# Topological Analysis of Metal-Organic Frameworks with Polytopic Linkers and/or Multiple Building Units and the Minimal Transitivity Principle 

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## 1. INTRODUCTION

A central problem in chemistry is that of describing and organizing the structure (atomic arrangement) of chemical compounds. In the particular case of crystals, it has long been recognized that the structures can often be abstracted as underlying nets that are special kinds of periodic graphs. ${ }^{1}$ The pioneer in this endeavor was Wells, ${ }^{2}$ who focused mainly on the descriptions of the nets themselves. Later workers paid attention to the description of structures of complex solids in terms of the nets of simpler solids, such as diamond or PtS . ${ }^{3-6}$ This was the so-called "ball and spoke" approach to crystal structure and, to a lesser extent, design. Very little effort beyond Wells' early work was devoted to the systematic enumeration and classification of nets themselves.

The later development of the chemistry of metal-organic frameworks (MOFs) ${ }^{7}$ led to the realization that crystalline materials could be assembled from well-defined molecular clusters (rather than from single atoms) of simple geometrical shapes-so-called secondary building units (SBUs)-that were organic or metal-containing. ${ }^{8}$ Thus, what was wanted was a theory and practice of synthesis in which clusters abstracted as shapes such as triangles, squares, tetrahedra, and octahedra were linked into periodic structures. This discipline we called

[^0]reticular chemistry. ${ }^{9}$ It was realized that for forming structures by linking a single SBU or two SBUs of different shapes the most important nets were those with one kind of link (in the jargon of graph theory, edge transitive). Many nets admit a tiling (a face-to-face packing of generalized polyhedra or cages); for these a transitivity pqrs can be defined. ${ }^{10}$ This states that topologically there are $p$ kinds of vertices, $q$ kinds of edges, $r$ kinds of faces (of the tiles), and $s$ kinds of tiles. Transitivity has been used as a measure of "regularity" of a net; thus, the five regular nets have transitivity $11111 .^{11}$ The edge-transitive nets have $p q=11$ or 21 and they have been systematically enumerated. ${ }^{12}$ A summary of their properties and their importance for design has been given. ${ }^{13}$ These nets have minimal transitivity (smallest possible) for uninodal $(p=1)$ and binodal nets $(p=2)$. In this paper, we extend the concept of minimal transitivity to include more complex (i.e., more kinds of vertices) nets.

An increasing number of MOFs are being made in which either three or more metal-containing SBUs are joined by simple links or the linkers themselves have complicated structures with more than one branch point corresponding to a vertex of a net. In general, the nets describing the topology of such structures have higher transitivity $p q$ with $p>2$ and $q \geq p$ - 1. It is with such structures and, more particularly, their topologies that this review is concerned. The importance of knowing these topologies in theoretical design of materials was nicely illustrated in a recent work on hypothetical covalent organic frameworks (COFs) based on nets with transitivity 3 2. ${ }^{14}$

Many of the more commonly occurring nets are collected in a searchable database and identified by widely used RCSR symbols (most are randomly assigned and have no mnemonic function). ${ }^{15}$ When we refer in the following text to the abstract graph, we use the terms vertex and edge; when referring to an embedding (a spatial graph in graph theory) or crystal structure, we use node or branch point, and link. When we refer to the shape of the coordination figure of a vertex of a net, we are, of course, referring to an embedding, more specifically, to a maximum symmetry embedding. For example, in the fourcoordinated (abbreviated 4-c) net with RCSR symbol pts, there are two kinds of vertex. In the maximum symmetry embedding, the site symmetries at the nodes are $m m m\left(D_{2 h}\right)$ and $\overline{4} m 2$ $\left(D_{2 d}\right)$. The former is compatible with square (or rectangular) coordination but not with tetrahedral coordination; the latter is compatible with tetrahedral or planar coordination, but in fact, planar coordination is impossible in practice.

In a recent review we illustrated the abstraction or deconstruction procedure for a variety of MOF structures. ${ }^{16}$ Often, as in the case of simple symmetric metal-containing SBUs joined by ditopic or tritopic linkers, the procedure is unambiguous. The iconic MOFs, MOF-5 ${ }^{17}$ and HKUST-1, ${ }^{18}$ are shown in Figure 1. In MOF-5, octahedrally shaped $\mathrm{Zn}_{4} \mathrm{O}\left(-\mathrm{CO}_{2}\right)_{6}$ SBUs with six points of extension (carboxylate C atoms) are linked by terephthalate (dicarboxylate) linkers. The underlying net is, as shown in the figure, a simple cubic net with six-coordinated ( $6-\mathrm{c}$ ) vertices that has the symbol pcu. In HKUST-1, the SBU is the paddle-wheel $\mathrm{Cu}_{2}\left(-\mathrm{CO}_{2}\right)_{4}$ with four points of extension arranged at the vertices of a square. The linker is a tricarboxylate with a 3-c branch point. The underlying net is accordingly a $(3,4)$-coordinated [written $(3,4)-c]$ net with the RCSR symbol tbo. In both of these cases, the net is the simplest possible (minimal transitivity) -there is just one kind of link; i.e., all links (edges of the net) are related


Figure 1. (a) The components of MOF-5 (section 1$)^{17}$ showing the abstraction of the $\mathrm{Zn}_{4} \mathrm{O}\left(-\mathrm{CO}_{2}\right)_{6} \mathrm{SBU}$ as an octahedron, the ditopic terephthalate linker as a rod, and their assembly into the pcu net shown here in augmented form. (b) The components of HKUST- $1^{18}$ showing the $\mathrm{Cu}_{2}\left(-\mathrm{CO}_{2}\right)_{4}$ paddle wheel abstracted as a square, the tritopic linker as a triangle, and their combination to form the tbo net shown in augmented form tbo-a.
by symmetry. Many isoreticular (same topology) compounds have subsequently been synthesized by design. ${ }^{17,18}$ It is generally more informative to illustrate nets in their augmented versions ${ }^{19}$ in which vertices of the original net are replaced by their vertex figures as shown in the figure.

For MOFs with more complicated linkers, the process of deconstruction is less obvious and a variety of different procedures have been carried out by different authors in the past. This has had a number of unfortunate practical consequences, such as the failure to recognize that a particular structure type or, even on occasion, a particular structure has been synthesized before or failure to recognize that two structures assigned the same topology are in fact fundamentally different. We describe our preferred procedure for deconstructing these and related structures. Specifically, we present the case for considering each branch point of the linker explicitly as a vertex of the underlying net. The alternative, favored by some authors, of considering a $k$-topic linker as one $k$-c vertex of a net often fails to distinguish between fundamentally different topologies that occur. We emphasize that no information is lost by explicitly using all branch points of the linker in the analysis, and indeed, valuable extra information is gained. One example, elaborated on later, concerns MOFs constructed with square metal SBUs and planar tetratopic linkers. For many of these, the 4-c net is the cubic net of NbO (RCSR symbol nbo), and this is usually recorded as the crystal topology. But the linker (discussed further in section 3.1) with two 3-c branch points is incompatible with square site symmetry and at least three distinct $(3,4)-\mathrm{c}$ topologies have been observed. Two of
these have the same symmetry and have not been distinguished in every case. Curiously, in the analogous case of hexatopic linkers, the linker is rarely considered as a single 6-c node of a net. Indeed, in many cases it is divided into two parts, one of which is considered to be part of the metal SBU.

A simple solution to these problems is to give both the basic net and the derived net. Here we use the idea long ago developed in descriptive chemistry of basic and derived crystal structures. ${ }^{20}$ Thus, the structure of ZnS (diamond) is a basic structure and a derived structure is that of $\mathrm{CuFeS}_{2}$ (chalcopyrite). In a similar way, in the example given above, the net of the binary compound NbO (given as nbo-b in RCSR), one 4-c node, say Nb , is replaced in the derived net by two 3-c nodes. In another example, discussed in detail later (see Figure 50), the structure has a basic net pcu-b of NaCl in which one vertex, say Cl , is replaced in the derived net by a hexatopic linker with four 3-c nodes. The topology of the derived structure is that of calcite, $\mathrm{CaCO}_{3}$, in which C is $3-\mathrm{c}$ (to O ) and each of the three O is also $3-\mathrm{c}$ ( to $2 \mathrm{Ca}+\mathrm{O}$ ). It is clearly more informative to give the full structure of $\mathrm{CaCO}_{3}$ than simply to state that Ca and $\mathrm{CO}_{3}$ have a NaCl structure. It is useful to recognize that the symmetry of a derived net must always be the same or a subgroup of the original, and the symmetry of the crystal is either the same or a subgroup of the symmetry of the derived net. Generally, but not always, the basic nets are the edge-transitive nets. ${ }^{13}$ If they are uninodal, the derived net is obtained by splitting one-half of the vertices into groups of linked vertices of lower coordination (e.g., one 4-c to two linked 3-c); if they are binodal, one type of vertex is likewise split. We give many examples of basic and derived nets in this review, which is about structure and its description rather than the synthesis and properties of MOFs, which have been reviewed elsewhere. ${ }^{7}$ In this we follow the example of a celebrated review of real and potential zeolite framework topologies. ${ }^{21}$ We generally illustrate just the local geometry (linker and metal SBUs) of the MOF and a maximum symmetry embedding of the net.

We should mention that the advantage of explicitly considering two linked 3-c branch points in a crystal structure as two 3 -c vertices of a net, rather than subsuming them into one 4 -c vertex, was clearly demonstrated earlier for hydrogenbonded networks. ${ }^{22}$

We uncover a richness and diversity of nets of considerable aesthetic appeal; many have not been found or described before. We believe that they will become as much an essential vocabulary of chemists as the structures of molecules like $\mathrm{C}_{60}$ or adamantane. Strikingly, we also discover that in the great majority of cases the nets are topologically as simple as possible. By this we mean that they have minimal transitivity compatible with the local structure and stoichiometry. These special nets are essential to the description and design of MOF structures. As a distinguished crystal chemist remarked many years ago: "The synthesis of new structures requires not only chemical skill but also some knowledge of the principal topological possibilities. ${ }^{23}$ The explosive growth in theoretical evaluation of potential materials ${ }^{14,24}$ equally requires the knowledge of the possibilities, particularly of those most amenable to realization in synthesis, i.e., those with minimal transitivity.

The discussion is limited to MOFs with finite metal SBUs. Materials containing infinite SBUs such as rods need a somewhat different treatment and the preferred method of deconstruction is often less obvious. ${ }^{25}$

## 2. MOFS WITH MULTIPLE SBUS

Here we describe the nets of some MOFs with two different metal-containing SBUs, in all but one case, linked by tritopic linkers. There are generally more than one example of a MOF with a given topology. The nets have minimal transitivity and some are also met in subsequent sections on the structures of MOFs with polytopic linkers.

### 2.1. A MOF with Triangular and Square SBUs

A compound that proved to be the forerunner of a large group of MOFs has two Cu-containing SBUs: a $\mathrm{Cu}_{2}$ paddle wheel and a $\mathrm{Cu}_{3}$ SBU with three points of extension. ${ }^{26}$ These are linked by a tritopic linker, as shown in Figure 2. We believe the structure


Figure 2. Deconstruction of a MOF (section 2.1$)^{26}$ with two metal SBUs and a tritopic linker (a) into a (3,4)-c net (ntt) and (b) into first a TBU with 24 points of extension and then combining with a metal SBU with three points of extension to give a $(3,24)$-c net (rht).
is best described as a (3,4)-c trinodal net, symbol ntt, with minimal transitivity 32 (clearly there must be at least three vertices in the net and with three vertices there must be at least two edges). In the maximum symmetry embedding of the net (Figure 3) $124-\mathrm{c}$ nodes are linked into a cage with the 4-c nodes at the vertices of a cuboctahedron. The cages in turn are arranged as in cubic close packing and there is a large "octahedral" hole in that packing (shown as a green sphere in the figure). The nodes corresponding to the tritopic linker form a 24 -vertex rhombicuboctahedron (vertices in the center of the edges of the cuboctahedron), and these polyhedra are linked in groups of three by the node corresponding to the 3-c Cu SBU. Accordingly, an alternative description of the structure is as a binodal ( 3,24 )-c net known to RCSR as rht. However, the same net occurs in a very large family of MOFs with hexatopic linkers for which this description is surely less appropriate.


Figure 3. The net ntt in augmented form ntt-a. The yellow balls center cages with 12 square nodes (blue). The pale green ball centers an "octahedral" hole.

The cage with 12 paddle-wheel units is a very common tertiary building unit (TBU) in MOF chemistry. ${ }^{16}$ It has long been known as a metal-organic polyhedron (MOP-1) ${ }^{27}$ and will be met several times again in later sections.

### 2.2. Other MOFs with Triangular and Square SBUs

The MOF of the previous section had a tritopic linker joined to one 3-c and two 4-c SBUs. Another structure type has been reported for MOFs in which a tritopic linker is joined to two 3c and one 4-c SBUs. ${ }^{28,29}$ The SBUs (Figure 4) are $\mathrm{Zn}_{2}\left(-\mathrm{CO}_{2}\right)_{3}$


Figure 4. A tritopic linker joined to two $3-\mathrm{c} \mathrm{Zn}_{2}$ and one 4-c $\mathrm{Zn}_{2}$ paddle wheels in a tfe structured MOF (section 2.2). ${ }^{28}$
with three points of extension and $\mathrm{Zn}_{2}\left(-\mathrm{CO}_{2}\right)_{4}$ with four points of extension. The net, tfe, is again cubic, and in maximum symmetry there are cubic cages as in ntt net. Now, however, the 3-c and 4-c nodes corresponding to the Zn SBUs are at the positions of the vertices of rhombic dodecahedron cages (Figure 5) - the polyhedra dual to the cuboctahedra of the ntt net.


Figure 5. The net tfe in a symmetric embedding as the augmented form te-a.

### 2.3. A MOF with Triangular and Square SBUs and Hexatopic Linker

The next MOF, SDU-1, ${ }^{30}$ has metal SBUs like those in the previous section, i.e., one $\mathrm{Zn}_{2}\left(-\mathrm{CO}_{2}\right)_{4}$ with four points of extension and $\mathrm{Zn}_{2}\left(-\mathrm{CO}_{2}\right)_{3}$ with three points of extension. Now there is a hexatopic linker with four 3-c branch points (Figure 6). Taking the Zn SBUs as $3-\mathrm{c}$ and 4 -c nodes and the


Figure 6. The linker (branch points green) connected to 3-c (blue nodes) and 4-c (red nodes) in SDU-1 (section 2.3). ${ }^{30}$
linkers as four 3-c nodes, one finds the net is again the primitive cubic (3,4)-c net tfe described in the previous section. However, in the basic net the 3-c Zn SBU and the 3-c node at the center of the linker are topologically the same, so to distinguish them, a "binary" (as far as those two 3-c nodes are concerned) or, perhaps better, "colored" (say red and blue) version of lower symmetry structure tfe-b must be used. This is in just the same way as to distinguish Na and Cl in NaCl : one goes from the primitive cubic pcu to the face-centered cubic pcu-b net. Figure 7, which might be compared with Figure 3, shows this "colored" version of the net, which now has a facecentered cell with double cell edge length. Notice that in both the $\mathbf{n t t}$ and $\mathbf{t f e}-\mathbf{b}$ nets one can identify a tertiary building unit (TBU) with 24 vertices, and if that is used, the underlying topology is rht in both cases, but clearly it is more useful to distinguish these two topologies. Figure 8 compares the cages in the two structures.

### 2.4. MOFs with Square and Tetrahedral SBUs

We describe just the simplest structure found in MOFs with square and tetrahedral SBUs. This was first reported ${ }^{31}$ for USF3, a Zn MOF with a tritopic linker, and subsequently ${ }^{32}$ for a Cd MOF. Other reported ${ }^{31,33}$ topologies for squares and tetrahedra linked by tritopic linkers are not discussed. An example of a linker with these SBUs is shown in Figure 9, and the net mmm


Figure 7. The net $\mathbf{t f e}$ in binary and augmented form tfe-b-a. The red squares and blue triangles are at the positions of the metal SBUs in the crystal structure.


Figure 8. The cages in (a) ntt-a and (b) tfe-a are compared.
(transitivity 32 ) is illustrated in Figure 10. This net is met again later in MOFs with octatopic linkers (section 6).
2.5. MOFs Based on Square and Trigonal Prismatic SBUs

The next MOF, named UMCM-150, is based on $\mathrm{Cu}_{2}\left(-\mathrm{CO}_{2}\right)_{4}$ paddle wheels with four points of extension and related $\mathrm{Cu}_{3}\left(-\mathrm{CO}_{2}\right)_{6}$ SBUs with six points of extension. ${ }^{34}$ These are


Figure 9. The linker and metal SBUs in USF-3 (section 2.4). ${ }^{31}$


Figure 10. A symmetrical embedding of the net mmm in augmented form mmm-a. The view is almost down the tetragonal $c$ axis.
linked by a tritopic linker (Figure 11) into a trinodal (3,4,6)-c net agw. This net again has minimal transitivity (32) and is


Figure 11. (Left) The linker in UMCM-150 (section 2.5) ${ }^{34}$ and its adjoining SBUs ( $\mathrm{Cu}_{2}$ blue and $\mathrm{Cu}_{3}$ red). (Right) The corresponding nodes and links of the underlying net.
shown in a maximum symmetry embedding in Figure 12. A second MOF with the same SBUs linked by a longer linker has been reported as NJU-Bai3. ${ }^{35}$
2.6. MOFs Based on Square and Octahedral SBUs

A Zn MOF with square 4-c and octahedral 6-c SBUs joined by a tritopic linker (Figure 13) has been reported. ${ }^{29}$ The 4-c SBU is again a paddle wheel, but the 6-c SBU is novel with an octahedral shape and is also shown in Figure 13. The underlying net is again a minimal transitivity (32) net with RCSR symbol idp illustrated in Figure 14. An isoreticular compound with a different linker has also been reported. ${ }^{36}$ In


Figure 12. The net agw in a maximum symmetry embedding of its augmented form agw-a.


Figure 13. Fragments of a MOF (section 2.6). ${ }^{29}$ (a) The tritopic linker joined to two 6-c and one 4-c SBU. (b) The 6-c SBU joined to six tritopic linkers. 3-c branch points are indicated by green balls.


Figure 14. The net idp shown in its augmented form idp-a in a maximum symmetry embedding.
both cases, in the real crystal structure there are two kinds of links to the 6-c node (see Figure 13b). However, in the net these become the same. Accordingly, the crystals have lower symmetry (I23) than that of the net (Im $\overline{3}$ ).
2.7. MOFs Based on Tetrahedral and Trigonal Prismatic SBUs

An isoreticular series of MOFs, named asc-1, asc-2, and asc-3, are constructed from tetrahedral and trigonal prismatic SBUs combined with ditopic and tritopic linkers. ${ }^{37}$ The SBUs are a tetrahedrally coordinated single Zn (or Cd ) atom and a $\mathrm{Cr}_{3}$ unit of three octahedra sharing a common vertex ( O atom) with six points of extension. The tritopic linker joins three Zn atoms, but each Zn atom is also linked to two 6-c nodes, so the basic topological unit is a 4-c vertex linked to two 3-c and two 6-c vertices (Figure 15). The resulting net, asc (Figure 16), is very simple and again of minimal transitivity 32.


Figure 15. Fragments of the asc-1 structure (section 2.7). ${ }^{37}$ (a) A 6-c $\mathrm{Cr}_{3}$ SBU connected to six tetrahedra Zn atoms by a ditopic linker. (b) $\mathrm{ZnO}_{2} \mathrm{~N}_{2}$ tetrahedron (blue) linked to two $\mathrm{Cr}_{3}$ SBUs and to two tritopic linkers; 3-c branch points are indicated by large green spheres.


Figure 16. A maximum symmetry embedding of the asc net in its augmented form asc-a.

### 2.8. A MOF Based on Square Pyramidal and Octahedral SBUs

An interesting structure has a net based on the ntt net of section 2.1. In that net, nodes, say A , corresponding to the linker are joined to $3-\mathrm{c}$ SBU nodes, B, and 4-c SBU nodes, C. In the MOF of this section ${ }^{38}$ there is in addition links by ditopic linkers between B nodes and between C nodes, so there are topologically four kinds of links: $\mathrm{A}-\mathrm{B}, \mathrm{A}-\mathrm{C}, \mathrm{B}-\mathrm{B}$, and $\mathrm{C}-\mathrm{C}$. The SBUs now become $5-\mathrm{c}$ and $6-\mathrm{c}$. The minimal possible transitivity is now 34 and this is what is observed in the real crystal structure. The SBUs are illustrated in Figure 17 and the


Figure 17. Fragments of the structure of a MOF (section 2.8). ${ }^{38}$ (a) A pair of linked 5-c SBUs each linked to a tritopic linker with 3-c branch points shown as green balls. (b) A central 6-c SBU joined to three others and to three tritopic linkers.


Figure 18. The net ott shown in a maximum symmetry embedding in augmented form ott-a. The group of eight octahedra shown at the top right occurs in the "octahedral" hole in the center of the group of six cages (centered by yellow balls).
net ott is shown in Figure 18. The cages with 12 nodes, now corresponding to 5 -c SBUs, are the same as in ntt, but "the octahedral hole" now has a group of eight octahedra linked as vertices of a cube as indicated in the figure.

## 3. MOFS WITH TETRATOPIC LINKERS

Many MOFs have been made using tetratopic linkers with one planar or tetrahedral branch point. Some were described earlier. ${ }^{16}$ When the structures are analyzed, that branch point invariably corresponds to a 4-c vertex of a net. These generally have well-documented binodal nets such as pts and are not discussed here. Instead, we focus on tetratopic linkers with two 3-c branch points (Figure 19). The nets of these compounds


Figure 19. The limiting shapes (left, rectangular; right, tetrahedral) of tetratopic linkers with two 3-c branch points.
that take into account the 3-c nodes explicitly are generally derived from a basic net by replacing a $4-\mathrm{c}$ node, either planar or tetrahedral, with two 3-c nodes. The advantage of using the derived net description is that it can distinguish between the possibilities for derived nets that often have the same symmetry, and of course, the knowledge of the basic net is kept.

One can easily design tetratopic linkers that might be assigned other topologies. For example, the porphyrin-based linker ${ }^{39}$ in Figure 20 might be described as having four 3-c


Figure 20. A tetracarboxylate linker ${ }^{39}$ joined to metal SBUs centered at the magenta balls. It could be abstracted as one of the two shapes shown on the right.
branch points rather than one 4-c one. However, the square of nodes in the former is just the augmented version of the latter, which we argue is essentially the same underlying topology. ${ }^{16}$ Accordingly, we suggest that, in complicated linkers (they are rare) where branch points form a polygon or polyhedron, that figure be collapsed to a single point. This is in fact just what is done with finite metal SBUs such as paddle wheels in which the four points of extension form a square.

### 3.1. Paddle Wheels and Other Square SBUs Joined by Planar Tetratopic Linkers

A large number of MOFs have been reported in which square $\mathrm{Cu}_{2}$ paddle-wheel SBUs are joined by mostly planar tetracarboxylate linkers with two $3-\mathrm{c}$ branch points. ${ }^{40,41}$ Possibly the first of these was MOF-505 (Figure 21), ${ }^{40 a}$ the


Figure 21. (a) The MOF-505 structure (section 3.1). ${ }^{40 \mathrm{a}} \mathrm{Cu}$ atoms, blue; C , black; O red. (b) The linker attached to four paddle wheels. The magenta sphere is at a $4-\mathrm{c}$ node of the underlying net and the green spheres at $3-\mathrm{c}$ branch points of the linker. (c) Two possible abstractions of the linker + SBUs according to whether (top) or not (bottom) the 3-c branch points are included.
underlying net of which was described as 4-c nbo with the linker forming one 4-c node. With one exception, noted below, all subsequent papers that have identified nets also consider the linker as a 4-c vertex in the net and the nets are generally, but not universally, correctly identified. The 4-c nets with square coordination that occur are the uninodal edge-transitive nets nbo and lvt and the binodal edge-transitive nets ssa and ssb. ${ }^{42}$ A recent paper did indeed follow our recommendation to consider the 3-c nodes explicitly. ${ }^{40 \mathrm{k}}$ Then it was discovered that there are two different structures (IZE-1 and IZE-2) that can be distinguished as having distinct (3,4)-c derived nets (fof and fog) but that have the same basic 4-c nbo net and indeed have the same intrinsic symmetry. Most of the observed nbo-derived MOFs have the fof underlying net, but at least two others, JUC$62^{40 e}$ (described as nbo) and UWDM-1 ${ }^{401}$ (no topology assigned), also have the fog net. This observation, that two distinct (3,4)-c nets derive from the same basic 4-c net, makes a compelling case for deconstructing MOFs in the way we recommend. It is also helpful to distinguish these MOFs, such as those with fof or fog topology, from those ${ }^{43}$ in which paddle wheels are joined by ditopic linkers to produce an nbo topology. Figure 22 shows the augmented nets fof-a and fog-a.


Figure 22. Two nets, shown in augmented form and both with $R \overline{3} m$ symmetry derived from the nbo net.

There are generally more than one net derived from a basic net. For example, in the net ssb there are two topologically distinct vertices with square coordination. Each of these in turn can be replaced by a pair of $3-\mathrm{c}$ vertices in two distinct ways while preserving the symmetry to give four derived nets as shown in Figure 23.


Figure 23. (3,4)-c nets derived from ssb by splitting one 4-c vertex into two $3-\mathrm{c}$ vertices. All nets have the same symmetry, $14 / \mathrm{mmm}$, and all have two kinds of vertices and two kinds of links.

A surprising number of topologies have been found in practice. NOTT-109 ${ }^{40 \mathrm{~h}}$ has the (3,4)-c underlying stx net derived from the $4-\mathrm{c}$ net $\mathbf{s s b}$. DUT- $12^{40 \mathrm{oo}}$ has a topology based on a second net derived from ssb, viz., stu. Clearly to distinguish these two one must find the $(3,4)-\mathrm{c}$ net. PCN-12 $2^{40 \mathrm{c}}$ and ZJU- $25^{40 \mathrm{n}}$ have the underlying ( 3,4 )-c net sty (Figure 24) derived from the $4-\mathrm{c}$ net ssa. Interestingly, sty appears to be the only minimal transitivity ( 3,4 )-c net that can be derived from ssa.


Figure 24. The net sty shown in augmented form sty-a.
DUT- $10^{400}$ has a net, lil, derived from the edge-transitive uninodal net, lvt. The same net is found in ZJU-30 ${ }^{40 \mathrm{p}}$ now as a pair of interpenetrating structures. Interestingly, the basic net, lvt, has symmetry $I 4_{1} /$ amd, but this is reduced to Imma in the derived net and this is the symmetry of DUT-10. However, in ZJU-30 the interpenetrating lil nets are related by a $\overline{4}$ axis, so the symmetry again becomes tetragonal ( $\bar{I} \overline{4} m 2$ ). There is a second minimal transitivity (3,4)-c net with the same symmetry (Imma) derived from lvt, lim, which has been identified in multiply interpenetrating cyano-bridged copper azolate frameworks. ${ }^{44}$ These nets are illustrated in Figure 25. We include


Figure 25. Two minimal transitivity nets with symmetry Imma derived from the basic net lvt.
here also in this section a Mg MOF, SNU-25, with a simple single-atom SBU with planar links to a tetratopic linker, as shown in Figure $26 .{ }^{45}$ This also has lil topology, again with two frameworks interpenetrating.


Figure 26. Linker and SBU of a Mg MOF, SNU-25 (section 3.1), ${ }^{45}$ with lil topology. Large green balls are N atoms at branch points of the linker.

Recently three isoreticular MOFs (fcu-MOF-1, MMPF-3, and DUT-49) were constructed from tetracarboxylate linkers joining SBUs with four planar points of extension. ${ }^{41}$ Figure 27 illustrates the deconstruction into a $(3,4)-\mathrm{c}$ net, tfb , also shown in augmented form in the figure. Interestingly, this is yet another net derived from nbo by splitting one 4-c vertex into two 3-c vertices. The authors used neither the (3,4)-c nor the 4 c description but instead identified the topology as derived from linkage of tertiary building units (TBUs) of six paddlewheel clusters (centered by yellow balls in the figure). The TBUs are linked as in the $12-\mathrm{c}$ net fcu (hence the name). This third mode of description reinforces our case for the need for an agreed protocol for deconstructing MOF structures. An interesting question is that of why one or other of the nets ( $\mathbf{t f b}$, fof, and fog) identified here as derived from nbo is found in practice.

We remark that despite the variety of observed derived topologies (seven mentioned in this section), they are all minimal transitivities (22). There are of course exceptions, but they are rare. PCN- $12^{40 \mathrm{c}}$ has the minimal transitivity net sty; however, it has an isomeric form, PCN-12', of considerable complexity, most unusual for a MOF, with eight vertices and ten edges (transitivity 810 , in the RCSR database as pcn). IZE-1 and IZE-2 are isomers of MOFs with chemically identical frameworks, both with minimal transitivity (22) nets, but there is a third isomer, IZE-3, with net hyx that has transitivity $33 .{ }^{40 \mathrm{k}}$

The cds net is another common net that like nbo has all vertices in square coordination in a maximum symmetry embedding. This, however, has transitivity 12 . If a node with square geometry is linked by a tetratopic linker with two 3-c branch points, again a structure with a (3,4)-c underlying net will be produced. The simplest such net, gwg, illustrated in Figure 28, has monoclinic symmetry, in contrast to the tetragonal symmetry of cds, although it does have the minimal derived transitivity 23 . Two recent examples, ${ }^{46}$ one of which was described by the authors as cds, ${ }^{46 a}$ do in fact have the gwg topology and symmetry.


Figure 27. (Top) Abstraction of the linker and SBU of fcu-MOF-1 (section 3.1). ${ }^{41 \mathrm{a}}$ (Bottom) The underlying net shown in augmented form tfb-a. The yellow balls are arranged as in cubic closest packing.


Figure 28. The net gwg, shown in augmented form gwg-a, derived from cds by splitting square vertices into pairs of triangular vertices (symmetry $P 2_{1} / c$ ).

### 3.2. Paddle-Wheel SBUs Joined by Tetrahedral Tetratopic Linkers

Not all tetracarboxylate linkers are planar. We have previously cited cases in which the linker considered as a 4-c node is tetrahedral and combined with the square paddle wheel gives
structures based on the 4-c pts net. ${ }^{16}$ However, just as for nbo, there is more than one way of deriving (3,4)-c nets by splitting the tetrahedral vertex into two $3-\mathrm{c}$ vertices, so the description with 3-c vertices is again preferred. Two of the simplest ways (sur and tfk) are shown in Figure 29. The reported compounds ${ }^{400,47}$ have the sur topology. The figure also shows the two simplest ways of splitting the planar ("square") vertex (dmd and tifi).

Besides pts, there is a second way of linking tetrahedral and square vertices in an edge-transitive net; this is pth ("hexagonal PtS"). It has lower symmetry and occurs much more rarely than pts, but examples are known. One such has paddle wheels linked by the same kind of tetrahedral linker that consists of


Figure 29. Six $(3,4)-\mathrm{c}$ nets derived from pts by dividing the tetrahedral 4-c vertex into two 3-c vertices (top) and dividing the planar vertex (bottom). Nets are shown in their augmented forms.
two 3-c branching points. ${ }^{48}$ Although the net was described as "hexagonal PtS" a better description is as a (3,4)-c net. As shown in Figure 30, there are two simple ways of splitting the


Figure 30. Two nets derived from pth by splitting the tetrahedral vertices into two 3-c ones. Compare with Figure 29.
tetrahedral vertex into two 3-c ones. Both preserve the symmetry of pth $\left(P 6_{2} 22\right)$. The observed structure is based on phw (see Figure 30). Again, the (3,4)-c net needs to be specified to distinguish between these two possibilities.

### 3.3. MOFs with Tetrahedral Vertices Linked by Tetratopic Linkers

An interesting Co MOF with an unusual metal SBU and tetratopic linker was reported recently. ${ }^{49}$ The metal SBU is a pair of $\mathrm{CoO}_{6}$ octahedra sharing a corner, as shown in Figure 31.


Figure 31. The linker (left) and 4-c SBU (right) of a MOF (section 3.3) ${ }^{49}$ with the zyl topology.

Each SBU is connected tetrahedrally to four tetratopic linkers with overall tetrahedral shape, as also shown in the figure. The basic 4-c net is that of lonsdaleite, lon, which has transitivity 1 2. The derived net $\mathbf{z y l}$ (Figure 32) is even less minimal, as it has transitivity 34; however, it seems not to be possible to construct a $(3,4)$-c derived net based on lon of lower transitivity. The symmetry of zyl is $\mathrm{Cmc}_{1}$ and that of the crystal is only $P 2_{1}$.

A very simple MOF in which single tetrahedrally coordinated Zn atoms are linked by a dicarboxylate linker is again derived from the basic pts net. The linker is dimethylbenzenedicarboxylate. Each carboxylate C atom is linked through O to two different Zn atoms and thus acts as a 3-c linker, as shown in Figure $33 .{ }^{50}$ The derived net, obtained by replacing the planar


Figure 32. The net zyl derived from lon (lonsdaleite) in augmented form zyl-a.


Figure 33. Fragments of the structure of Zn (dimethylbenzenedicarboxylate) ${ }_{2}$ (section 3.3$)^{50}$ illustrating the 3-c and 4-c nodes of the dmd net (Figure 29). Zinc, blue; carbon, black; oxygen, red.
vertices of pts, is now dmd (Figure 29). The same net is found with a tetrahedrally linked Mn atom joined by a tetracarboxylate linker. ${ }^{40 \mathrm{q}}$

Cyanides with tetratopic links present some fascinating structures. In an early example of "crystal engineering" the Iwamoto group over 30 years ago prepared cyanides based on the pts net. These had straightforward square and tetrahedral SBUs joined by the $\mathrm{C}-\mathrm{N}$ link. ${ }^{3}$ The tetratopic linker TCNQ (tetracyanoquinodimethane, Figure 34) has led to some unusually interesting salts, particularly of Cu and Ag , in which the metal atoms are tetrahedrally coordinated. ${ }^{51}$ The first structure, that of $\mathrm{AgTCNQ},{ }^{51 a}$ has a rather complicated ptsderived structure with transitivity 34 , dmh. $\mathrm{CuTCNQCl} 2_{2}$ and $\mathrm{AgTCNQCl}_{2}$ have two forms: the latter ${ }^{51 \mathrm{~d}}$ with the dmd net and the former ${ }^{51 e}$ with tfi (interpenetrated). All these topologies are illustrated in Figure 29. More recently, Cu salts of tetrafluoro-TCNQ have been reported. ${ }^{51 f}$ Structures 14 have the tfi topology, and 5 and 6 have dmg topology. To refer to all these structures collectively as pts does seem like an oversimplification.

### 3.4. MOFs with Octahedral Vertices Linked by Tetratopic Linkers

Two MOFs with the same underlying net have been reported for octahedral SBUs linked by tetrahedral tetratopic linkers. For one, the node is a simple octahedrally coordinated metal


Figure 34. Part of the structure of $\operatorname{AgTCNQ}$ (section 3.3). ${ }^{51 \mathrm{a}}$ Carbon, black; nitrogen, green; $\mathrm{AgN}_{4}$ tetrahedra, blue. The larger spheres indicate the 3-c branch points. The TCNQ unit is accurately planar.
atom. ${ }^{52}$ For the other, the SBU is the $\mathrm{Zn}_{4}$ cluster of MOF-5 (Figure 1) as shown in Figure $35 .{ }^{53}$ The basic net is the edge-


Figure 35. The linker and SBUs of a MOF (section 3.4$)^{53}$ with the act topology.
transitive (4,6)-c net iac and the derived net act shown in Figure 36. This complicated high-symmetry net does not appear to have been recognized before, but the basic net and its derived net again have minimal transitivity (21 and 22, respectively).

Another MOF, DUT-13, in which the same SBU is linked by a tetrahedral tetracarboxylate linker (Figure 37) has a different topology. ${ }^{54}$ Now the basic net is the common corundum net, cor, which has nonminimal transitivity 22 . The derived net, $\mathbf{t t u}$ (Figure 38), does have the minimal transitivity, 23 , for a net derived from that basic net.

Another MOF with tetratopic linker has a number of features of special interest. ${ }^{55}$ The metal SBU consists of three $\mathrm{InO}_{6}$ octahedra sharing a common vertex and linked to six carboxylate units (Figure 39). The points of extension (carboxylate C atoms) form a trigonal prism, as in the familiar basic chromium acetate unit, but the linkage is topologically cubic, as shown in Figure 39, and the basic net soc is an edgetransitive way of linking square and octahedron and is found in complex cyanides. ${ }^{56}$ In the most symmetrical embedding of basic net the vertex figure of the $6-\mathrm{c}$ node is an elongated octahedron, and the site symmetry is $\overline{3} m$, compatible with an octahedral linkage but incompatible with trigonal prismatic. However, there are two simple ways, edq and cdj, of replacing the square vertex with two triangular vertices to produce a net with transitivity 22 . Both are cubic, but with different symmetries, and the symmetries at the $6-\mathrm{c}$ sites now are


Figure 36. The net act in its maximum symmetrical form as the augmented net act-a.


Figure 37. The linker and SBUs of DUT-13 (section 3.4$)^{54}$ with the ttu topology. Compare with Figure 35.
different: 32 and $\overline{3}$, respectively. The former is now compatible with trigonal prismatic coordination, which is in fact now the case. Figure 40 shows the augmented versions of the basic net and its two simplest derived nets, one suitable for linking trigonal prismatic SBUs and the other for linking octahedral SBUs. The derived nets edq and cdj are a rare example of a pair of nets with identical coordination sequences and vertex symbols, so they are easy to confuse if the intrinsic symmetry is not considered. The cages in the structure are topologically equivalent to pentagonal dodecahedra $5^{3}$, and the structures differ in the two possible orientations of these, as shown in


Figure 38. The net $\mathbf{t t u}$ shown in augmented form ttu-a.

Figure 41. Clearly these two are just the simplest of an infinite family of such nets.

### 3.5. A MOF with Tritopic and Tetratopic Linkers

In DUT-25, both a tritopic and a tetratopic linker with two 3-c branch points were used to link an octahedral $\mathrm{Zn}_{4}$ SBU. ${ }^{57}$ There are accordingly three nodes in the net. One, say A , is $6-\mathrm{c}$ and linked to the 3-c tritopic linker node, B, and also to the 3-c branch point, C , of the tetratopic linker. There must be then at least three vertices and three edges (corresponding to the $\mathrm{A}-\mathrm{B}$, $\mathrm{A}-\mathrm{C}$ and $\mathrm{C}-\mathrm{C}$ links). Fragments of the structure are shown in Figure 42. The net they form has indeed minimal transitivity 3


Figure 39. (a) An $\mathrm{In}_{3} \mathrm{SBU}$ (section 3.4$)^{55}$ showing the trigonal prismatic geometry of the points of extension. (b) A fragment of the structure showing one SBU linked to six others in an octahedral geometry.

3; it has RCSR symbol ttz and is illustrated in Figure 43. Interestingly, as the authors note, upon removal of the 3-c node corresponding to the tritopic linker, the net would be fof (although they referred to the basic net nbo).

### 3.6. MOFs with Cubic SBUs Joined by Tetratopic Linkers

Several recent papers report MOFs with an 8-c $\mathrm{Zr}_{6}$ SBU (Figure 44) joined by tetracarboxylate linkers. ${ }^{39,58}$ In two cases the linker is based on a porphyrin, and as shown in Figure 44, the points of extension form a square. The net is one of the edge-transitive ways of joining cube and square shapes with RCSR symbol csq, as the authors recognize. ${ }^{39,58 a}$ However, in the third case the linker (Figure 44) has a pyrene core, and we prefer to also recognize two 3-c branch points, as shown in Figure $44 .{ }^{58 \mathrm{~b}}$ A simple advantage of this is that the linker no longer has square symmetry, and there are two simple derived nets, xly and $\mathbf{x l z}$, in which the long axis of the linker is aligned parallel or perpendicular to the hexagonal $\mathbf{c}$ axis, as shown in Figure 45. The observed orientation, ${ }^{58 \mathrm{~b}} \mathrm{xly}$, results in a more open framework. The advantage of this approach was further illustrated in recent unpublished work ${ }^{46 \mathrm{~b}}$ at Shantou University in which a pyrene tetracarboxylate linker produced a MOF


Figure 40. Augmented forms of the basic net soc and the derived nets cdj and edq. Note that the blue octahedra in cdj-a and soc-a become trigonal prisms in edq-a.
based on the basic net cds, which has the monoclinic symmetry of the derived net $\mathbf{g w g}$ (cf. the last paragraph of section 3.1).
3.7. Nets Derived by Replacing a 4-c Vertex with Two 3-c Vertices

Table 1 gives RCSR symbols for nets derived from some basic nets by replacing a $4-\mathrm{c}$ vertex by two linked $3-\mathrm{c}$ vertices. In almost every case the increase in transitivity is minimal: by 11 for uninodal basic nets and 01 for binodal basic nets.


Figure 41. Nets cdj and edq shown as tilings. The blue and red tiles are topologically the same as pentagonal dodecahedra $5^{3}$.


Figure 42. Parts of the structure of DUT-25 (section 3.5). ${ }^{57}$ (a) The tritopic linker. The large magenta ball is a 3 -c branch point. (b) The tetratopic linker. Green balls ( N atoms) are 3-c branch points. (c) The $\mathrm{Zn}_{4}$ SBU linked to six 3-c branch points. The large red ball ( O atom) is at the $6-\mathrm{c}$ node.


Figure 43. The net ttz in augmented form ttz-a.


Figure 44. (a) The $\mathrm{Zr}_{6}$ SBU in MOF-545 (section 3.6$)^{39}$ with eight carboxylate C atoms (black) as points of extension. (b) The linker in NU$1000,{ }^{58 \mathrm{~b}}$ with branch points shown as green balls. (c) The linker in MOF-545 ${ }^{39}$ showing branch points (large spheres) forming a square (cf. Figure 20).


Figure 45. The nets xlz and xly shown in augmented form.

## 4. MOFS WITH PENTATOPIC LINKERS

Two groups have prepared isoreticular MOFs (PMOF-3 and PCN-124) using a tetracarboxylate linker that also contains a pyridyl group. ${ }^{59}$ The metal SBU is the $\mathrm{Cu}_{4}\left(-\mathrm{CO}_{2}\right)_{4}$ paddle wheel with a fifth link from one Cu to the pyridyl N atom. Thus, the metal SBU is a 5-c node. The linker has 3-c branch points, so the resulting net is ( 3,5 )-c and has RCSR symbol pzh. Figure 46 shows the deconstruction of the linker, and Figure 47 shows the net in augmented form. The figure also shows that the net has large cages with 12 paddle-wheel SBUs (red in the figure) located at the vertices of a truncated octahedron, so again the MOP-1 TBU of section 2.1 is now arranged in a body-centered cubic array (the symmetry is $\operatorname{Im} \overline{3} m)$. There are three kinds of nodes, the 3-c nodes are of two kinds, say A and B. Node A is linked to two B and to the 5c node C. Node B is linked to one A and two C. Accordingly, there must be at least three kinds of nodes and three kinds of links ( $\mathrm{A}-\mathrm{B}, \mathrm{A}-\mathrm{C}$, and $\mathrm{B}-\mathrm{C}$ ). The net does indeed have this minimal transitivity. The authors described the topology as a $(3,36)$-c net (RCSR symbol txt) based on the observation that there are 12 links from the 5-c nodes (red in Figure 47) and 24 links from the 3-c nodes (green) of the TBU each going to one of the second kind of $3-\mathrm{c}$ vertex (shown as blue).

## 5. MOFS WITH HEXATOPIC LINKERS

Hexatopic linkers can take a variety of topologies and shapes. We do not consider a single 6-c vertex (a star in graph theory) and only consider topologies without rings (trees in graph

Table 1. Basic Nets with 4-c Vertices and Derived Nets with Two Linked 3-c Vertices

| basic net | transitivity | coord | replace | derived nets | transitivity |
| :---: | :---: | :---: | :---: | :---: | :---: |
| nbo | 11 | 4 | square | fof, ${ }^{\text {a }}$ fog, ${ }^{\text {a }}$ tfb ${ }^{\text {a }}$ | 22 |
| lvt | 11 | 4 | square | lil, ${ }^{\text {a }} \mathrm{lim}^{\text {a }}$ | 22 |
| rhr | 11 | 4 | square | ucp | 22 |
| cds | 12 | 4 | square | $\mathrm{gwg}^{\text {a }}$ | 23 |
| dia | 11 | 4 | tetrahedron | tfa | 22 |
| qtz | 11 | 4 | tetrahedron | tfq | 22 |
| sod | 11 | 4 | tetrahedron | xbl | 22 |
| lon | 12 | 4 | tetrahedron | zyl ${ }^{\text {a }}$ | 34 |
| pts | 21 | 44 | square | $\mathrm{dmd},{ }^{\text {a }}$ fi ${ }^{\text {a }}$ | 22 |
|  |  |  | square | $\mathrm{dmg},{ }^{\text {a }} \mathrm{dmh}{ }^{\text {a }}$ | 33,34 |
|  |  |  | tetrahedron | sur, ${ }^{a}$ tfk | 22 |
| pth | 21 | 44 | square | hst | 22 |
|  |  |  | tetrahedron | phw, ${ }^{\text {a }}$ phx | 22 |
| ssb | 21 | 44 | square 1 | stu, ${ }^{\text {a }}$ stw | 22 |
|  |  |  | square 2 | stj,stx ${ }^{\text {a }}$ | 22 |
| ssa | 21 | 44 | square 1 | sty ${ }^{\text {a }}$ | 22 |
| stp | 21 | 64 | square | ttp, ttx | 22 |
| soc | 21 | 64 | square | edq, ${ }^{\text {a }}$ cdj | 22 |
| scu | 21 | 84 | square | tty | 22 |
| csq | 21 | 84 | square | xly, ${ }^{a} \mathrm{xlz}$ | 22 |
| ftw | 21 | 124 | square | ttv | 22 |
| iac | 21 | 64 | tetrahedron | $\mathrm{act}^{\text {a }}$ | 22 |
| toc | 21 | 64 | tetrahedron | xab | 22 |
| cor | 22 | 64 | tetrahedron | $\mathrm{ttu}^{\text {a }}$ | 23 |

${ }^{a}$ Nets identified in crystal structures and discussed in the text.
theory). The overall symmetric shapes are planar hexagon, octahedron, or trigonal prism (Figure 48), all of which are observed in practice, although for most work to date on MOFs the hexagonal shape (Figure 48f) predominates.

### 5.1. MOFs with 6-c SBUs and Hexatopic Linkers

In three cases, at least, in which octahedral $\mathrm{Zn}_{4} \mathrm{O}\left(-\mathrm{CO}_{2}\right)_{6}$ SBUs were joined by such linkers, the structures have been described in terms of $6-\mathrm{c}$ nets. ${ }^{60}$ In one early case (MODF$1^{60 \mathrm{a}}$ ) the linker is trigonal prismatic in overall shape (Figure 48b). The basic 6 -c net is edge-transitive nia with octahedral and trigonal-prismatic nodes in the structure. Considered as a derived $(3,6)-\mathrm{c}$ net, however, it is a rather high transitivity structure, as the net mod has transitivity 45 . This is another example that shows that the minimal transitivity principle is not universally obeyed.

In the other MOFs with octahedral SBUs (MOF-1 ${ }^{60 \mathrm{~b}}$ and JUC- $100^{60 \mathrm{c}}$ ) the basic net is pcu with all octahedral nodes. The linker is illustrated in Figure 49. The net is more appropriately


Figure 46. Deconstruction of the linker in PMOF-3 (section 4). ${ }^{59 a}$


Figure 47. The underlying net, pzh, of PMOF-3 in augmented form, pzh-a.
described as the derived (3,6)-c net $\mathbf{z x c}$. It is interesting that $\mathbf{z x c}$ is exactly the net of the three kinds of atoms in calcite, $\mathrm{CaCO}_{3}$, as illustrated in Figure 50. The same structure occurs in NU-$108-\mathrm{Zn},{ }^{61}$ and in this instance, the topology was described in terms of the ( 3,6 )-c net (not identified). zxc has minimal transitivity 32.

It is interesting that the group in Figure 48e is chiral (it is the shape familiar to chemists as that of octahedral complexes of bidentate ligands). The linker unit in Figure 49 is likewise chiral, but the net is not chiral, as in assembling the zxc net (symmetry $R \overline{3} c$ ) units of both hands are used. If units of just one hand were used, the likely net is tsh, an alternative possibility with minimal transitivity (32) and symmetry R32. We have not found an example of that structure, but it could be an attractive target for designed synthesis given an enantiopure linker of sufficient rigidity.


Figure 48. Some topologies and shapes for hexatopic linkers: $(a-c)$ trigonal prisms, ( $\mathrm{d}, \mathrm{e}$ ) octahedra, and ( f ) hexagon.


Figure 49. Linker of a MOF (section 5.1$)^{60 \mathrm{~b}}$ with zxc net.

Three MOFs with a nia-derived structure are JUC-101, JUC$102,{ }^{62 a}$ and UTSA-62. ${ }^{62 b}$ In these compounds, the metal SBU has trigonal prismatic points of extension and the linker is again of the octahedral shape shown in Figure 48e. Figure 51 illustrates a fragment of the crystal structure. The derived net is jjt . Again the linker is chiral but the net is not. The overall symmetry is $P \overline{6} 2 c$. But there is a chiral derived net also of minimal transitivity. This is tsb, with symmetry $P 6_{3} 22$. However, if that net is examined, it can be seen that the "trigonal prismatic" site now has links more suitable for an octahedral SBU. This is the same phenomenon as remarked on in section 3.4 (in that case an octahedral node morphed into a trigonal prismatic one). The two nets are illustrated in Figure 52 in augmented forms, which emphasize the difference in the 6-c nodes.


Figure 50. The net zxc-a and the calcite structure (Ca, red; C, blue; O, green).


Figure 51. The linker and SBUs of JUC-101 (section 5.1). ${ }^{62 a}$ The metal SBUs (groups of three octahedra) have trigonal prismatic points of extension.

A hexatopic linker with a topology (two 4-c branch points as in Figure 48d) different from those discussed so far was used in the construction of IMP-15. ${ }^{63}$ The linker is shown in Figure 53. It is linked to $\mathrm{Zn}_{4} \mathrm{O}\left(-\mathrm{CO}_{2}\right)_{6}$ SBUs with six octahedrally disposed points of extension, and with the linker considered as a 6-c node, the structure was described as based on pcu. However, a better description recognizes the 4-c branch points explicitly and then the net is fsn (Figure 54). This (4,6)-c net is the net of the atoms in the pyrite form of $\mathrm{FeS}_{2}$ and of the Si and P atoms in $\mathrm{SiP}_{2} \mathrm{O}_{7}\left(-\mathrm{O}-\right.$ acting as links). ${ }^{64}$ Again, surely one would prefer to consider the individual atoms in $\mathrm{FeS}_{2}$ as nodes of a net rather than a description as a NaCl packing of Fe and $\mathrm{S}_{2}$ groups (cf. the description of $\mathrm{CaCO}_{3}$ at the beginning of this section).


Figure 52. Two nets derived from nia by replacing the octahedral nodes with four 3-c nodes.


Figure 53. (Left) The linker in IMP-15 (section 5.1). ${ }^{63}$ Magenta balls are at the center of $\mathrm{Zn}_{4} \mathrm{O}\left(-\mathrm{CO}_{2}\right)_{6}$ SBUs (cf. Figure 1); the large blue balls are Si . (Right) The nodes in the underlying (4,6)-c net.

### 5.2. MOFs with Square SBUs and Hexatopic Linkers

The bulk of the work with hexatopic linkers that has been reported has been on linking $\mathrm{Cu}_{2}$ or $\mathrm{Zn}_{2}$ paddle-wheel SBUs with essentially planar linkers, as shown in Figure 55. The topology of the structure formed considered as a ( 3,4 )-c net is ntt, the same as described in section 2.1 for a MOF with two metal SBUs. The first compound reported ${ }^{65 a}$ was also described as the ( 3,24 )-c net rht with the 3 -c node corresponding to the center of the linker and the rest of the linker fused into the 24-c TBU. All the subsequent authors have adopted that description


Figure 54. The augmented version (fsn-a) of the (4,6)-c net fsn.


Figure 55. A hexatopic linker (section 5.2) ${ }^{65 \mathrm{a}}$ joined to paddle-wheel SBUs with branch points of the underlying net shown as green and magenta balls (respectively 3-c and 4-c vertices). C, black; O, red; Zn , blue.
and the dozens of compounds produced are generically referred to as rht-MOFs (sic).

An advantage of the alternative (3,4)-c ntt net description is that it explicitly recognizes the two separate links in the linker, and these have been systematically and independently varied to give a wide range of relative cavity sizes. ${ }^{61,651}$ Figure 56 illustrates parts of two real MOFs with different linkers (Figure 57). These structures are among those with the highest porosities and surface area per unit mass. ${ }^{651}$

Remarkably, for none of these many ntt/rht compounds that have been reported ${ }^{61,65}$ has the linker been described as a $6-\mathrm{c}$ node of a framework. We can attempt to "back-derive" a basic $(4,6)$-c net from $\mathbf{n t t}$. Figure 58 shows a fragment of $\mathbf{n t t}$. If the group of four $3-\mathrm{c}$ vertices are replaced by a $6-\mathrm{c}$ vertex, the resulting net has a topology in which two different 4-c vertices are linked to the same set of four 6 -c vertices as shown in Figure 58. As a result, in barycentric coordinates, in which each vertex has coordinates that are the average of those of its neighbors, the pairs of vertices have the same coordinates (collide). A net of this type is said to be "non-crystallographic" (NC), as it contains symmetries that do not correspond to crystallographic symmetries. Thus, it should be clear that simply interchanging the two $4-\mathrm{c}$ vertices and keeping the rest fixed is an automorphism ("symmetry") of the graph. On the other hand, a crystallographic symmetry acts on the (embedded) graph as a rigid body. Such noncrystallographic symmetries are analogous to the symmetries of flexible molecules which are well-known to have symmetries other


Figure 56. Two MOFs (section 5.2$)^{61,651}$ with ntt topology.
than the familiar point groups of rigid molecules. We refer the reader to the recent literature for more information on this topic. ${ }^{66}$ One way to deal with NC nets of this type is to simply merge the two colliding vertices. In the net under discussion, the result is a (3,4)-c net, in fact, the familiar tbo (Figure 1). Clearly, this is not a very reasonable deconstruction of the structures of $\mathbf{n t t}$ MOFs.

However, there is an edge-transitive (4,6)-c net (RCSR symbol she) with vertices that have planar coordination, and it is natural to ask why a net derived from this topology is never found. The answer should be familiar to the reader who has read the foregoing material. If the $6-\mathrm{c}$ node is replaced by a coplanar group of four 3-c vertices in the most symmetrical (minimal transitivity) way, the coordination of the 4-c node morphs from planar to tetrahedral, so the derived net, symbol het, is suitable for linking tetrahedral SBUs with planar


Figure 57. The linkers of the MOFs (section 5.2) ${ }^{61,651}$ in Figure 56: (left) NU-110651 and (right) NU-108. ${ }^{61}$


Figure 58. (Left) A fragment of the ntt net showing 4-c vertices (red) and a group of four 3-c vertices with one colored blue at the center. (Right) The (4,6)-c net of the red and blue vertices.
hexatopic linkers. The nets she and het in the augmented form are shown in Figure 59. We have not found such a MOF yet but remark that, in contrast to the familiar planar paddle wheel, neutral tetrahedral metal SBUs are rare-but see the next section (section 5.3).


Figure 59. (Left) The net she shown in augmented form. (Right) The derived (3,4)-c net, het, shown in augmented form. Note that the green hexagons are replaced by planar groups of four triangles and the red squares in she-a morph into red tetrahedra in het-a.

A linker of dimensions that are too small to allow planarity of the carboxylate groups was used to link paddle-wheel SBUs into a new topology in UTSA-20. ${ }^{67}$ The linker, with the octahedral shape of Figure 48e, is shown in Figure 60. Now the (3,4)-c net is zyg, as shown in Figure 61. Again we find the apparently paradoxical result that the octahedral linker is replacing a site of


Figure 60. Linker used to construct a MOF, UTSA-20 (section 5.2), ${ }^{67}$ with zyg topology.


Figure 61. The net zyg in augmented form.
trigonal prismatic coordination of the basic binodal (4,6)-c net, which is $\mathbf{s t p}$, the default (edge-transitive) net for linking square and trigonal-prismatic units. zyg has transitivity 32 , again minimal.

There is, however, a basic net with transitivity 21 for linking squares and octahedra, namely, soc (Figure 40). The simplest derived net is obtained by replacing the $6-\mathrm{c}$ vertex by four $3-\mathrm{c}$ nodes, i.e., corresponding to the same shape as the linker in the previous paragraph. One then gets the chiral derived net hey (symmetry I432) with transitivity 32 illustrated in augmented form in Figure 62. It may be seen that in a reasonable


Figure 62. The net hey in augmented form.
embedding (in this case, all links of equal length) the 4-c nodes (square in the figure) come close together and thus might be considered unfavorable for a MOF topology. However, there is an example, UTSA-61, with this topology. ${ }^{68}$ The linker is the same as in NU-108 (Figure 57), ${ }^{61}$ which forms a ntt net with a square paddle-wheel SBU. In UTSA-61, the metal SBU is $\mathrm{YbO}\left(-\mathrm{CO}_{2}\right)_{4}$ with the noncarboxylate O atoms linked by $\mathrm{O}-$ $\mathrm{H}-\mathrm{O}$ hydrogen bonds, as shown in Figure 63. It is reasonable to assume that this drives the formation of the hey topology (previously unobserved) in this instance.


Figure 63. A pair of $\mathrm{YbO}\left(-\mathrm{CO}_{2}\right)_{4}$ SBUs linked by an $\mathrm{O}-\mathrm{H}-\mathrm{O}$ bond in UTSA-61 (section 5.2). ${ }^{68}$ Large spheres, Yb ; small sphere in center, presumed H atom position (not located experimentally).

### 5.3. A MOF with Tetrahedral SBU and Hexatopic Linker

A MOF with the basic $(4,6)-\mathrm{c}$ cor net was constructed with the octahedrally shaped linker of Figure 49 and a tetrahedral SBU shown in Figure $64 .{ }^{60 \mathrm{~b}}$ A fragment of the derived net tfu is illustrated in Figure 65. cor has nonminimal transitivity 22; however, tfu does have minimal transitivity (33) for a net


Figure 64. A tetrahedral SBU used to construct a MOF (section $5.3)^{60 \mathrm{~b}}$ with net tfu derived from the $(4,6)$-c net cor.
derived from cor by splitting the $6-\mathrm{c}$ vertex into four 3-c vertices.


Figure 65. A fragment of the net tfu in augmented form.

### 5.4. Basic Nets with 6-c Vertices and Their Derived Nets

Table 2 lists some basic nets with $6-\mathrm{c}$ vertices and their derived nets. We call attention again to the fact that octahedral and trigonal-prismatic vertices can change into each other when going from a binodal to a trinodal net. Thus, in design of syntheses or evaluation of theoretical possibilities, it is best to look directly at the derived nets. Table 2 lists the derived nets of this section and also some other possibilities. Data for all the derived nets are to be found in the RCSR database.

Table 2. Some Basic Nets and Nets Derived by Splitting 6-c Vertices ${ }^{a}$ into either Two 4-c or Four 3-c Vertices

| basic net | transitivity | coord | replace | with | derived nets | transitivity |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| pcu | 11 | 6 | octah | $3-\mathrm{c}$ | zxc, ${ }^{\text {b }}$ tsh | 32, 32 |
|  |  |  | octah | $4-\mathrm{c}$ | $\mathrm{fsn}^{\text {b }}$ | 32 |
| acs | 11 | 6 | prism | 3-c | tsg | 32 |
|  |  | 6 | prism | $4-\mathrm{c}$ | tsj | 32 |
| nia | 21 | 6 | octah | 3-c | $\mathbf{j j t},{ }^{\text {b }}$ tsb | 32,32 |
|  |  |  | octah | $4-\mathrm{c}$ | xby | 22 |
|  |  |  | prism | 3-c | tsa | 32 |
|  |  |  | prism | $4-\mathrm{c}$ | xat | 22 |
| pyr | 21 | 36 | octah | 3-c | pyo | 32 |
| cor | 22 | 46 | octah | $3-\mathrm{c}$ | tfu ${ }^{\text {b }}$ | 33 |
| soc | 21 | 46 | octah | $3-\mathrm{c}$ | hey ${ }^{\text {b }}$ | 32 |
| toc | 21 | 46 | octah | 3-c | tot | 32 |
| stp | 21 | 46 | prism | $3-\mathrm{c}$ | $\mathrm{zyg}^{\text {b }}$ | 32 |
| she | 21 | 46 | hexagon | $3-\mathrm{c}$ | het | 32 |

$a_{\text {octah }}=$ octahedron, prism $=$ trigonal prism. ${ }^{b}$ indicates nets identified in crystal structures and discussed in the text.

## 6. MOFS WITH OCTATOPIC LINKERS

Structures reported with octatopic linkers are so far quite rare and as far as we know all carboxylates. There are four symmetrical ways of constructing octatopic linkers with only 3c and 4 -c branch points. These are shown in Figure 66 in which


Figure 66. Symmetrical shapes for octatopic linkers.
parts a and c differ only in the embedding shape (tetrahedral or planar central vertex) and parts $b$ and $d$ are derived from parts a and c by splitting a $4-\mathrm{c}$ node into two linked $3-\mathrm{c}$ nodes. Assuming that the linked SBUs are all the same, then the minimal transitivity is 32 for cases $a$ and $c$ and 33 for cases $b$ and d. Minimal transitivity nets are indeed found in every case but one.

In two isostructural compounds, MMPF-4 and MMPF-5, the porphyrin-based octacarboxylate linkers (Figure 67) are joined to $\operatorname{In}\left(-\mathrm{CO}_{2}\right)_{3}$ SBUs with three points of extension (the


Figure 67. A fragment of the structure of MMPF-5 (section 6). ${ }^{69}$ Large light blue balls are In atoms with three points of extension. Magenta balls are 3-c branch points, and the dark blue atom (metal in the porphyrin unit) is a 4 -c node.
carboxylate C atoms). ${ }^{69}$ In describing the structure the authors focused on polyhedron packing, but they also described it as the ( 3,8 )-c net the. However, if we include the branch points of the linker explicitly, as shown in Figure 67, the resulting net is the (3,4)-c net tfe already encountered as the net of SDU- $1{ }^{29}$ in section 2.2 (Figure 5). The net is shown in Figure 68, which


Figure 68. (a) The net tfe formed by the unit in Figure 67. (b) Showing how three 8 -vertex units share a common vertex.
also illustrates how three octatopic units meet at a common vertex. Thus, the net tfe with transitivity 32 can be considered as derived from the basic $(3,8)-\mathrm{c}$ net the with transitivity 21.

A very similar porphyrin-based octatopic linker was used in the construction of MOFs labeled ZJU-18, -19, and $-20 .^{70}$ In these compounds, the linker joins two distinct SBUs $\left(\mathrm{Mn}_{2}\right.$ and $\mathrm{Mn}_{3}$ ) each with four planar points of extension. Let A denote the 3-c branch points of the linker and $B$ the central $4-\mathrm{c}$ square node. If further the Mn SBUs are denoted C and D , the stoichiometry is $\mathrm{A}_{4} \mathrm{BCD}$. The net of the structure is found to be the binary (3,4)-c net tbo described earlier (Figure 1) with the $\mathrm{B}, \mathrm{C}$, and D nodes occupying topologically equivalent positions, as shown in Figure 69. To have an embedding with chemically different B, C, and D nodes, now a three-way coloring (say red, blue, and green) of the 4-c vertices, the symmetry must be lowered from $\mathrm{Fm} \overline{3} m$ (the symmetry of tbo) to Fmmm (the symmetry observed for the crystal).

An octatopic linker with different topology (that of Figure 66d) was used to join $\mathrm{Cu}_{2}$ paddle wheels in PCN-80. ${ }^{71}$ The linker is shown in Figure 70. In this case, the structure was deconstructed by the authors into a new (3,4)-c net lwg shown in augmented form in Figure 71. The basic net from which lwg may be considered to be derived is the $(4,8)$-c net scu.

It is natural to ask what is the net obtained by merging the two central 3-c vertices in lwg into one 4-c vertex. Not surprisingly, it becomes tbo again (compare Figures 69 and 71). If one distinguishes the new 4-c vertices from the original 4-c vertices of $\mathbf{l w g}$, one has a two-way coloring of the produced tbo net with symmetry reduced to $14 / \mathrm{mmm}$ (that of lwg).

Several MOFs have been constructed using an octatopic linker with the shape a of Figure $66{ }^{72}$ We illustrate that of NOTT-140 ${ }^{72 a}$ in Figure 72. The central 4-c node now has tetrahedral geometry and links together with square paddlewheel vertices in a different topology, mmm (already mentioned in section 2.4), derived again from scu.

We earlier ${ }^{16}$ described the deconstruction of a series of $\mathrm{MOFs}^{73}$ with a linker with shape b of Figure 66, i.e., with the 4 c node of the previous linker divided into two $3-\mathrm{c}$ nodes. The corresponding net is $\mathbf{m m l}$, which is of course derived from the same basic net, scu. Figure 73 compares the two nets.


Figure 69. Components of ZJU-18 (section 6). ${ }^{70}$ (a) The octatopic linker and (b) its skeleton. Blue balls are the 4-c SBUs shown in parts c and d. (e) The placing of the nodes and links in the crystal structure shown using actual crystal data. The net is tbo.


Figure 70. Deconstruction of the linker in PCN-80 (section 6). ${ }^{\text {11a }}$ Red balls are 3-c branch points of the linker; green balls are 4-c paddlewheel vertices.

## A MOF constructed from an octatopic linker has a structure

 that is apparently not based on a minimal transitivity net. ${ }^{74}$ The metal SBUs have trigonal prismatic points of extension and the linker, shown in Figure 74, has shape c in Figure 66. Accordingly, one gets a $(3,4,6)$-c net, wxs, but the linkers are of two topologically distinct kinds, and the transitivity is 55 rather than the expected minimal 32; nevertheless, the net shown in Figure 75 is very pleasing. If one considers the linkers as 8 -c nodes, the $(6,8)-\mathrm{c}$ net, msq, from which wxs is derived, has transitivity 32 . Topologically, one can see the difference in the 8 -c nodes from the connectivity: one 8 -c vertex has 14 next-

Figure 71. The net lwg in augmented version lwg-a.


Figure 72. The linker in NOTT-140 (section 6) ${ }^{72 a}$ and its deconstruction. Large balls: black, a C atom acting as a $4-\mathrm{c}$ node; green, 3-c branch points; magenta, 4-c paddle-wheel nodes.


Figure 73. The relationship between $\mathbf{m m m}$ and $\mathbf{m m l}$. The latter is derived from the former by splitting tetrahedral nodes into two triangular ones.


Figure 74. (a) The linker and SBUs in the MOF MMPF-2 (section 6). ${ }^{74}$ (b) In the skeleton, red balls are 6 -c nodes with trigonal prismatic geometry.
nearest neighbors (joined by a path of two edges) and the other has 20 next-nearest neighbors. It may be that this is the best that can be done. We are not aware of a binodal $(6,8)$-c net in which trigonal-prismatic nodes are linked with 8-c nodes with a vertex figure that is a rectangular parallelepiped. With the reservations made earlier, we know ${ }^{12}$ that there is only one edge-transitive ( 6,8 )-c and that is ocu, the default net for linking octahedral and hexahedral ("cubic") vertices. On the other hand, trigonal prisms and cubes have symmetries of incompatible systems (hexagonal and cubic), so it is possible that there is no suitable binodal net and that msq has the lowest transitivity of possible nets.

Our final example of a MOF with octatopic linkers, IFMC200, contains an unprecedented 24-c metal SBU with composition $\mathrm{Zn}_{16}\left(\mathrm{HPO}_{3}\right)_{4}\left(-\mathrm{CO}_{2}\right)_{24}$ with the 24 carboxylate C atoms as points of extension. ${ }^{75}$ This SBU (Figure 76) is centered at sites with symmetry $432(O)$, and the pattern of points of extension, shown as black lines in the figure, is that of the 24 -vertex rhombicuboctahedron. The carboxylate linker


Figure 75. The net wxs shown in augmented form wxs-a. The view direction is close to the tetragonal $c$ axis.


Figure 76. The Zn - and P-containing SBU in IFMC-2000 (section 6). ${ }^{75} \mathrm{PO}_{3}$, green; $\mathrm{ZnO}_{4}$, light blue; $\mathrm{ZnO}_{6}$, darker blue. Black spheres are carboxylate C atoms (points of extension) and red ones are O . The black lines linking points of extension outline a distorted rhombicuboctahedron.
(Figure 77), although it has a tetrahedrally coordinated atom in the center, is effectively planar (an octagon). Including the branch points of the linker as vertices, as shown in the figure, the net is found to be the $(3,4,24)-\mathrm{c} d d y$, a net of transitivity 3 2. In a maximum-symmetry embedding, shown as ddy-a in Figure 78, the coordination figure of the 24-c vertex becomes a truncated octahedron. It may be seen that each linker is attached twice to the same metal SBU; accordingly, if the linker is considered as a single vertex, it is $4-\mathrm{c}$ and the net is the $(4,12)$-c ftw.

## 7. THE MINIMAL TRANSITIVITY PRINCIPLE

We earlier introduced the concept of default nets, which are those that are expected to occur when linking one or two


Figure 77. The linker in IFMC-2000 (section 6). ${ }^{75}$ The large black ball (carbon) is the 4-c branch point, and the green balls are at 3-c branch points. Magenta balls are at the centers of 24-c SBUs.


Figure 78. (Left) A fragment of the augmented ddy net. (Right) A unit cell of the same.
components into a periodic net unless there is some peculiar shape of linker that prevents it. ${ }^{9,19}$ These are uninodal (for example, linking octahedra as in MOF-5) and binodal (for example, linking squares and triangles as in HKUST-1) edgetransitive nets with transitivity 11 and 21 , the minimum possible. Very many MOFs and related materials such as covalent organic frameworks (COFs) have structures based on edge-transitive nets.

In this paper, we have mainly focused on the nets of MOFs which have three kinds of nodes. In the first case (section 2), there were two kinds of metal SBUs, say A and B, and a polytopic linker C . There must be links $\mathrm{A}-\mathrm{C}$ and $\mathrm{B}-\mathrm{C}$ and so minimal possible transitivity 32.

In all the other MOFs there is generally one kind of metalcontaining SBU (we do not count metal atoms in a porphyrinbased organic linker ${ }^{39}$ here); call this A . The polytopic linkers may have one topological kind of branch point, say B , or two, say B and C (or more than two, but we have not found examples yet). We take explicit account of the types of link in a structure. Thus, in compounds with one SBU (A) and with tetratopic linkers (B) with two 3-c branch points, there must be two kinds of edges ( $\mathrm{A}-\mathrm{B}$ and $\mathrm{B}-\mathrm{B}$ ) in the graph and transitivity 22 is minimal. Accordingly, there are two requirements for minimal transitivity. First, each shape of cationic SBU and each distinct type of linker branch point must each correspond to just one vertex of the net. Second, each kind of link must correspond to just one edge of the net.

The following are possibilities encountered in real crystals and discussed in this review ( $\mathrm{MT}=$ minimal transitivity).
(i) A with links A-A (ditopic linker), MT 11 : nbo, pcu
(ii) $A B$ with links $A-B$, MT 2 1: csq, pth, pts, pyr, scu, soc, tbo, the
(iii) $A B$ with links $A-B$ and $B-B$, MT 22 : act, dmd, edq, fof, fog, lil, lim, phw, stu, stx, sty, sur, tfb, tfi, xly
(iv) ABC with links $\mathrm{A}-\mathrm{B}$ and $\mathrm{B}-\mathrm{C}$, MT 32 2: agw, asc, ddy, fsn, hey, idp, jjt, mmm, ntt, tfe, zxc, zyg
(v) ABC with links $\mathrm{A}-\mathrm{B}, \mathrm{B}-\mathrm{C}$, and $\mathrm{C}-\mathrm{C}$, MT 3 3: lwg, mml
(vi) ABC with links $\mathrm{A}-\mathrm{B}, \mathrm{A}-\mathrm{C}$, and $\mathrm{B}-\mathrm{C}$, MT 3 3: pzh
(vii) ABC with links $\mathrm{A}-\mathrm{B}, \mathrm{A}-\mathrm{C}$, and $\mathrm{C}-\mathrm{C}$, MT 33: ttz
(viii) ABC with links $\mathrm{A}-\mathrm{B}, \mathrm{A}-\mathrm{C}, \mathrm{B}-\mathrm{B}$, and $\mathrm{C}-\mathrm{C}, \mathrm{MT} 34$ : ott

We note also that in most of the nets of MOFs with rod SBUs, ${ }^{25}$ the rods are uninodal and are joined by just one kind of link, e.g., sra, umv, irl, snp, and wnf. ${ }^{16}$

The fact that so many MOFs have underlying nets that have minimal transitivity leads us to suggest that this is a general principle:

The underlying nets of MOFs and related materials tend to be nets of minimal transitivity.

This is, in a sense, a specific case of Pauling's Rule of Parsimony, which states that "the number of essentially different kinds of constituents in a crystal tends to be small". ${ }^{76}$

There are of course exceptions, but they are rare (we estimate less than $10 \%$ of the MOFs examined for this review), hence the word "tend" in the previous paragraph.

The nets ssa and ssb, in which two topologically distinct square nodes are linked by one kind of edge (transitivity 21 ), are not really minimal because there are nets (nbo is one) in which all square nodes are equivalent and have transitivity 11. Indeed, as far as we know, no MOFs with 4-c nets have been reported with either ssa or ssb topology, but there are many with nbo topology. ${ }^{43}$ But, as we have shown above, $(3,4)-\mathrm{c}$ nets derived from ssa, ssb, as well as nbo can all be minimal and are all found in crystal structures.

The crystallographic restriction to certain symmetry types (e.g., no 5 -fold symmetry operations) applies equally to crystallographic nets. Accordingly, there can be no 5-c net with transitivity 11 and the minimal transitivity is 12 , as in the commonly found $5-\mathrm{c}$ nets ubt, bnn, and sqp. ${ }^{13,16}$ Likewise, the $(3,9)-\mathrm{c}$ nets xmz and gfy found in MOFs ${ }^{16}$ with transitivity 22 (rather than 21) are minimal, as there is similarly no 9 -fold crystallographic symmetry. A more subtle restriction, much harder to establish, is that there may not be a suitable minimal transitivity net for certain geometrical constraints. Thus, we remarked in section 6 that there may not be an edge transitive net for linking trigonal prismatic and hexahedral ("cubic") shapes. Likewise, we believe that there is not an edge-transitive ( 3,6 )-c net with trigonal prismatic coordination of the 6-c node. However, the net sit with that coordination and with transitivity 22 is found in MOFs, ${ }^{77}$ so this transitivity is probably the minimum possible for this coordination.

PCN-12 has the topology of type iii above and the underlying minimal transitivity net sty. ${ }^{40 \mathrm{c}}$ However, it has an isomeric form, PCN-12', of considerable complexity, most unusual for a MOF, with eight vertices and 10 edges (transitivity 810 , section 3.1 ). IZE-1 and IZE-2 are isomers of MOFs with chemically identical frameworks, both with minimal transitivity ( 22 ) nets, but there is a third isomer, IZE3 , with net hyx that has transitivity $33 .^{40 \mathrm{k}}$ But these, and some TCNQ salts (section 3.3), are rare exceptions.

There are many MOFs in which planar 4-c paddle-wheel SBUs are linked with tritopic linkers and which have the minimal transitivity (21) tbo or pto topology. ${ }^{18}$ We know of only one exception, a MOF with the fmj topology with transitivity $54 .^{78}$

One of the most striking exceptions to the minimal transitivity principle is MOF-177 and the isoreticular MOF180 and MOF-200. ${ }^{79}$ These have structures in which octahedral
$\mathrm{Zn}_{4}\left(-\mathrm{CO}_{2}\right)_{6}$ units are linked by tritopic linkers. One might expect structures based on the edge-transitive net pyr found in MOFs and coordination networks, ${ }^{80}$ but instead the net is qom with transitivity 5 . These are MOFs with ultrahigh porosities and exceptional potential for practical applications, and a satisfactory explanation of the occurrence of this topology would be most welcome. Perhaps this could be the exception that "proves the rule".

Zeolitic imidazolate frameworks (ZIFs) are also somewhat exceptions to the rule of minimal transitivity. In these compounds the linker functionalization acts to direct the structure, and a variety of topologies is found. ${ }^{81}$ But the great majority are based on vertex-transitive nets with transitivity $1 q$ with $q=1-4$.

## 8. CONCLUDING REMARKS

In this work we have outlined a consistent approach to the description on the structures of MOFs and related materials in terms of their underlying nets for cases in which these nets have more than two kinds of vertices. For MOFs formed from polytopic linkers, we recommend identifying both the basic net in which the linker is considered as a single node and the derived net in which branch points are identified explicitly. The advantages of the latter procedure are the following: (a) The intrinsic symmetry of the crystal is that of the derived net, which may be lower than that of the basic net. The net gwg, derived from cds, is an example in which a tetragonal basic net has only a monoclinic derived net of minimal transitivity. (b) Structures with different derived nets that may have the same symmetry can be differentiated. The nbo-derived and ptsderived nets are examples. (c) In derived nets formed by modifying the vertices B of a basic net AB , the coordination geometry of A may change. We have shown examples in which square and tetrahedral, and octahedral and trigonal prismatic interchange in this way (see, for example, Figures 40 and 59). The implications for design should be obvious.

We have shown also that most structures have nets of minimal transitivity. This is important for both theory and for experiment. Theoretically, one can evaluate potential structures on the basis of these nets. Experimentally, those structures can be the target of designed synthesis. The basic nets with transitivity 32 (type iv of section 7) are particularly important in this regard. ${ }^{14}$ RCSR lists 67 nets of this type, including the nets of some common crystal structures, such as those of spinel, $\mathrm{MgAl}_{2} \mathrm{O}_{4}$ (spl) and of cubic perovskite, e.g. $\mathrm{SrTiO}_{3}$ (xbo). A more complete enumeration is an important future task for theoretical crystal chemistry.

In all this work, nodes of the nets were determined from the crystal structures, as shown in many figures, and then the net topologies were determined using the program Systre (available from gavrog.org). ${ }^{82}$ For the work performed here, the program TOPOS (available at topos.ssu.samara.ru) could be used to either identify the net or provide Systre input for new nets. ${ }^{83}$ In this latter case, one should use the TOPOS "cluster representation".

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Notes
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## Biographies



Mian Li was born in Shantou, Guangdong, China, in 1982. He majored in chemistry and received his B.Sc. (2006) from Nanjing University, where he studied with Prof. Xiao-Zeng You and initiated his interest in structure-property relationships. He then worked as a research assistant with Prof. Dan Li in Shantou University, where he developed his research interest in MOFs, photochemistry and excited states, and theoretical and computational chemistry. He was inspired, since 2007, by Prof. Michael O'Keeffe to practice in the field of chemical geometry (topology).


Dan Li was born in Chaozhou, Guangdong, China, in 1964. He received his B.Sc. from Sun Yat-Sen University in 1984 and then served as a teaching assistant at Shantou University. He pursued his Ph.D. at The University of Hong Kong with Prof. Chi-Ming Che during 1988-1993. In April 1993, he returned to Shantou University after the completion of his doctoral degree. His current position is Professor in Chemistry, Director of Research Institute for Biomedical and Advanced Materials, and Vice President of Shantou University. He was a recipient of National Science Found for Distinguished Young Scholars of China in 2009. His research interest includes supramolecular coordination chemistry, photoluminescence, porosity, chirality, and especially the design, synthesis, and properties of luminescent $\mathrm{d}^{10}$ transition-metal coordination compounds, including MOFs.


Michael O'Keeffe was born in Bury St Edmunds, England, in 1934. He attended the University of Bristol (B.Sc. in 1954, Ph.D. in 1958, and D.Sc. in 1976). He is Regents' Professor of Chemistry at Arizona State University, where he has been since 1963. Past research has included investigations of conductivity, diffusion, defects, and nonstoichiometry in solids and experimental and theoretical studies of crystal chemistry. Over the last dozen years he has been applying the theory of periodic structures to the development of the theoretical basis of designed synthesis of materials, such as MOFs, consisting of linked molecular fragments of predetermined shapes (reticular chemistry).


Omar M. Yaghi was born in Amman, Jordan, in 1965. He received his Ph.D. from the University of Illinois—Urbana (1990) with Prof. Walter G. Klemperer. He was an NSF Postdoctoral Fellow at Harvard University (1990-1992) with Professor Richard H. Holm. He has been on the faculties of Arizona State University (1992-1998), University of Michigan (1999-2006), and University of California, Los Angeles (2007-2012). His current position is the James and Neeltje Tretter Professor of Chemistry, University of California, Berkeley, and Faculty Scientist at Lawrence Berkeley National Laboratory. His work encompasses the synthesis, structure, and properties of inorganic compounds and the design and construction of new crystalline materials. He has shown that organic and inorganic molecules can be stitched together into extended porous structures called metal-organic frameworks, zeolitic imidazolate frameworks, and covalent organic frameworks.

## ACKNOWLEDGMENTS

M.O'K. is supported by the World Class University program (R-31-2008-000-10055-0) and by the U.S. National Science Foundation (grant DMR 1104798). He also acknowledges helpful correspondence about the structures of TCNQ-based salts with Kim Dunbar and Zhongyue Zhang. D.L. is supported by the National Basic Research Program of China (973

Program, 2012CB821706) and the National Natural Science Foundation of China (91222202 and 21171114).

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[^0]:    Received: July 19, 2013
    Published: November 5, 2013

