that has the same intrinsic symmetry as the net it carries. A *natural* tiling has the further property that no one face of a tile is larger than
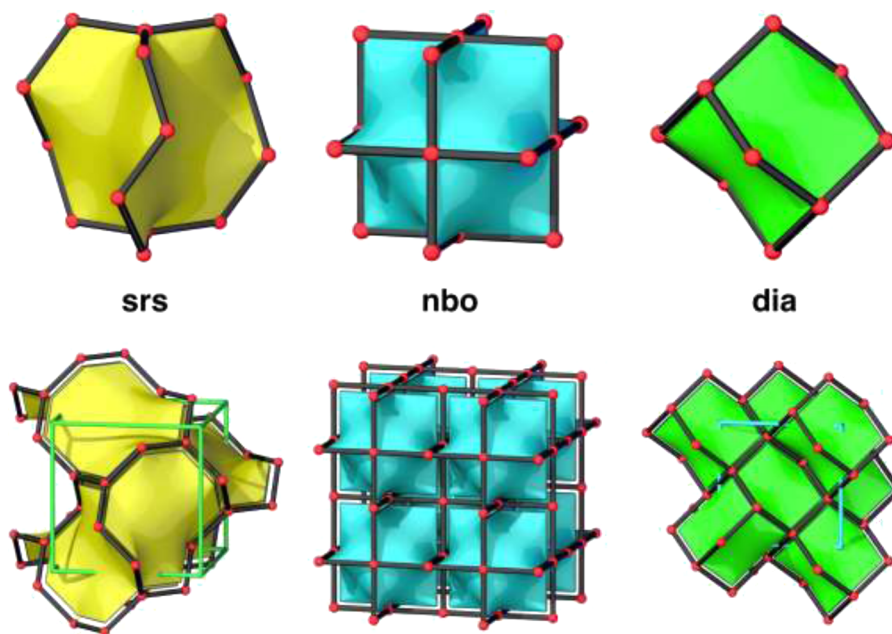

FIG. 3. Top: examples of tiles with two-coordinated vertices. Bottom: fragments of tilings by these tiles with tiles slightly shrunk.

all rest. A familiar example of a tiling is that associated with the cubic closest sphere packing (the face-centered cubic lattice). Space is divided up into tetrahedra and octahedra sharing faces.

In this contribution, I identify some of the nets of most importance to reticular chemistry. By "most important" I mean those which can be predicted to occur in a designed synthesis of a target MOF. These are also the nets of theoretical studies that screen hypothetical materials, that might plausibly be synthesized, for suitable properties such as selective absorption of gases.

Mathematicians recognize just one regular tiling of three-dimensional Euclidean space—the tiling by cubes. Instead, we defined *regular nets* which have embeddings in which the coordination figures (patterns of nearest neighbors) are regular polygons or polyhedra required by the symmetry.[16] The only regular coordination figures compatible with crystallographic symmetry are the triangle, square, tetrahedron, octahedron, and cube. We exclude the hexagon as 6-fold axes must all be parallel and the regular net with that coordination is in fact the net of the two-dimensional hexagonal lattice. The only quasi regular (vertex- and edge- but not face-transitive) polyhedron compatible with crystallographic symmetry (not icosahedral) is the cuboctahedron. It is easy to show that the corresponding nets all exist and that they are unique.[16] They are illustrated in Figure 4 in what we call the *augmented* form with the nodes replaced by the coordination figure and the RCSR symbol augmented by **-a**.[14] This allows one to readily see the coordination figure. It also emphasizes that our interest in such structures is as methods of linking finite geometric shapes into networks. There are just five, and their natural tilings turned out to be the only natural tilings with transitivity 1 1 1 1.[16] They are (symbol, coordination, coordination figure) **srs**, 3-c, triangle; **nbo**, 4-c, square; **dia** (diamond), 4-c, tetrahedron; **pcu** (primitive cubic lattice), 6-c, octahedron; and **bcu** (body-centered cubic lattice), 8-c, cube. The quasiregular net is **fcu** (face-centered cubic lattice), 12-c, cuboctahedron. This last has the only natural tiling with transitivity 1 1 1 2.

This makes a nice extension from the well-known tilings of the sphere and the plane which have transitivities *p q r* (*p* kinds of vertex, *q* kinds of edge, and *r* kinds of face = tile). Thus, the 5 regular polyhedra have transitivity 1 1 1 and the two quasi-regular polyhedra have transitivities 1 1 2.[18] The three regular tilings of the plane have transitivities 1 1 1 and the quasi-regular one (the kagome net) has transitivity 1 1 2. We have illustrated all these structures, which have been known for a long time, in an earlier review.[17]
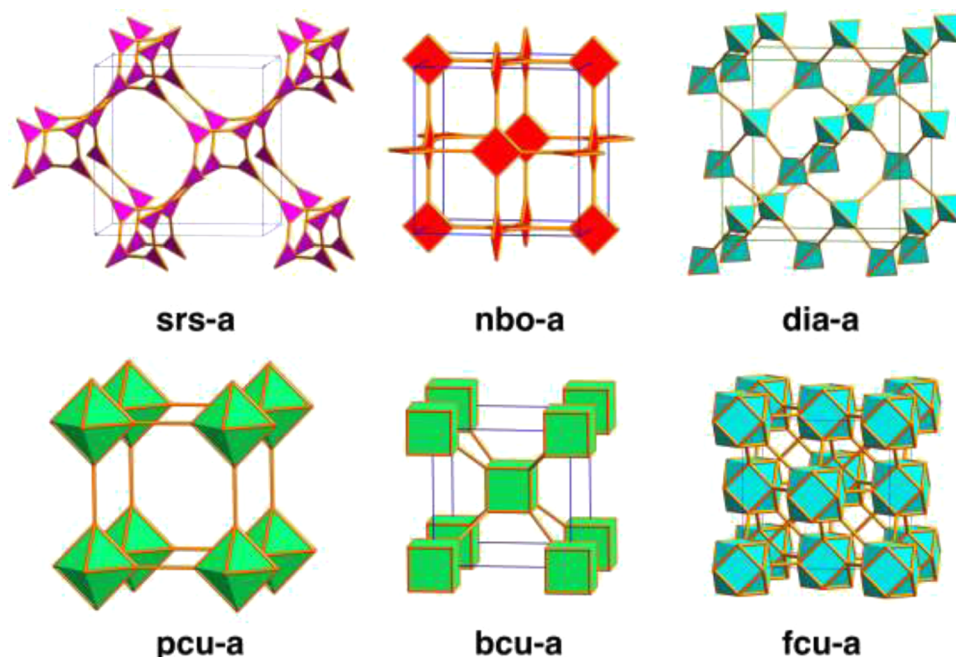

FIG. 4. The regular and quasiregular nets shown in augmented form (**-a**).

In the basic, and most common, type of MOF a metal SBU is kinked with ditopic or polytopic linkers. In geometric terms, we are linking one or two kinds of shape. The simplest way of doing this is with just one kind of link that will result in a structure based on an edge-transitive net. Edge-transitive structures are special. For example, there is an infinity of vertex- or face-transitive polyhedra (prisms and antiprisms and their duals), but only nine edge-transitive polyhedra.[17] Similarly, there are over a thousand vertex-transitive sphere packings (the exact number depends a little on how they are counted) but only 18 of these are edge-transitive.[18]

We have made a systematic enumeration of edge-transitive, three-periodic nets. First, by examining possible combinations of special positions in space groups[16,18] and then, by enumeration of edge-transitive tilings.[19] Accordingly, we are fairly confidant that we know all edge-transitive three-periodic nets that admit tilings. These are the core of the special set of basic nets of importance in crystal chemistry and nearly all unknown before our work. A. F. Wells who was the pioneer in the net approach to crystal chemistry devoted his attention almost exclusively to 3-c and 4-c nets.[20] It is satisfying that so many of these basic nets have subsequently been found in crystal chemistry.[3,4] They have been reviewed and illustrated before.[17]

We think that there is only one edge-transitive three-periodic 3-c net, but it would be nice to have a graph-theoretical proof of that. For higher coordination numbers, it is not clear if the number of edge-transitive nets is bounded. We have described infinite families of high-coordination edge-transitive *lattice* nets that have just one vertex in the repeat unit.[21] There are 14 edge-transitive 4-c nets in RCSR.

Our enumeration found two edge-transitive nets for linking triangle and square nodes, and these are ubiquitous in MOF chemistry, but there is a third edge-transitive (3,4)-c net (**mhq**) that has been reported for linking square and 3-c node.[22] This was not found in our enumeration of edge-transitive tilings.[19] The reason for its not being found is that the 3-c node has non-planar coordination and rings of the structure are catenated with each other to a remarkable extent, preventing the formation of tiles (tile faces cannot have links passing through them). Actually, this net has the interesting property that it has collisions in barycentric coordinates, but is nevertheless crystallographic.[8]

There are surely edge-transitive nets waiting to be discovered, and MOFs based on these nets are synthesized. In response for a request for a net suitable for linking trigonal prisms and tetrahedra, the net **tpt** was found (not yet, I think, synthesized). This net was not on our original list because it does not have a tiling as its rings are self-catenated.

We know of no edge-transitive net for linking triangle and trigonal prism, but an edge 2-transitive net was found by in the following way. In a bipartite net with stoichiometry AB_2, there must be at least three vertices in the repeat unit. No edge-transitive (3,6)-c of this sort appears to exist but an edge 2-transitive net **sit** was found with nodes in triangular and trigonal-prismatic coordination. It is a rare example of a polar net (symmetry *Imm*2). Only recently was it pointed out to me, by Davide Proserpio, that we had in fact reported a MOF with this structure some years ago, and that about a dozen examples of MOFs with this topology are known. Interestingly, they are all of structures based on intergrown (catenated) pairs of nets (**sit-c**) of opposite polarity and ideal symmetry *Imma*.

The RCSR database lists only 65 edge-transitive nets out of more than 2000 nets in total. Most of these are illustrated in Ref. 17. Of these, 10 are chiral (**srs** and **qtz**, the quartz net, are notable examples) and none are polar.

The nets with transitivity 1 1 and 2 1 (edge-transitive nets) of the previous section are the basic nets of reticular chemistry. They might be supplemented by a small group of nets that must have two links because of the crystallographic restriction to point symmetries with 1-, 2-, 3-, 5-, or 6-fold rotations (proper and improper). Commonly occurring uninodal nets of this sort with transitivity 1 2 are the 5-c nets **bnn** (trigonal bipyramidal coordination), and **ubt** and **sqp** (square pyramidal coordination), and the 9-c net **ncb** (tricapped trigonal prism coordination). Similarly, there are binodal nets with transitivity 2 2 such as the (3,9)-c **xmz** and **gfy**.[4] These can be targets of designed synthesis as in a recent spectacular synthesis of MOFs based on the (3,18)-c net **gea** with transitivity 2 2.[23] We include these under the heading of minimal transitivity nets.

A special, and large, class of MOFs are those in which there are just two SBUs, but one, the organic linker has multiple branch points.[4] It is common to consider, say, a tetratopic or hexatopic

linker as a single 4-c or 6-c node of an underlying net. However, if the linker has multiple branch points as shown in Figure 2, it is important to consider the branch points explicitly in the topology. First, consider a common case of a planar tetratopic linker joining square paddlewheels. One might expect, and indeed very often gets, the regular 4-c net **nbo** as the underlying topology. Actually, one gets the binary version **nbo-b** in which the two kinds of node are distinguished ("colored") reducing the symmetry, as in the binary compound NbO itself. If the linker is of the shape shown in Figure 2, with the 4-c node split into two 3-c nodes, the structure must be of lower symmetry (a 4-c node with square symmetry is being replaced with a two-node unit that has rectangular symmetry). Considering the 3-c nodes explicitly, we get a (3,4)-c net *derived* from the *basic* **nbo** net. The derived net may have as minimum transitivity 2 2. Some dozens of compounds of this sort have been made. Most do indeed have **nbo**-derived nets of minimal transitivity, but of three distinct topologies (**fof**, **fog**, **tfb**), although the authors of the compounds in question generally do not recognize this.[4,24] It is interesting that the binodal edge-transitive 4-c nets, **ssa** and **ssb**,[19] have only been found in MOFs with tetratopic linkers and derived nets with transitivity 2 2 **sty** (from **ssa**) and **stu** and **stx** (from **ssb**).[4]

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