

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

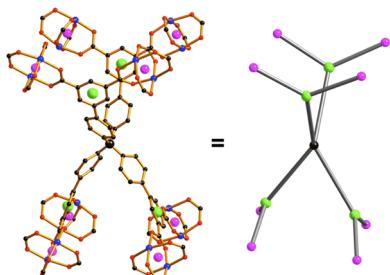
Mian Li,[†] Dan Li,[†] Michael O’Keeffe,^{*,‡,§} and Omar M. Yaghi^{§,||}

[†]Department of Chemistry, Shantou University, Guangdong 515063, P. R. China

[‡]Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, United States

[§]Graduate School of E�WS (WCU), KAIST, 373-1, Guseng Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea

^{||}Department of Chemistry, University of California—Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460, United States



CONTENTS

1. Introduction	1343	5.1. MOFs with 6-c SBUs and Hexatopic Linkers	1357
2. MOFs with Multiple SBUs	1345	5.2. MOFs with Square SBUs and Hexatopic Linkers	1359
2.1. A MOF with Triangular and Square SBUs	1345	5.3. A MOF with Tetrahedral SBU and Hexatopic Linker	1362
2.2. Other MOFs with Triangular and Square SBUs	1346	5.4. Basic Nets with 6-c Vertices and Their Derived Nets	1362
2.3. A MOF with Triangular and Square SBUs and Hexatopic Linker	1346	6. MOFs with Octatopic Linkers	1363
2.4. MOFs with Square and Tetrahedral SBUs	1346	7. The Minimal Transitivity Principle	1365
2.5. MOFs Based on Square and Trigonal Prismatic SBUs	1347	8. Concluding Remarks	1367
2.6. MOFs Based on Square and Octahedral SBUs	1347	Author Information	1367
2.7. MOFs Based on Tetrahedral and Trigonal Prismatic SBUs	1348	Corresponding Author	1367
2.8. A MOF Based on Square Pyramidal and Octahedral SBUs	1349	Notes	1367
3. MOFs with Tetratopic Linkers	1349	Biographies	1367
3.1. Paddle Wheels and Other Square SBUs Joined by Planar Tetratopic Linkers	1349	Acknowledgments	1368
3.2. Paddle-Wheel SBUs Joined by Tetrahedral Tetratopic Linkers	1352	References	1368
3.3. MOFs with Tetrahedral Vertices Linked by Tetratopic Linkers	1353		
3.4. MOFs with Octahedral Vertices Linked by Tetratopic Linkers	1353		
3.5. A MOF with Tritopic and Tetratopic Linkers	1355		
3.6. MOFs with Cubic SBUs Joined by Tetratopic Linkers	1355		
3.7. Nets Derived by Replacing a 4-c Vertex with Two 3-c Vertices	1356		
4. MOFs with Pentatopic Linkers	1357		
5. MOFs with Hexatopic Linkers	1357		

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

Received: July 19, 2013

Published: November 5, 2013



*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 pqr 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 1 1 1 1.¹¹ The edge-transitive nets have $pq = 11$ 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 pq 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 four-coordinated (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 *mmm* (D_{2h}) and $\bar{4}m2$ (D_{2d}). 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-5¹⁷ and HKUST-1,¹⁸ are shown in Figure 1. In MOF-5, octahedrally shaped $Zn_4O(-CO_2)_6$ 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-c) vertices that has the symbol **pcu**. In HKUST-1, the SBU is the paddle-wheel $Cu_2(-CO_2)_4$ 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

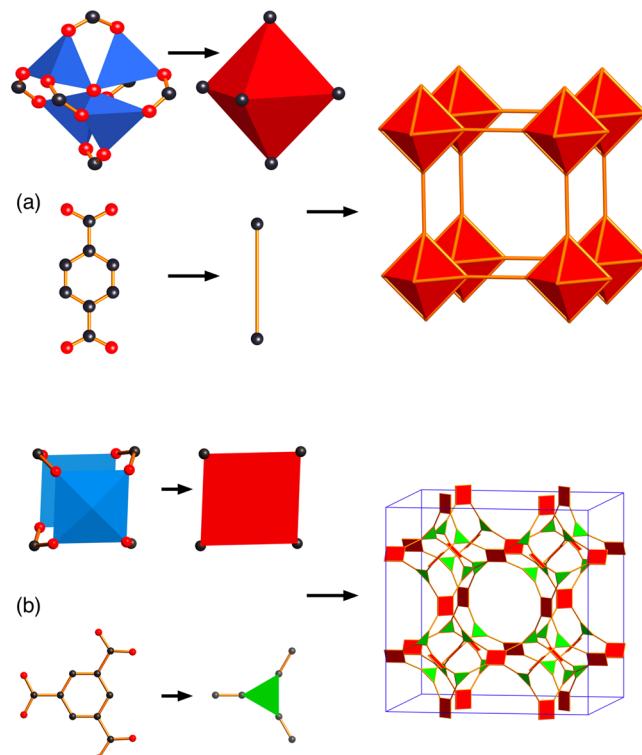


Figure 1. (a) The components of MOF-5 (section 1)¹⁷ showing the abstraction of the $Zn_4O(-CO_2)_6$ SBU as an octahedron, the ditopic terephthalate linker as a rod, and their assembly into the **pcu** net shown here in augmented form. (b) The components of HKUST-1¹⁸ showing the $Cu_2(-CO_2)_4$ paddle 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* versions¹⁹ 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)-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 CuFeS₂ (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, CaCO₃, in which C is 3-c (to O) and each of the three O is also 3-c (to 2Ca + O). It is clearly more informative to give the full structure of CaCO₃ than simply to state that Ca and CO₃ 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 hydrogen-bonded 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 C₆₀ 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 Cu₂ paddle wheel and a Cu₃ SBU with three points of extension.²⁶ These are linked by a tritopic linker, as shown in Figure 2. We believe the structure

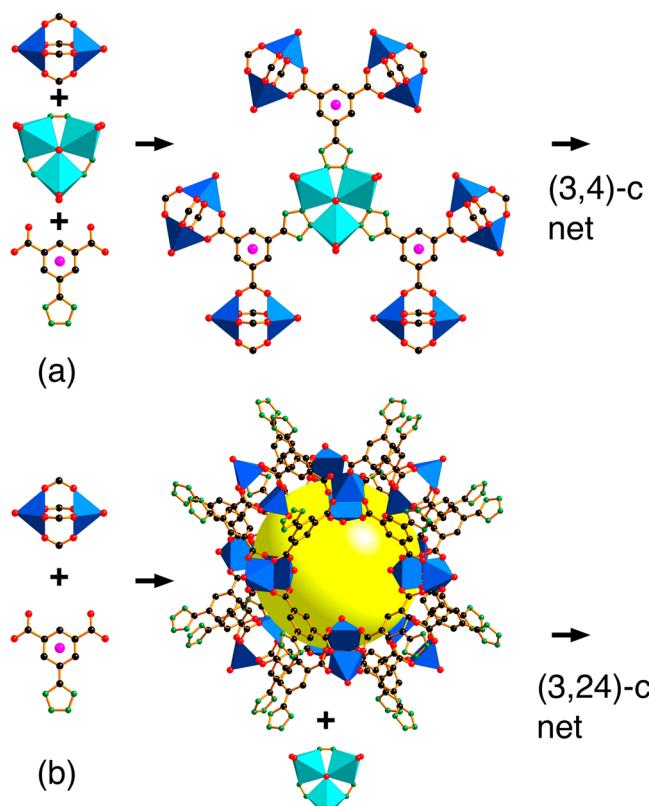


Figure 2. Deconstruction of a MOF (section 2.1)²⁶ with two metal SBUs and a tritopic linker (a) into a (3,4)-c net (ntt) and (b) into first a TBU with 24 points of extension and then combining with a metal SBU with three points of extension to give a (3,24)-c net (rht).

is best described as a (3,4)-c trinodal net, symbol **ntt**, with minimal transitivity 3 2 (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) 12 4-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.

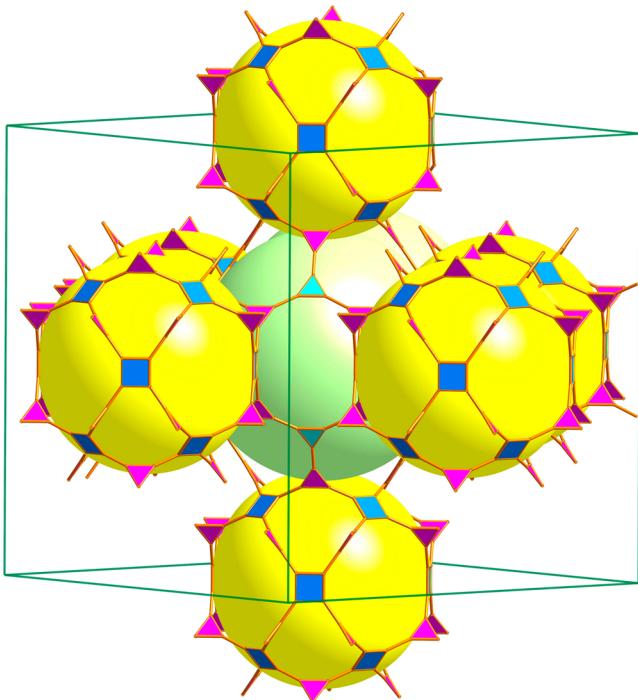


Figure 3. The net **ntt** in augmented form **ntt-a**. The yellow balls center cages with 12 square nodes (blue). The pale green ball centers an “octahedral” hole.

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 3-c and one 4-c SBUs.^{28,29} The SBUs (Figure 4) are $\text{Zn}_2(-\text{CO}_2)_3$

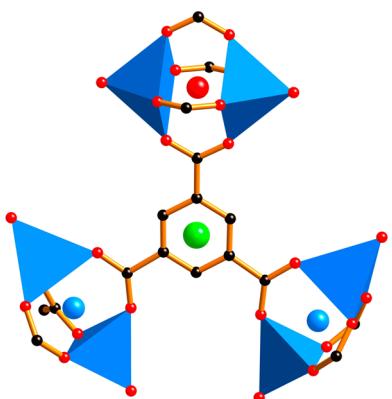


Figure 4. A tritopic linker joined to two 3-c Zn_2 and one 4-c Zn_2 paddle wheels in a **tfe** structured MOF (section 2.2).²⁸

with three points of extension and $\text{Zn}_2(-\text{CO}_2)_4$ 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.

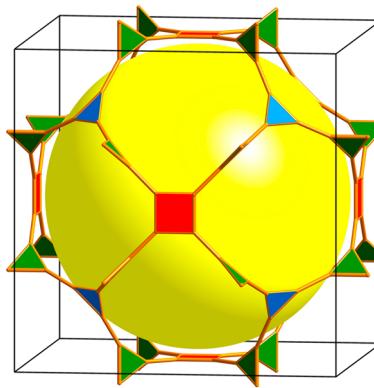


Figure 5. The net **tfe** in a symmetric embedding as the augmented form **tfe-a**.

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 $\text{Zn}_2(-\text{CO}_2)_4$ with four points of extension and $\text{Zn}_2(-\text{CO}_2)_3$ 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-c and 4-c nodes and the

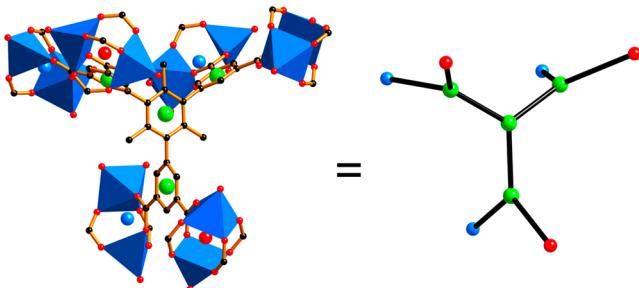


Figure 6. The linker (branch points green) connected to 3-c (blue nodes) and 4-c (red nodes) in SDU-1 (section 2.3).³⁰

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 face-centered cell with double cell edge length. Notice that in both the **ntt** and **tfe-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 reported³¹ for USF-3, a Zn MOF with a tritopic linker, and subsequently³² 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**

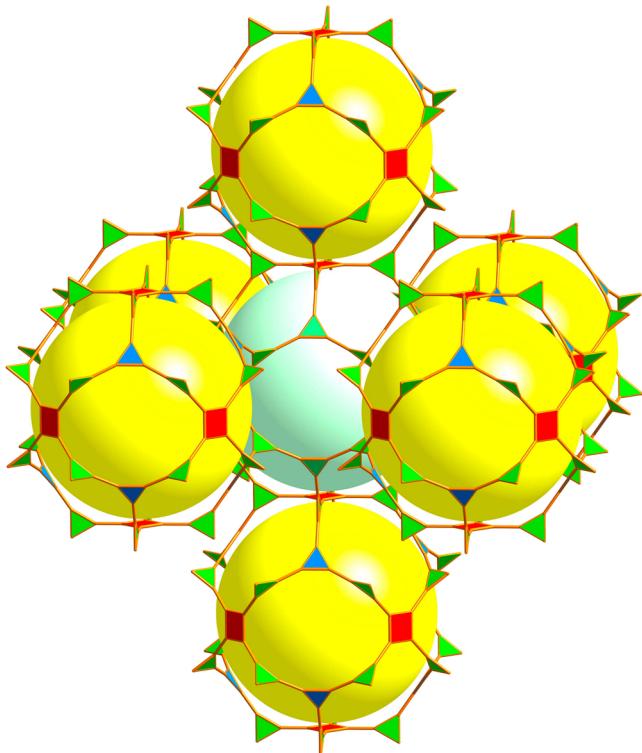


Figure 7. The net **tfe** in binary and augmented form **tfe-b-a**. The red squares and blue triangles are at the positions of the metal SBUs in the crystal structure.

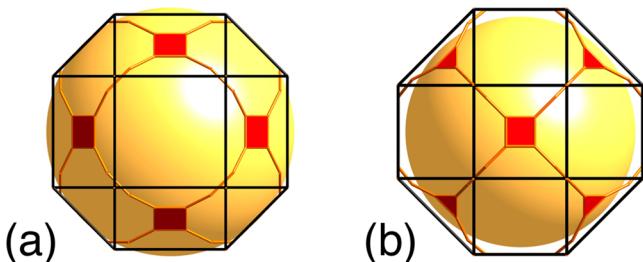


Figure 8. The cages in (a) **ntt-a** and (b) **tte-a** are compared.

(transitivity 3 2) 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 UCMC-150, is based on $\text{Cu}_2(-\text{CO}_2)_4$ paddle wheels with four points of extension and related $\text{Cu}_3(-\text{CO}_2)_6$ SBUs with six points of extension.³⁴ These are

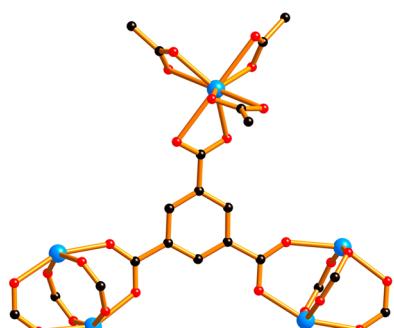


Figure 9. The linker and metal SBUs in USF-3 (section 2.4).³¹

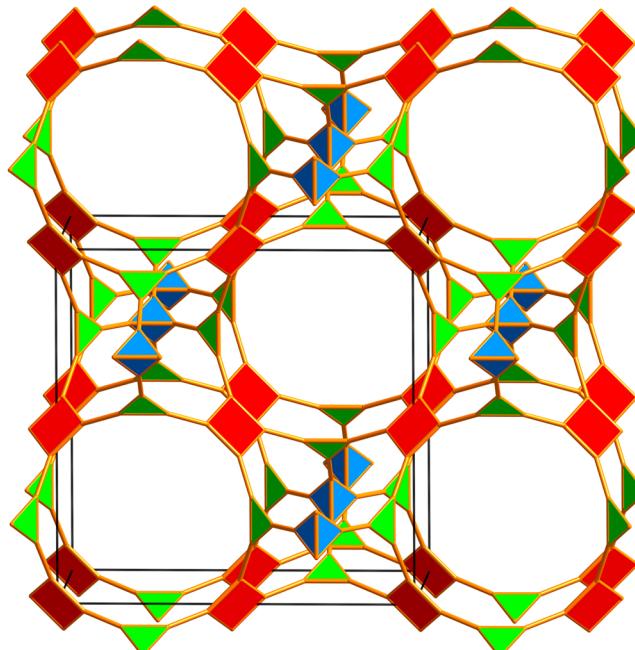


Figure 10. A symmetrical embedding of the net **mmm** in augmented form **mmm-a**. The view is almost down the tetragonal *c* axis.

linked by a tritopic linker (Figure 11) into a trinodal (3,4,6)-c net **agw**. This net again has minimal transitivity (3 2) and is

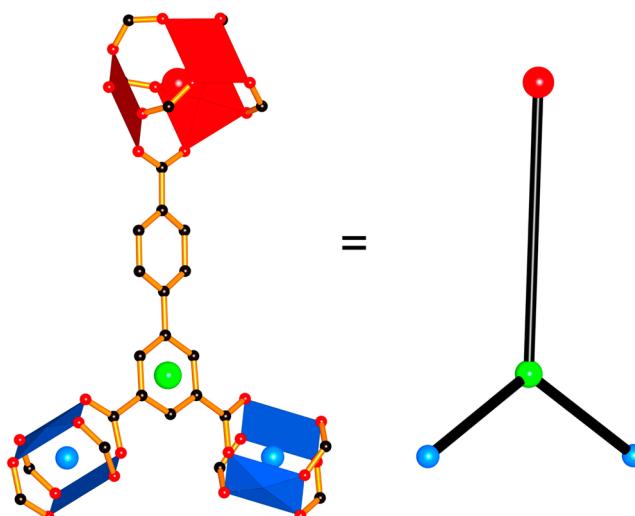


Figure 11. (Left) The linker in UCMC-150 (section 2.5)³⁴ and its adjoining SBUs (Cu_2 blue and Cu_3 red). (Right) The corresponding nodes and links of the underlying net.

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 (3 2) net with RCSR symbol **idp** illustrated in Figure 14. An isoreticular compound with a different linker has also been reported.³⁶ In

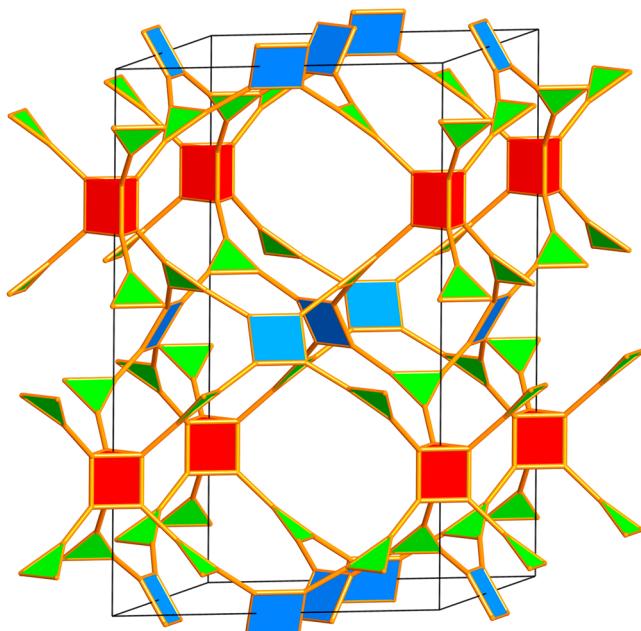


Figure 12. The net agw in a maximum symmetry embedding of its augmented form agw-a.

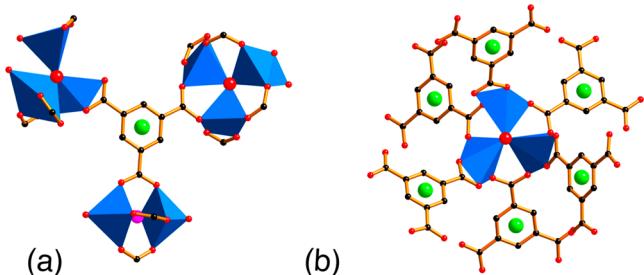


Figure 13. Fragments of a MOF (section 2.6).²⁹ (a) The tritopic linker joined to two 6-c and one 4-c SBU. (b) The 6-c SBU joined to six tritopic linkers. 3-c branch points are indicated by green balls.

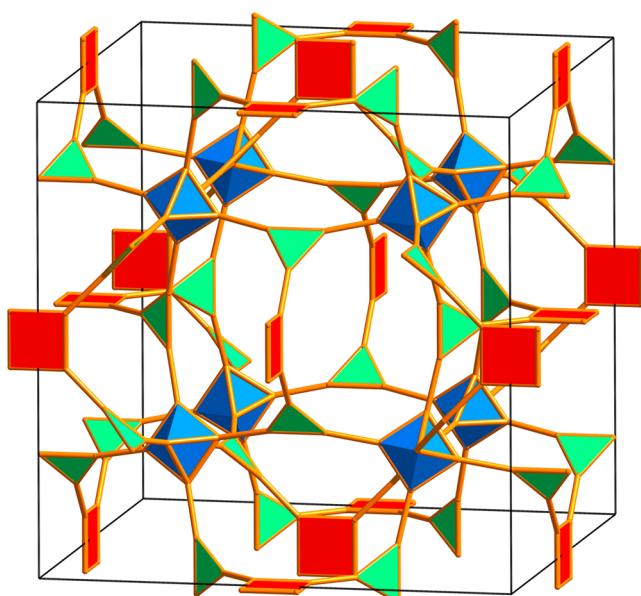


Figure 14. The net idp shown in its augmented form idp-a in a maximum symmetry embedding.

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 ($I\bar{2}3$) than that of the net ($Im\bar{3}$).

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 Cr₃ 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 3 2.

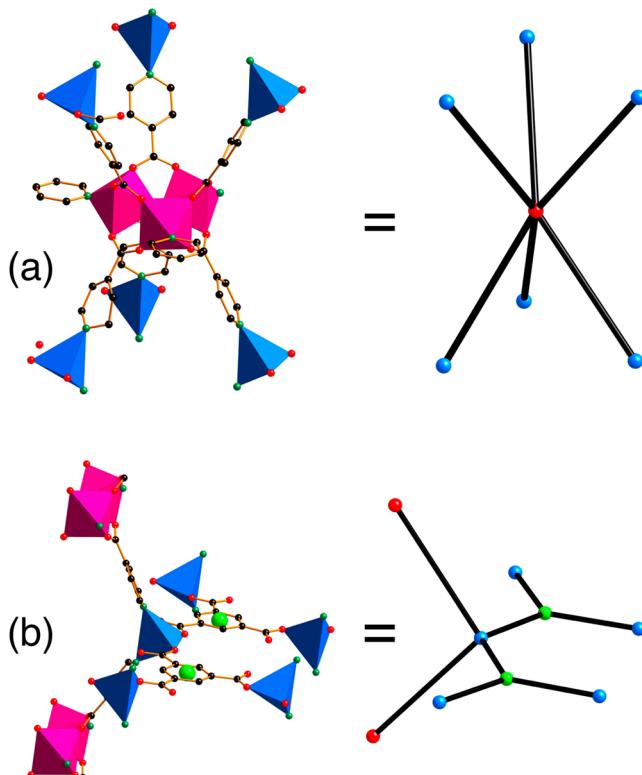


Figure 15. Fragments of the asc-1 structure (section 2.7).³⁷ (a) A 6-c Cr₃ SBU connected to six tetrahedra Zn atoms by a ditopic linker. (b) ZnO₂N₂ tetrahedron (blue) linked to two Cr₃ SBUs and to two tritopic linkers; 3-c branch points are indicated by large green spheres.

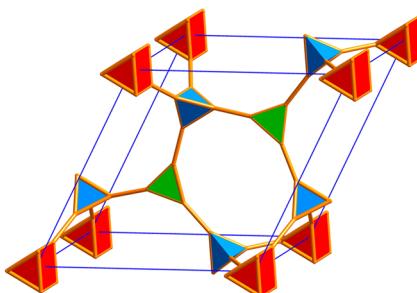


Figure 16. A maximum symmetry embedding of the asc net in its augmented form asc-a.

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-c SBU nodes, B, and 4-c SBU nodes, C. In the MOF of this section³⁸ there is in addition links by ditopic linkers between B nodes and between C nodes, so there are topologically four kinds of links: A–B, A–C, B–B, and C–C. The SBUs now become 5-c and 6-c. The minimal possible transitivity is now 3 4 and this is what is observed in the real crystal structure. The SBUs are illustrated in Figure 17 and the

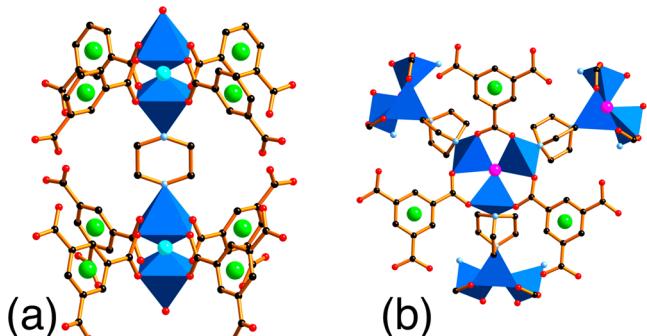


Figure 17. Fragments of the structure of a MOF (section 2.8).³⁸ (a) A pair of linked 5-c SBUs each linked to a tritopic linker with 3-c branch points shown as green balls. (b) A central 6-c SBU joined to three others and to three tritopic linkers.

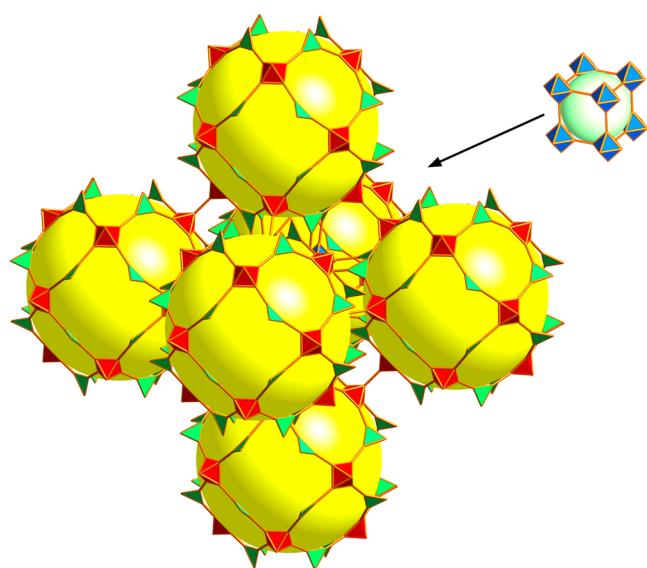


Figure 18. The net **ott** shown in a maximum symmetry embedding in augmented form **ott-a**. The group of eight octahedra shown at the top right occurs in the “octahedral” hole in the center of the group of six cages (centered by yellow balls).

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

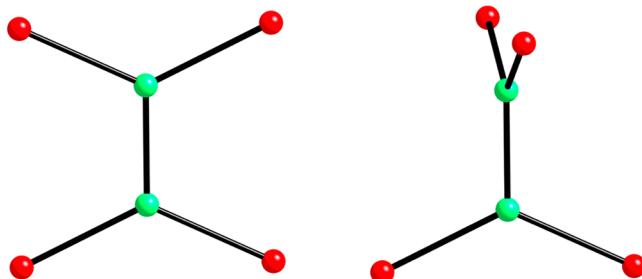


Figure 19. The limiting shapes (left, rectangular; right, tetrahedral) of tetratopic linkers with two 3-c branch points.

that take into account the 3-c nodes explicitly are generally derived from a basic net by replacing a 4-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 linker³⁹ in Figure 20 might be described as having four 3-c

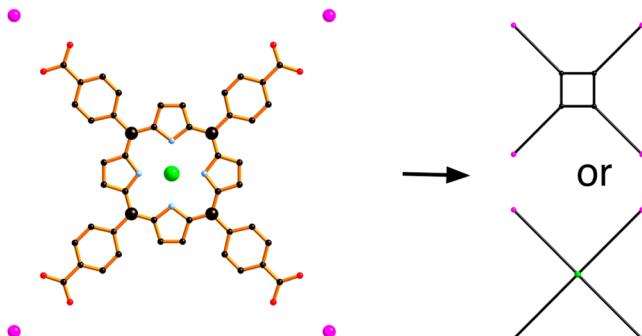


Figure 20. A tetracarboxylate linker³⁹ joined to metal SBUs centered at the magenta balls. It could be abstracted as one of the two shapes shown on the right.

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 Cu₂ paddle-wheel SBUs are joined by mostly planar tetracarboxylate linkers with two 3-c branch points.^{40,41} Possibly the first of these was MOF-505 (Figure 21),^{40a} the

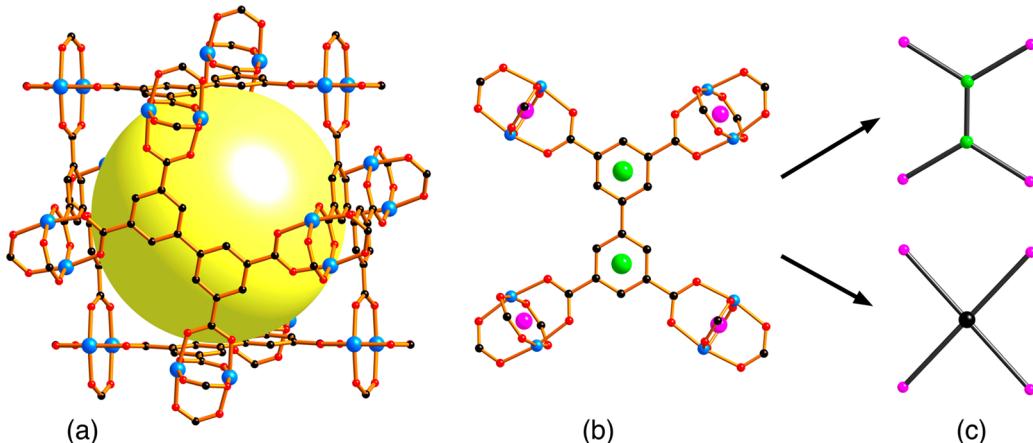


Figure 21. (a) The MOF-505 structure (section 3.1).^{40a} Cu atoms, blue; C, black; O red. (b) The linker attached to four paddle wheels. The magenta sphere is at a 4-c node of the underlying net and the green spheres at 3-c branch points of the linker. (c) Two possible abstractions of the linker + SBUs 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.^{40k} 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^{40e} (described as **nbo**) and UWDM-1^{40l} (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 those⁴³ 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**.

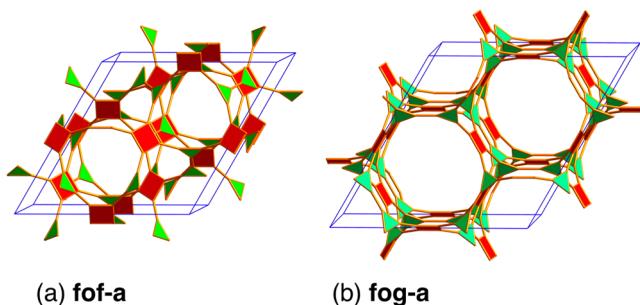


Figure 22. Two nets, shown in augmented form and both with $\bar{R}\bar{3}m$ symmetry derived from the **nbo** net.

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-c vertices in two distinct ways while preserving the symmetry to give four derived nets as shown in Figure 23.

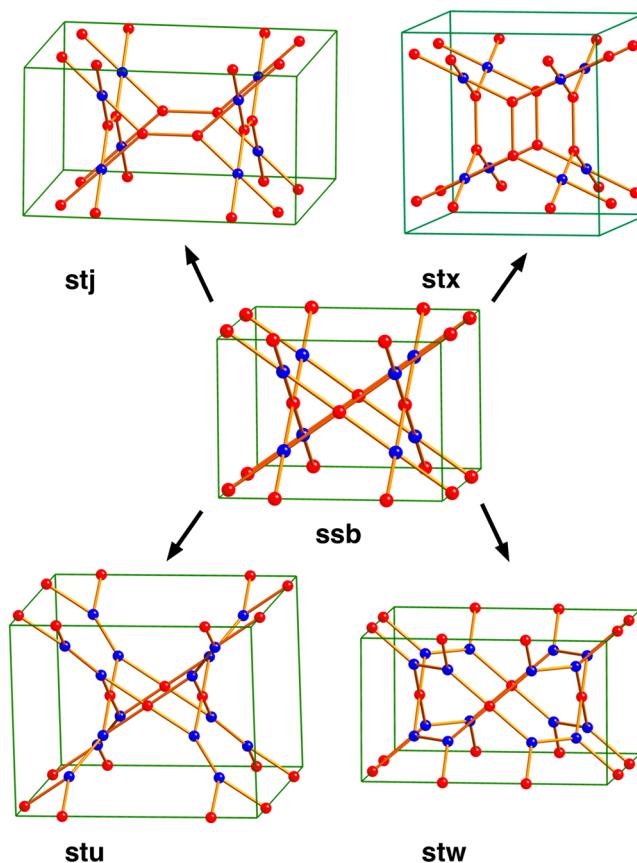


Figure 23. (3,4)-c nets derived from **ssb** by splitting one 4-c vertex into two 3-c vertices. All nets have the same symmetry, $I\bar{4}/m\bar{m}\bar{m}$, and all have two kinds of vertices and two kinds of links.

A surprising number of topologies have been found in practice. NOTT-109^{40h} has the (3,4)-c underlying **stx** net derived from the 4-c net **ssb**. DUT-12^{40o} has a topology based on a second net derived from **ssb**, viz., **stu**. Clearly to distinguish these two one must find the (3,4)-c net. PCN-12^{40c} and ZJU-25⁴⁰ⁿ have the underlying (3,4)-c net **sty** (Figure 24) derived from the 4-c net **ssa**. Interestingly, **sty** appears to be the only minimal transitivity (3,4)-c net that can be derived from **ssa**.

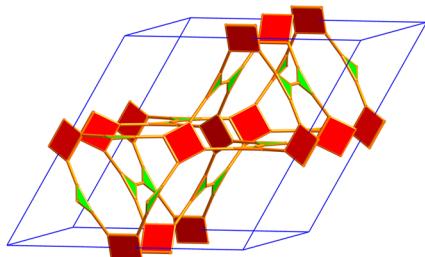


Figure 24. The net **sty** shown in augmented form **sty-a**.

DUT-10^{40o} has a net, **lil**, derived from the edge-transitive uninodal net, **Ivt**. The same net is found in ZJU-30^{40p} now as a pair of interpenetrating structures. Interestingly, the basic net, **Ivt**, has symmetry $I4_1/AMD$, 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 $\bar{4}$ axis, so the symmetry again becomes tetragonal ($\bar{4}m2$). There is a second minimal transitivity (3,4)-c net with the same symmetry (**Imma**) derived from **Ivt**, **lim**, which has been identified in multiply interpenetrating cyano-bridged copper azolate frameworks.⁴⁴ These nets are illustrated in Figure 25. We include

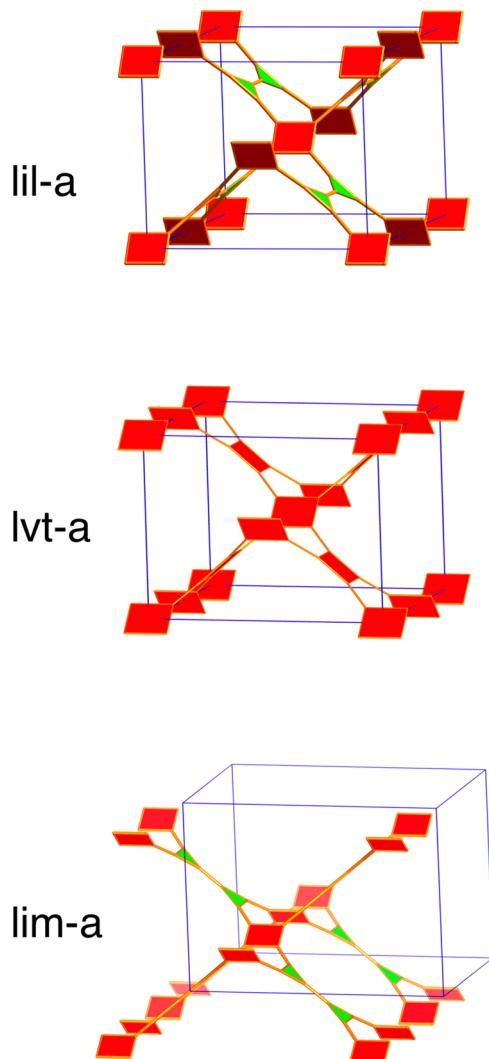


Figure 25. Two minimal transitivity nets with symmetry **Imma** derived from the basic net **Ivt**.

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.

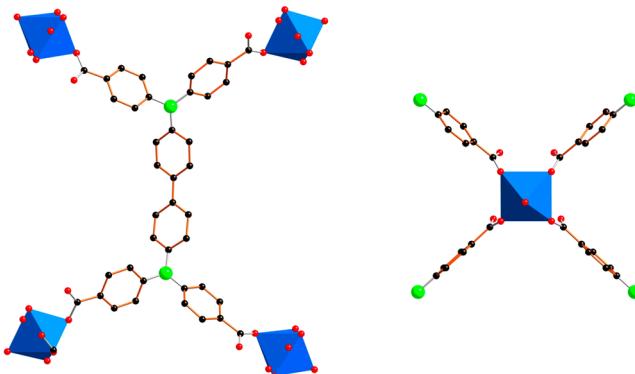


Figure 26. Linker and SBU of a Mg MOF, SNU-25 (section 3.1),⁴⁵ with **lil** topology. Large green balls are N atoms at branch points of the linker.

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)-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-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 (**tfb**, **fob**, 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 (2 2). There are of course exceptions, but they are rare. PCN-12^{40c} 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 8 10, in the RCSR database as **pcn**). IZE-1 and IZE-2 are isomers of MOFs with chemically identical frameworks, both with minimal transitivity (2 2) nets, but there is a third isomer, IZE-3, with net **hyx** that has transitivity 3 3.^{40k}

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 1 2. 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 2 3. Two recent examples,⁴⁶ one of which was described by the authors as **cds**,^{46a} do in fact have the **gwg** topology and symmetry.

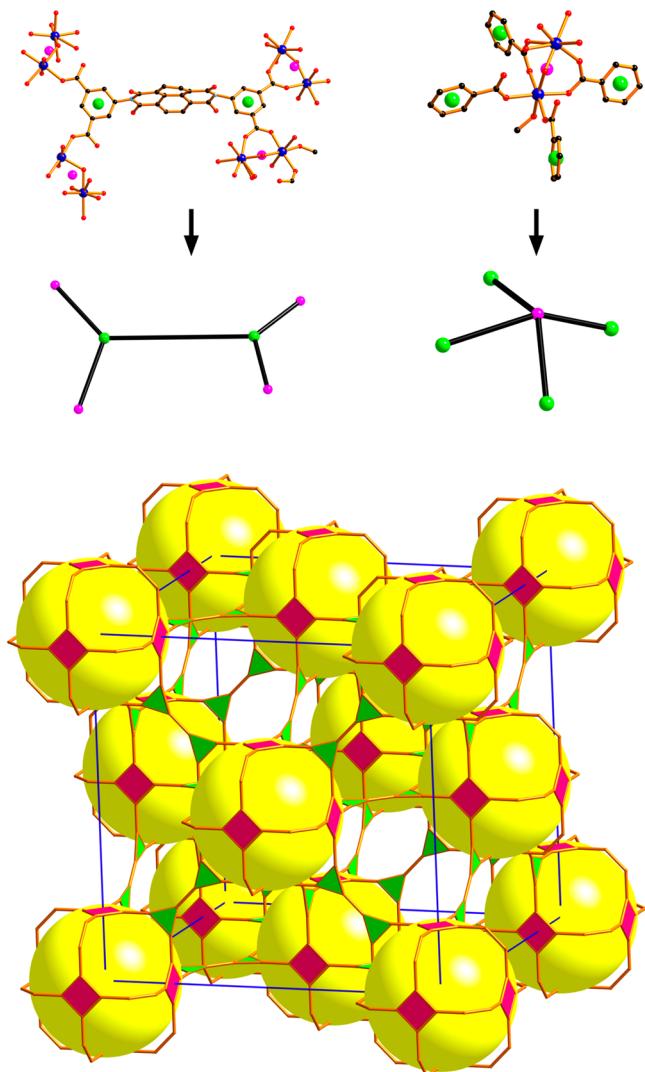


Figure 27. (Top) Abstraction of the linker and SBU of fcu-MOF-1 (section 3.1).^{41a} (Bottom) The underlying net shown in augmented form tfb-a. The yellow balls are arranged as in cubic closest packing.

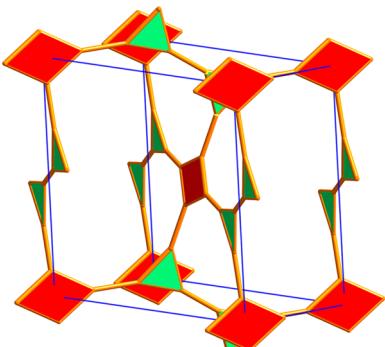


Figure 28. The net gwg, shown in augmented form gwg-a, derived from cds by splitting square vertices into pairs of triangular vertices (symmetry $P2_1/c$).

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-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^{40,47} have the **sur** topology. The figure also shows the two simplest ways of splitting the planar (“square”) vertex (**dmd** and **tfi**).

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

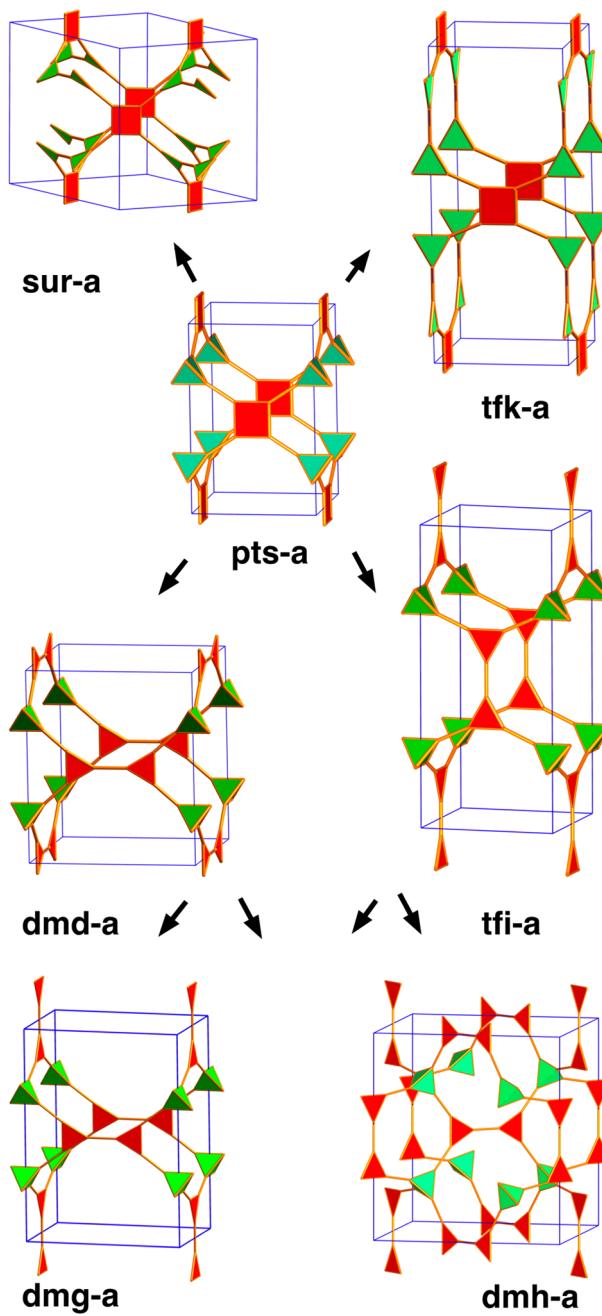


Figure 29. Six (3,4)-c nets derived from pts by dividing the tetrahedral 4-c vertex into two 3-c vertices (top) and dividing the planar vertex (bottom). Nets are shown in their augmented forms.

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

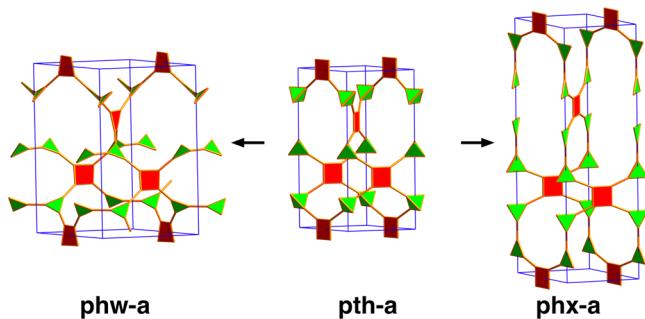


Figure 30. Two nets derived from **pth** by splitting the tetrahedral vertices into two 3-c ones. Compare with Figure 29.

tetrahedral vertex into two 3-c ones. Both preserve the symmetry of **pth** ($P6_222$). 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 CoO_6 octahedra sharing a corner, as shown in Figure 31.

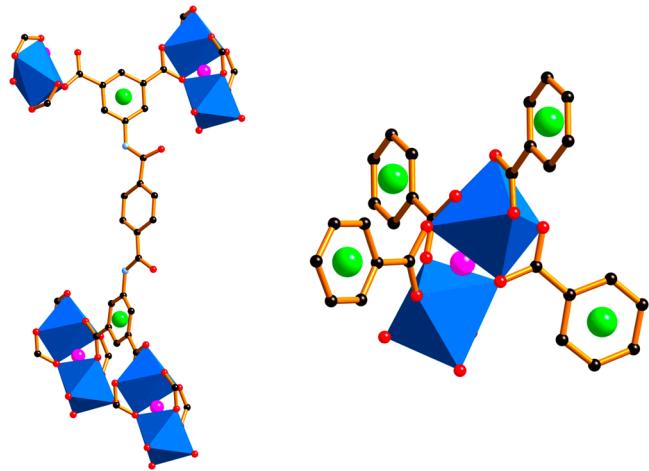


Figure 31. The linker (left) and 4-c SBU (right) of a MOF (section 3.3)⁴⁹ with the **zyl** topology.

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, **ion**, which has transitivity 1 2. The derived net **zyl** (Figure 32) is even less minimal, as it has transitivity 3 4; however, it seems not to be possible to construct a (3,4)-c derived net based on **ion** of lower transitivity. The symmetry of **zyl** is $Cmc2_1$ and that of the crystal is only $P2_1$.

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

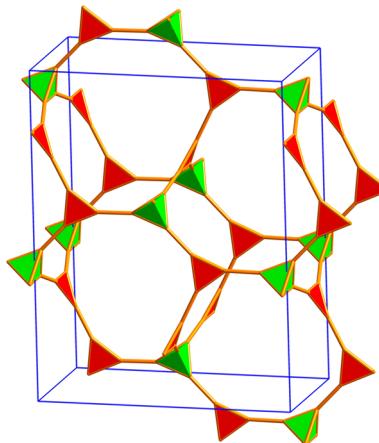


Figure 32. The net **zyl** derived from **ion** (lonsdaleite) in augmented form **zyl-a**.

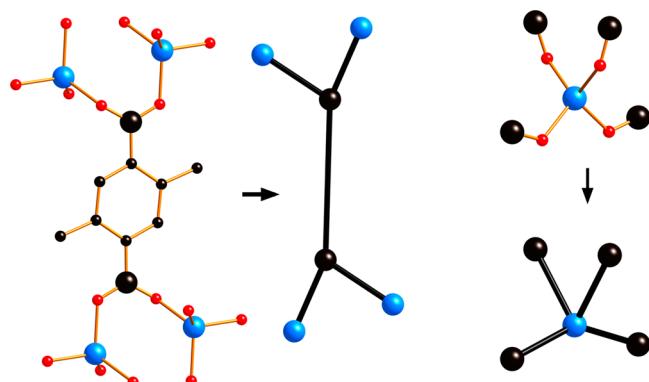


Figure 33. Fragments of the structure of $\text{Zn}(\text{dimethylbenzenedicarboxylate})_2$ (section 3.3)⁵⁰ illustrating the 3-c and 4-c nodes of the **dmd** net (Figure 29). Zinc, blue; carbon, black; oxygen, red.

vertices of **pts**, is now **dmd** (Figure 29). The same net is found with a tetrahedrally linked Mn atom joined by a tetracarboxylate linker.^{40q}

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 C–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 AgTCNQ_{51a} has a rather complicated **pts**-derived structure with transitivity 3 4, **dmb**. CuTCNQCl_2 and AgTCNQCl_2 have two forms: the latter^{51d} with the **dmd** net and the former^{51e} with **tfi** (interpenetrated). All these topologies are illustrated in Figure 29. More recently, Cu salts of tetrafluoro-TCNQ have been reported.^{51f} Structures 1–4 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

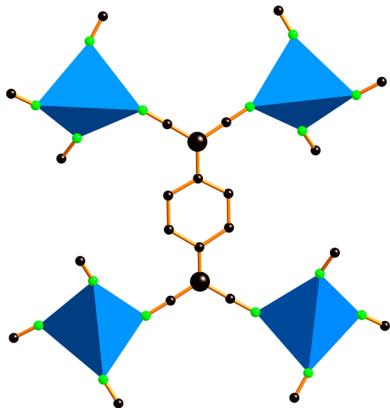


Figure 34. Part of the structure of AgTCNQ (section 3.3).^{51a} Carbon, black; nitrogen, green; AgN₄ tetrahedra, blue. The larger spheres indicate the 3-c branch points. The TCNQ unit is accurately planar.

atom.⁵² For the other, the SBU is the Zn₄ cluster of MOF-5 (Figure 1) as shown in Figure 35.⁵³ The basic net is the edge-

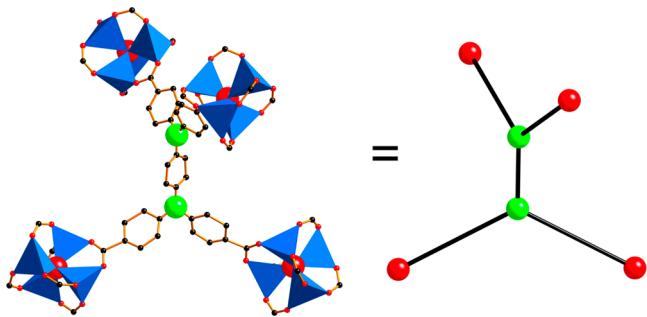


Figure 35. The linker and SBUs of a MOF (section 3.4)⁵³ with the act topology.

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 (2 1 and 2 2, 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 2 2. The derived net, ttu (Figure 38), does have the minimal transitivity, 2 3, 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 InO₆ 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 edge-transitive 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-c node is an elongated octahedron, and the site symmetry is $\bar{3}m$, 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 2 2. Both are cubic, but with different symmetries, and the symmetries at the 6-c sites now are

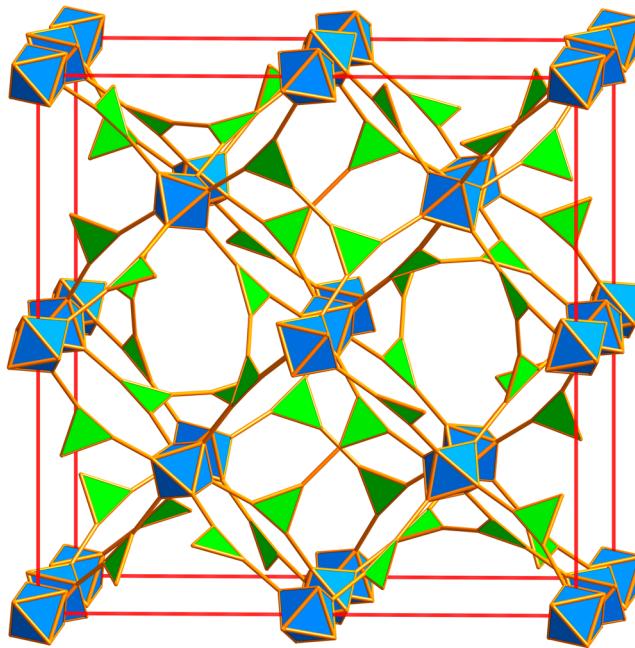


Figure 36. The net act in its maximum symmetrical form as the augmented net act-a.

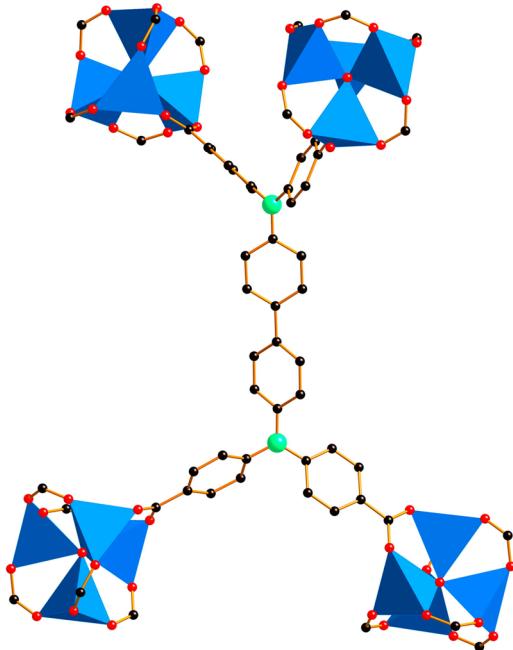


Figure 37. The linker and SBUs of DUT-13 (section 3.4)⁵⁴ with the ttu topology. Compare with Figure 35.

different: 32 and $\bar{3}$, 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 S³, and the structures differ in the two possible orientations of these, as shown in

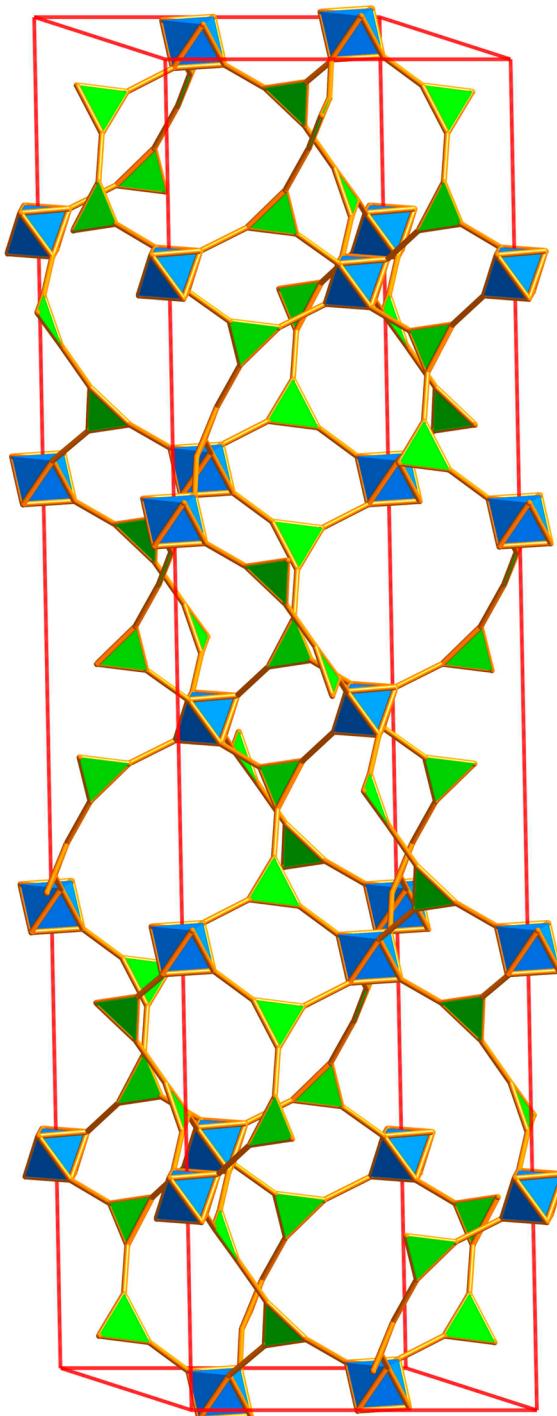


Figure 38. The net ttu shown in augmented form ttu-a.

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 Zn_4 SBU.⁵⁷ There are accordingly three nodes in the net. One, say A, is 6-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 A–B, A–C and C–C links). Fragments of the structure are shown in Figure 42. The net they form has indeed minimal transitivity 3

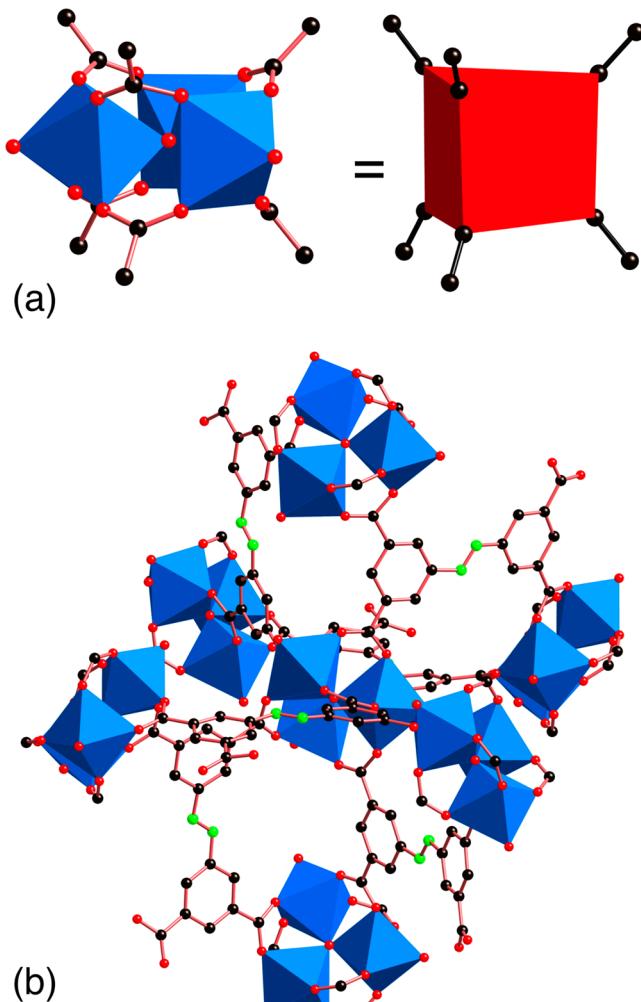


Figure 39. (a) An In_3 SBU (section 3.4)⁵⁵ showing the trigonal prismatic geometry of the points of extension. (b) A fragment of the structure showing one SBU linked to six others in an octahedral geometry.

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 Tetrapotic Linkers

Several recent papers report MOFs with an 8-c 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.^{39,58a} 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.^{58b} A simple advantage of this is that the linker no longer has square symmetry, and there are two simple derived nets, **xly** and **xlz**, in which the long axis of the linker is aligned parallel or perpendicular to the hexagonal c axis, as shown in Figure 45. The observed orientation,^{58b} **xly**, results in a more open framework. The advantage of this approach was further illustrated in recent unpublished work^{46b} at Shantou University in which a pyrene tetracarboxylate linker produced a MOF

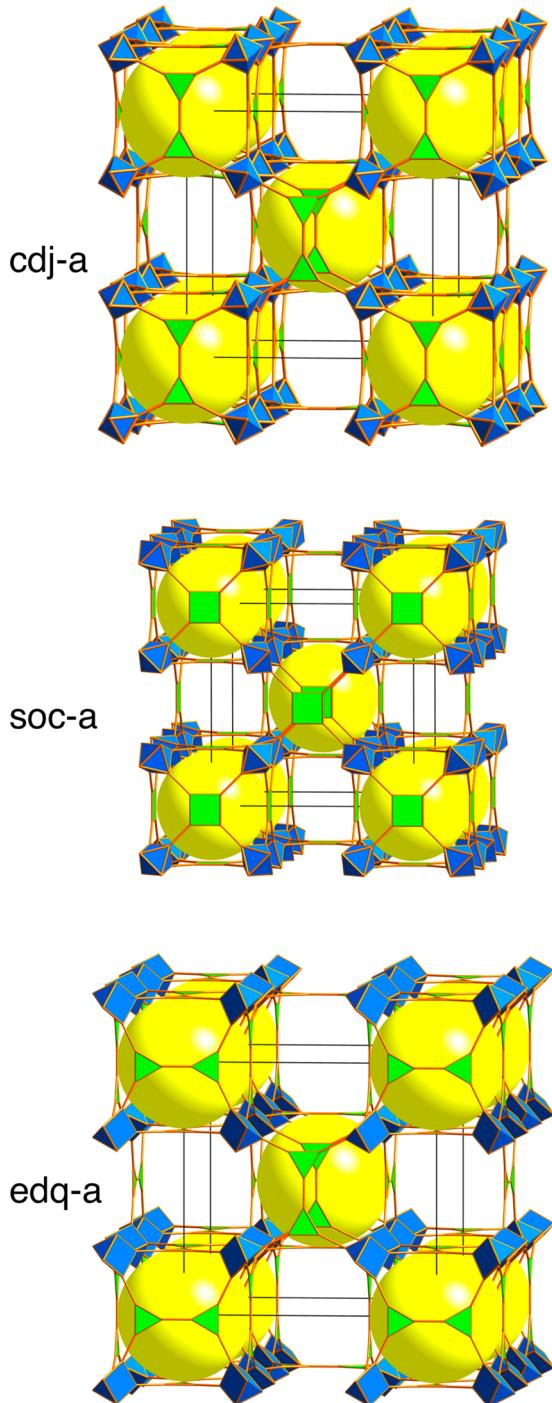


Figure 40. Augmented forms of the basic net **soc** and the derived nets **cdj** and **edq**. Note that the blue octahedra in **cdj-a** and **soc-a** become trigonal prisms in **edq-a**.

based on the basic net **cds**, which has the monoclinic symmetry of the derived net **gwg** (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-c vertex by two linked 3-c vertices. In almost every case the increase in transitivity is minimal: by 1 1 for uninodal basic nets and 0 1 for binodal basic nets.

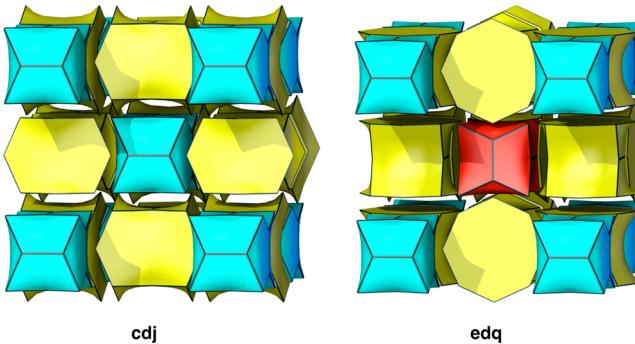


Figure 41. Nets **cdj** and **edq** shown as tilings. The blue and red tiles are topologically the same as pentagonal dodecahedra S^3 .

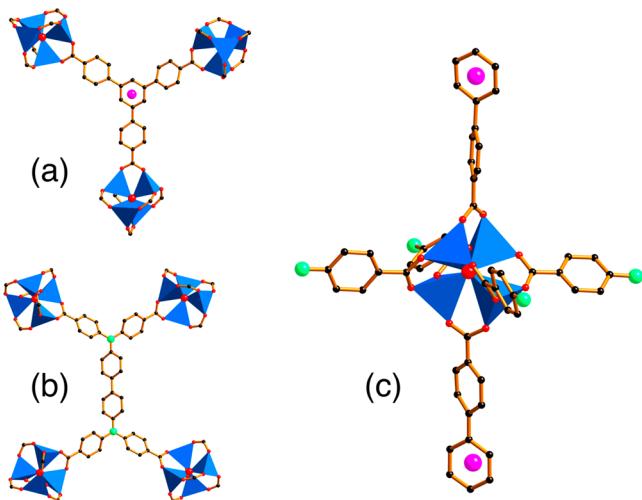


Figure 42. Parts of the structure of DUT-25 (section 3.5).⁵⁷ (a) The tritopic linker. The large magenta ball is a 3-c branch point. (b) The tetratopic linker. Green balls (N atoms) are 3-c branch points. (c) The Zn_4 SBU linked to six 3-c branch points. The large red ball (O atom) is at the 6-c node.

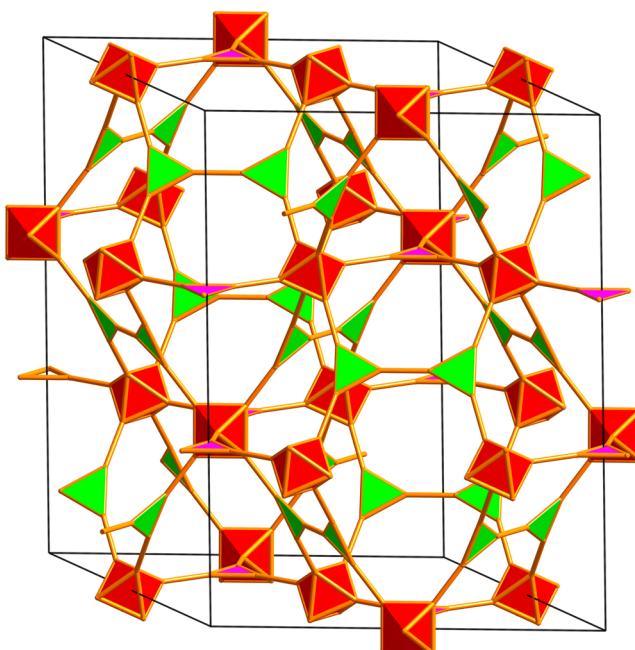


Figure 43. The net **ttz** in augmented form **ttz-a**.

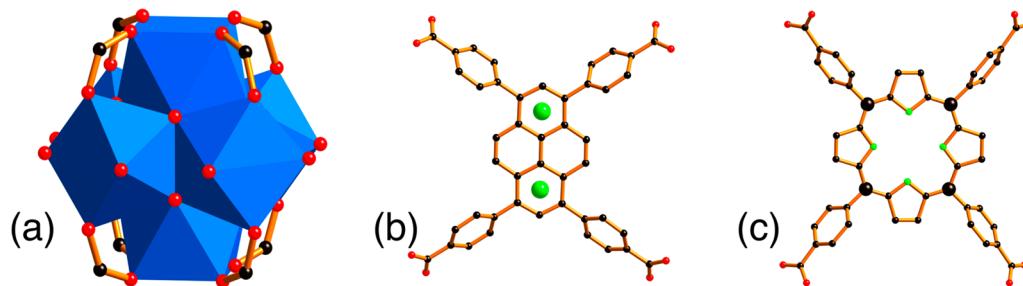


Figure 44. (a) The Zr_6 SBU in MOF-545 (section 3.6)³⁹ with eight carboxylate C atoms (black) as points of extension. (b) The linker in NU-1000,^{58b} with branch points shown as green balls. (c) The linker in MOF-545³⁹ showing branch points (large spheres) forming a square (cf. Figure 20).

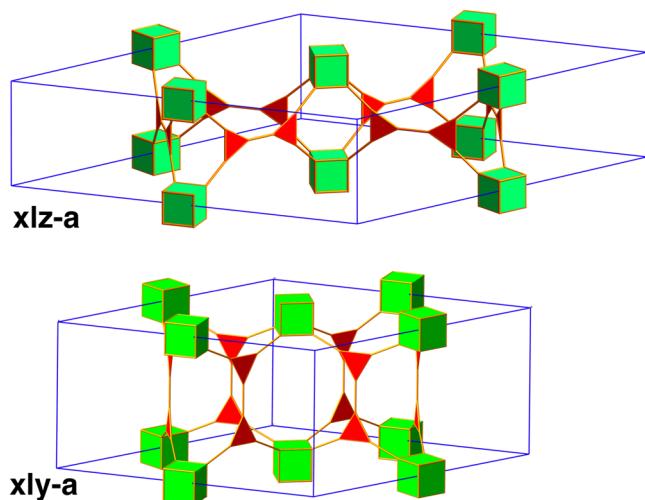


Figure 45. The nets xlz and xly shown in augmented form.

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 $\text{Cu}_4(-\text{CO}_2)_4$ 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 $\text{Im}\bar{3}m$). 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 5-c 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 (A–B, A–C, and B–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-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	1 1	4	square	fof, ^a fog, ^a tfb ^a	2 2
lvt	1 1	4	square	lil, ^a lim ^a	2 2
rhr	1 1	4	square	ucp	2 2
cds	1 2	4	square	gwg ^a	2 3
dia	1 1	4	tetrahedron	tfa	2 2
qtz	1 1	4	tetrahedron	tfq	2 2
sod	1 1	4	tetrahedron	xbl	2 2
lon	1 2	4	tetrahedron	zyl ^a	3 4
pts	2 1	4 4	square	dmd, ^a tfi ^a	2 2
			square	dmg, ^a dmh ^a	3 3, 3 4
			tetrahedron	sur, ^a tfk	2 2
pth	2 1	4 4	square	hst	2 2
			tetrahedron	phw, ^a phx	2 2
ssb	2 1	4 4	square 1	stu, ^a stw	2 2
			square 2	stj,stx ^a	2 2
ssa	2 1	4 4	square 1	sty ^a	2 2
stp	2 1	6 4	square	ttp, ttx	2 2
soc	2 1	6 4	square	edq, ^a cdj	2 2
scu	2 1	8 4	square	tty	2 2
csq	2 1	8 4	square	xly, ^a xlz	2 2
ftw	2 1	12 4	square	ttv	2 2
iac	2 1	6 4	tetrahedron	act ^a	2 2
toc	2 1	6 4	tetrahedron	xab	2 2
cor	2 2	6 4	tetrahedron	ttu ^a	2 3

^aNets 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 $\text{Zn}_4\text{O}(-\text{CO}_2)_6$ SBUs were joined by such linkers, the structures have been described in terms of 6-c nets.⁶⁰ In one early case (MODF-1^{60a}) 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)-c net, however, it is a rather high transitivity structure, as the net **mod** has transitivity 4.5. This is another example that shows that the minimal transitivity principle is not universally obeyed.

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

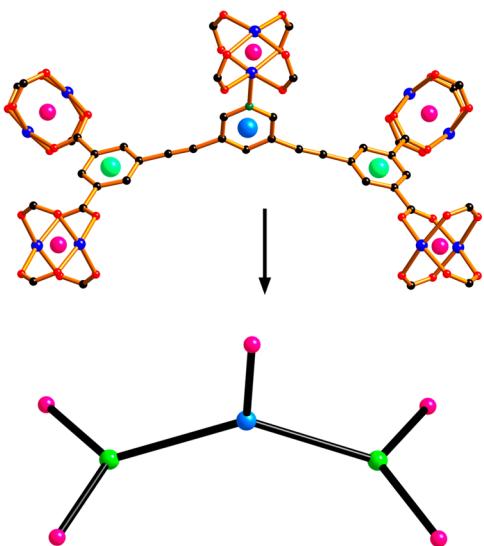


Figure 46. Deconstruction of the linker in PMOF-3 (section 4).^{59a}

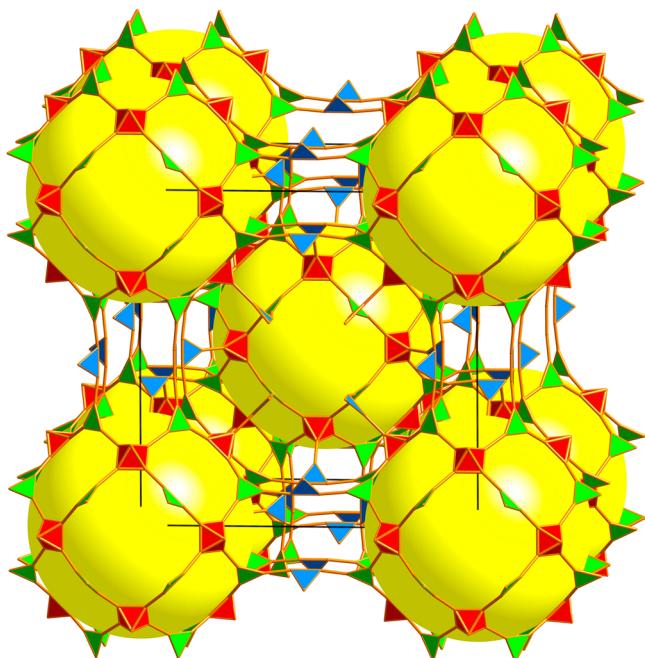


Figure 47. The underlying net, pzh, of PMOF-3 in augmented form, pzh-a.

described as the derived (3,6)-c net **zxc**. It is interesting that **zxc** is exactly the net of the three kinds of atoms in calcite, CaCO_3 , as illustrated in Figure 50. The same structure occurs in NU-108-Zn,⁶¹ and in this instance, the topology was described in terms of the (3,6)-c net (not identified). **zxc** has minimal transitivity 3 2.

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 $R\bar{3}c$) 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 (3 2) and symmetry $R\bar{3}2$. 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.

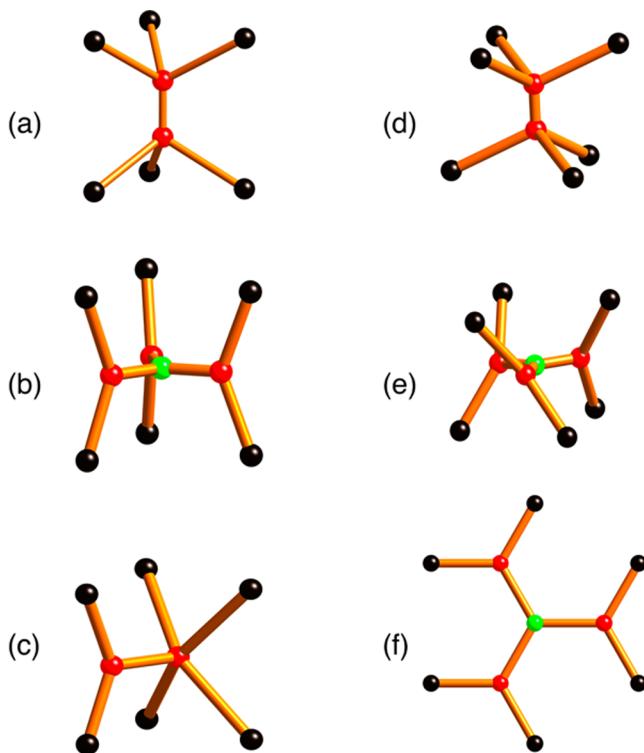


Figure 48. Some topologies and shapes for hexatopic linkers: (a–c) trigonal prisms, (d, e) octahedra, and (f) hexagon.

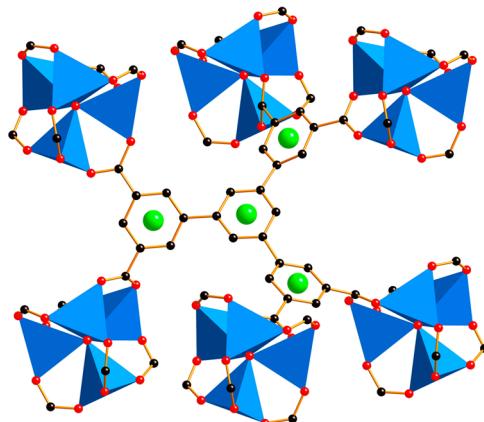


Figure 49. Linker of a MOF (section 5.1)^{60b} with **zxc** net.

Three MOFs with a **nia**-derived structure are JUC-101, JUC-102,^{62a} and UTSA-62.^{62b} 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 $P\bar{6}2c$. But there is a chiral derived net also of minimal transitivity. This is **tsb**, with symmetry $P6_322$. 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.

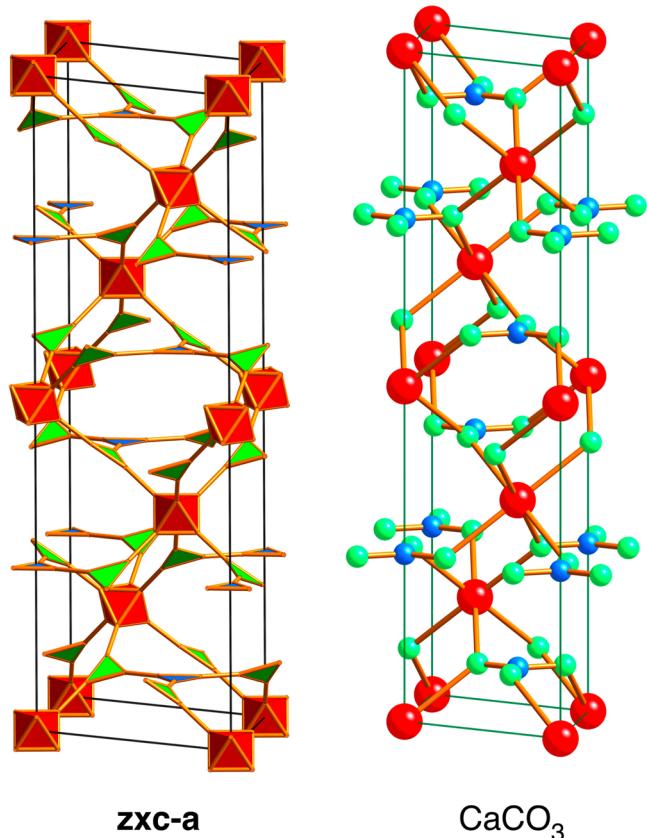


Figure 50. The net zxc-a and the calcite structure (Ca, red; C, blue; O, green).

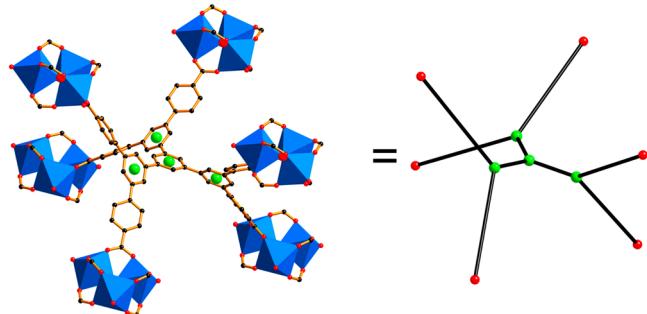


Figure 51. The linker and SBUs of JUC-101 (section 5.1).^{62a} The metal SBUs (groups of three octahedra) have trigonal prismatic points of extension.

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 $Zn_4O(-CO_2)_6$ 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 FeS_2 and of the Si and P atoms in SiP_2O_7 ($-O-$ acting as links).⁶⁴ Again, surely one would prefer to consider the individual atoms in FeS_2 as nodes of a net rather than a description as a NaCl packing of Fe and S_2 groups (cf. the description of $CaCO_3$ at the beginning of this section).

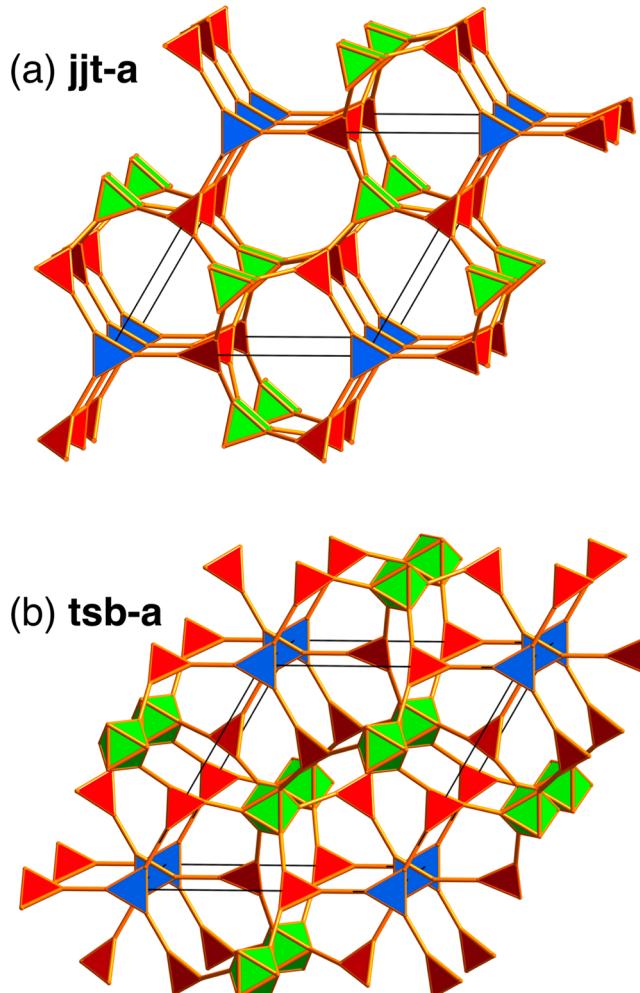


Figure 52. Two nets derived from nia by replacing the octahedral nodes with four 3-c nodes.

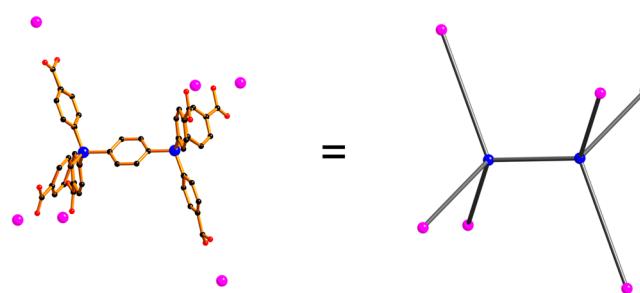


Figure 53. (Left) The linker in IMP-15 (section 5.1).⁶³ Magenta balls are at the center of $Zn_4O(-CO_2)_6$ SBUs (cf. Figure 1); the large blue balls are Si. (Right) The nodes in the underlying (4,6)-c net.

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 Cu_2 or 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^{65a} 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

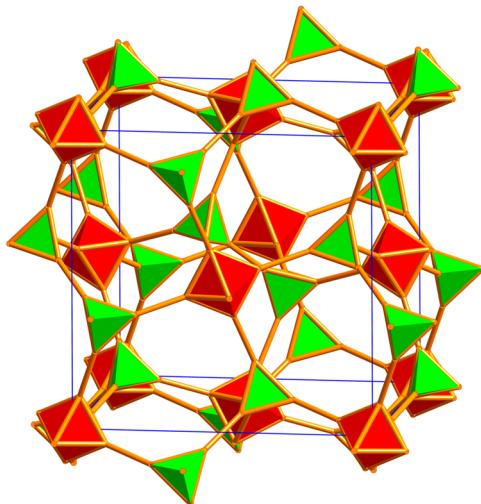


Figure 54. The augmented version (fsn-a) of the (4,6)-c net fsn.

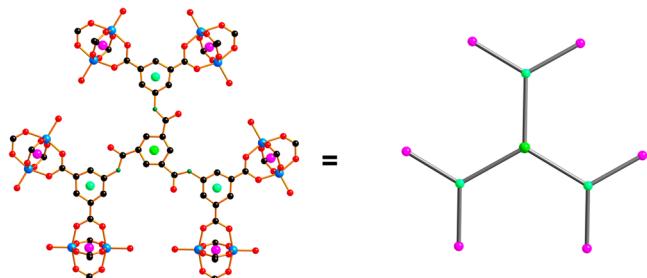


Figure 55. A hexatopic linker (section 5.2)^{65a} joined to paddle-wheel SBUs with branch points of the underlying net shown as green and magenta balls (respectively 3-c and 4-c vertices). C, black; O, red; Zn, blue.

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.^{61,65l} Figure S6 illustrates parts of two real MOFs with different linkers (Figure S7). These structures are among those with the highest porosities and surface area per unit mass.^{65l}

Remarkably, for none of these many **ntt/rht** compounds that have been reported^{61,65} has the linker been described as a 6-c node of a framework. We can attempt to “back-derive” a basic (4,6)-c net from **ntt**. Figure S8 shows a fragment of **ntt**. If the group of four 3-c vertices are replaced by a 6-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 S8. 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-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

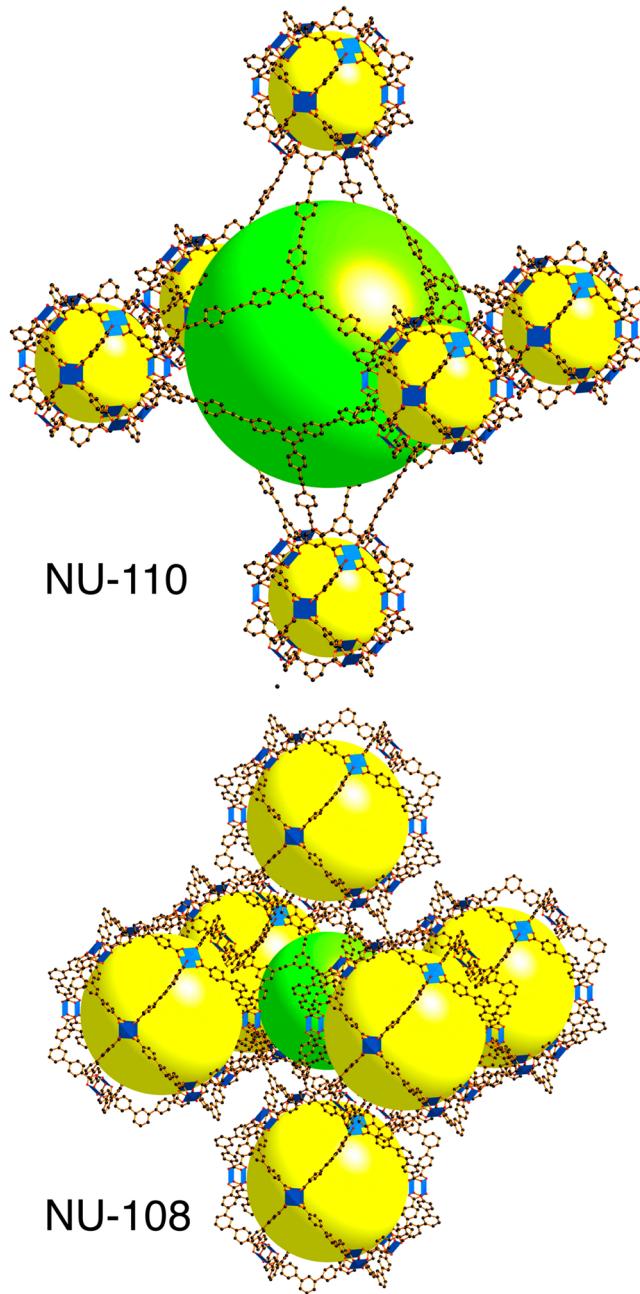


Figure 56. Two MOFs (section 5.2)^{61,65l} with **ntt** topology.

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 **ntt** 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-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*

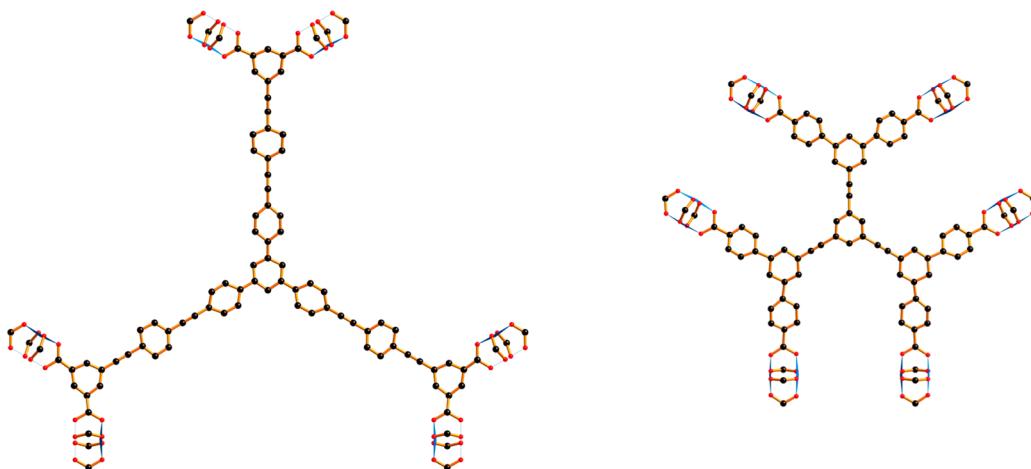


Figure 57. The linkers of the MOFs (section 5.2)^{61,65^l in Figure 56: (left) NU-110^{65^l and (right) NU-108.⁶¹}}

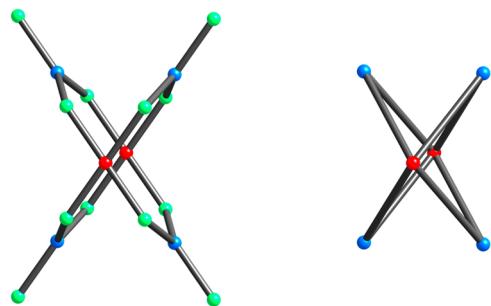


Figure 58. (Left) A fragment of the ntt net showing 4-c vertices (red) and a group of four 3-c vertices with one colored blue at the center. (Right) The (4,6)-c net of the red and blue vertices.

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).

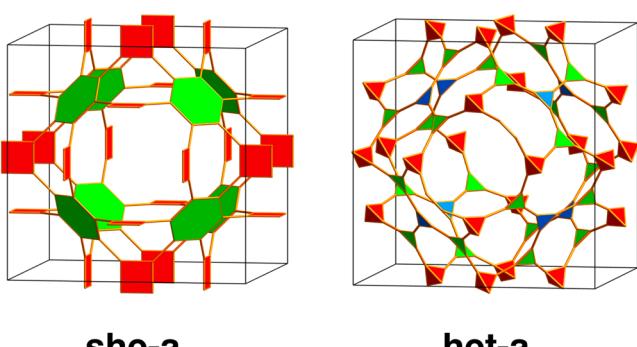


Figure 59. (Left) The net **she** shown in augmented form. (Right) The derived (3,4)-c net, **het**, shown in augmented form. Note that the green hexagons are replaced by planar groups of four triangles and the red squares in **she-a** morph into red tetrahedra in **het-a**.

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

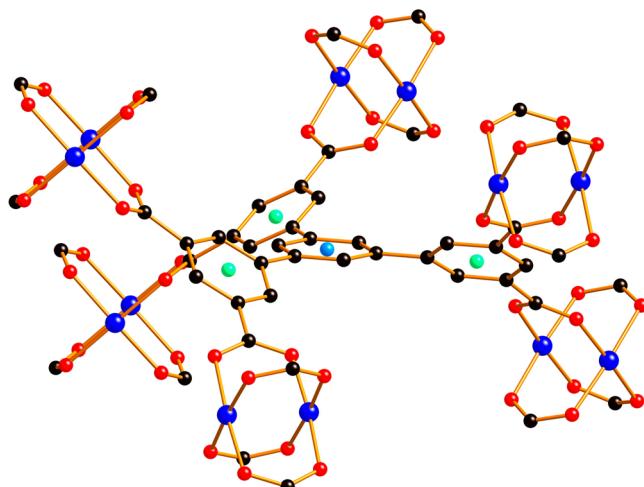


Figure 60. Linker used to construct a MOF, UTSA-20 (section 5.2),⁶⁷ with **zyg** topology.

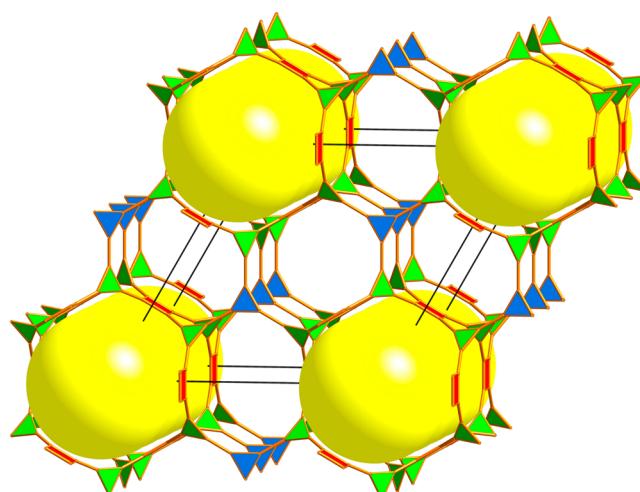


Figure 61. The net **zyg** in augmented form.

trigonal prismatic coordination of the basic binodal (4,6)-c net, which is **stp**, the default (edge-transitive) net for linking square and trigonal-prismatic units. **zyg** has transitivity 3 2, again minimal.

There is, however, a basic net with transitivity 2 1 for linking squares and octahedra, namely, **soc** (Figure 40). The simplest derived net is obtained by replacing the 6-c vertex by four 3-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 $I\bar{4}32$) with transitivity 3 2 illustrated in augmented form in Figure 62. It may be seen that in a reasonable

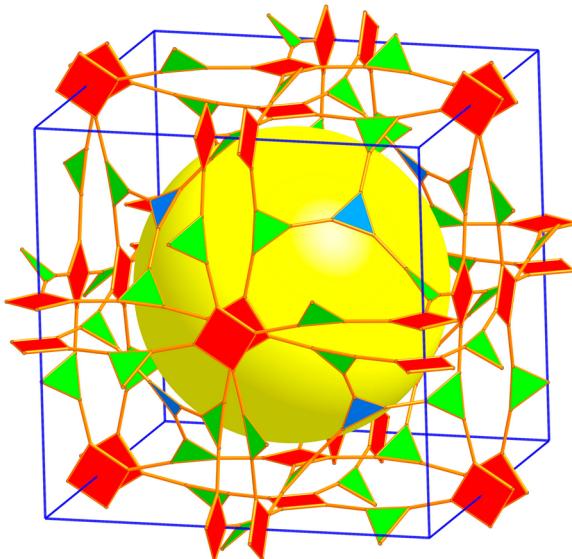


Figure 62. The net **hey** in augmented form.

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 $\text{YbO}(-\text{CO}_2)_4$ with the noncarboxylate O atoms linked by O–H–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.

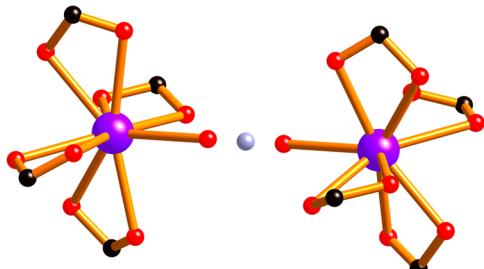


Figure 63. A pair of $\text{YbO}(-\text{CO}_2)_4$ SBUs linked by an O–H–O bond in UTSA-61 (section 5.2).⁶⁸ Large spheres, Yb; small sphere in center, presumed H atom position (not located experimentally).

5.3. A MOF with Tetrahedral SBU and Hexatopic Linker

A MOF with the basic (4,6)-c **cor** net was constructed with the octahedrally shaped linker of Figure 49 and a tetrahedral SBU shown in Figure 64.^{60b} A fragment of the derived net **tfu** is illustrated in Figure 65. **cor** has nonminimal transitivity 2 2; however, **tfu** does have minimal transitivity (3 3) for a net

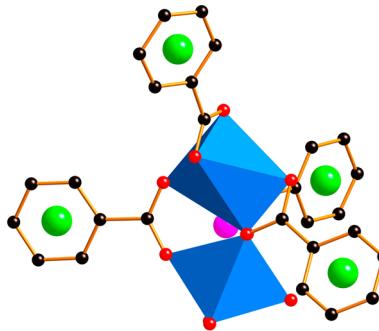


Figure 64. A tetrahedral SBU used to construct a MOF (section 5.3)^{60b} with net **tfu** derived from the (4,6)-c net **cor**.

derived from **cor** by splitting the 6-c vertex into four 3-c vertices.

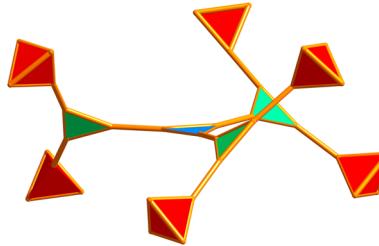


Figure 65. A fragment of the net **tfu** in augmented form.

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

Table 2 lists some basic nets with 6-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	1 1	6	octah	3-c	zxc , ^b tsh	3 2, 3 2
			octah	4-c	fsn ^b	3 2
acs	1 1	6	prism	3-c	tsg	3 2
		6	prism	4-c	tsj	3 2
nia	2 1	6	octah	3-c	jjt , ^b tsb	3 2, 3 2
			octah	4-c	xby	2 2
			prism	3-c	tsa	3 2
			prism	4-c	xat	2 2
pyr	2 1	3 6	octah	3-c	pyo	3 2
cor	2 2	4 6	octah	3-c	tfu ^b	3 3
soc	2 1	4 6	octah	3-c	hey ^b	3 2
toc	2 1	4 6	octah	3-c	tot	3 2
stp	2 1	4 6	prism	3-c	zyg ^b	3 2
she	2 1	4 6	hexagon	3-c	het	3 2

^aoctah = octahedron, prism = trigonal prism. ^bindicates 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 3-c and 4-c branch points. These are shown in Figure 66 in which

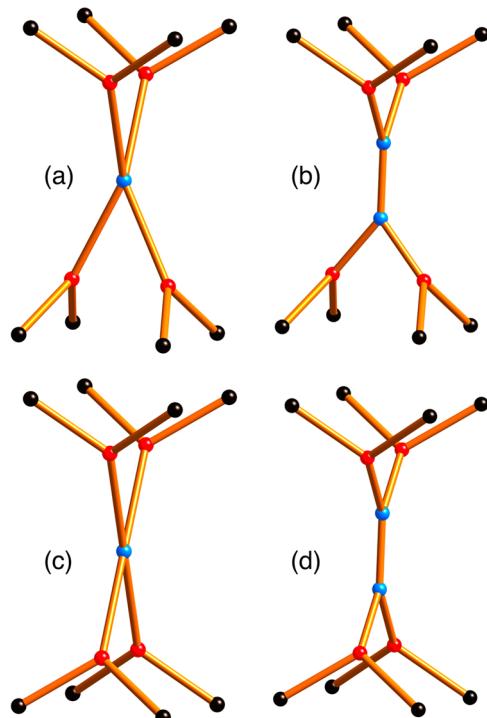


Figure 66. Symmetrical shapes for octatopic linkers.

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-c node into two linked 3-c nodes. Assuming that the linked SBUs are all the same, then the minimal transitivity is 3.2 for cases a and c and 3.3 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 $\text{In}(-\text{CO}_2)_3$ SBUs with three points of extension (the

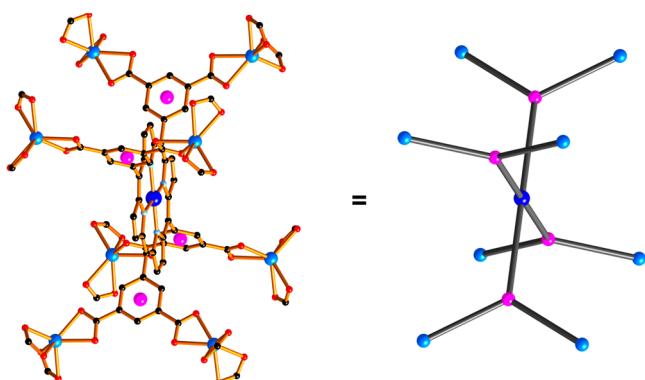


Figure 67. A fragment of the structure of MMPF-5 (section 6).⁶⁹ Large light blue balls are In atoms with three points of extension. Magenta balls are 3-c branch points, and the dark blue atom (metal in the porphyrin unit) is a 4-c node.

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-1²⁹ in section 2.2 (Figure 5). The net is shown in Figure 68, which

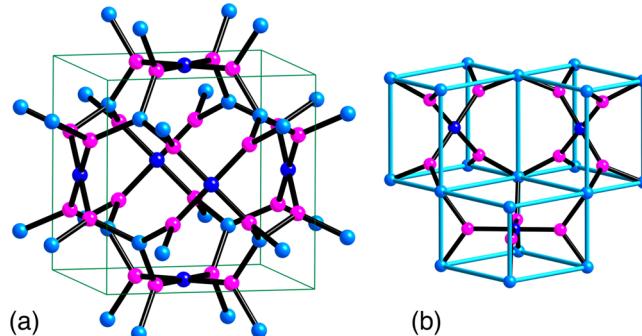


Figure 68. (a) The net **tfe** formed by the unit in Figure 67. (b) Showing how three 8-vertex units share a common vertex.

also illustrates how three octatopic units meet at a common vertex. Thus, the net **tfe** with transitivity 3.2 can be considered as derived from the basic (3,8)-c net **the** with transitivity 2.1.

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 (Mn_2 and 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-c square node. If further the Mn SBUs are denoted C and D, the stoichiometry is A_4BCD . The net of the structure is found to be the binary (3,4)-c net **tbo** described earlier (Figure 1) with the B, 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 $Fm\bar{3}m$ (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 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 **lwg**, one has a two-way coloring of the produced **tbo** net with symmetry reduced to $I\bar{4}/mm$ (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^{72a} in Figure 72. The central 4-c node now has tetrahedral geometry and links together with square paddle-wheel vertices in a different topology, **mmm** (already mentioned in section 2.4), derived again from **scu**.

We earlier¹⁶ described the deconstruction of a series of MOFs⁷³ with a linker with shape b of Figure 66, i.e., with the 4-c node of the previous linker divided into two 3-c nodes. The corresponding net is **mml**, which is of course derived from the same basic net, **scu**. Figure 73 compares the two nets.

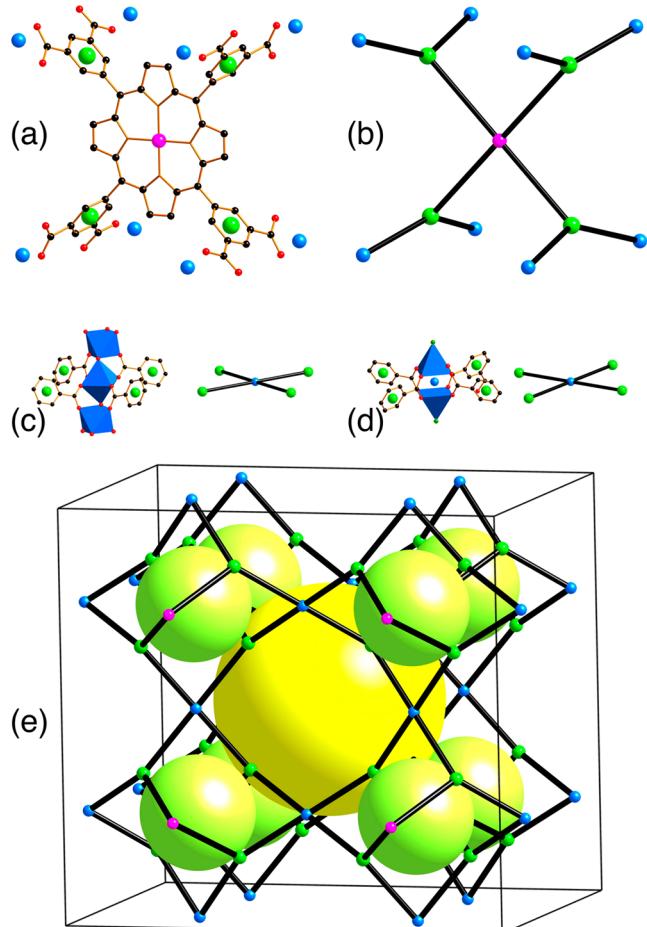


Figure 69. Components of ZJU-18 (section 6).⁷⁰ (a) The octatopic linker and (b) its skeleton. Blue balls are the 4-c SBUs shown in parts c and d. (e) The placing of the nodes and links in the crystal structure shown using actual crystal data. The net is tbo.

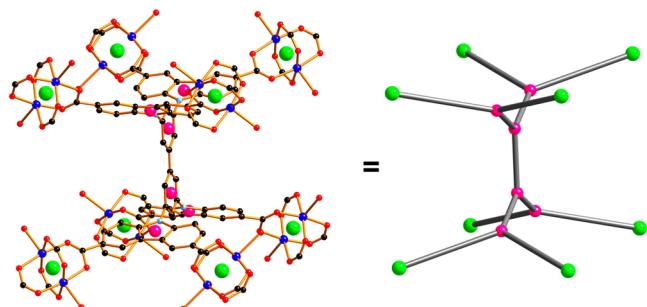


Figure 70. Deconstruction of the linker in PCN-80 (section 6).^{71a} Red balls are 3-c branch points of the linker; green balls are 4-c paddle-wheel vertices.

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)-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-

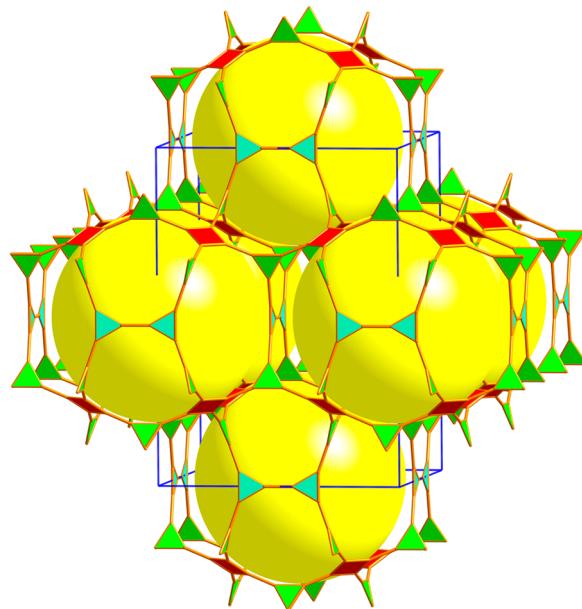


Figure 71. The net lwg in augmented version lwg-a.

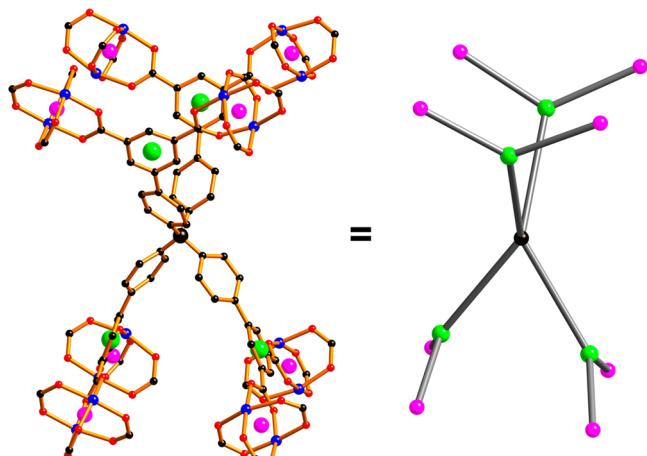


Figure 72. The linker in NOTT-140 (section 6)^{72a} and its deconstruction. Large balls: black, a C atom acting as a 4-c node; green, 3-c branch points; magenta, 4-c paddle-wheel nodes.

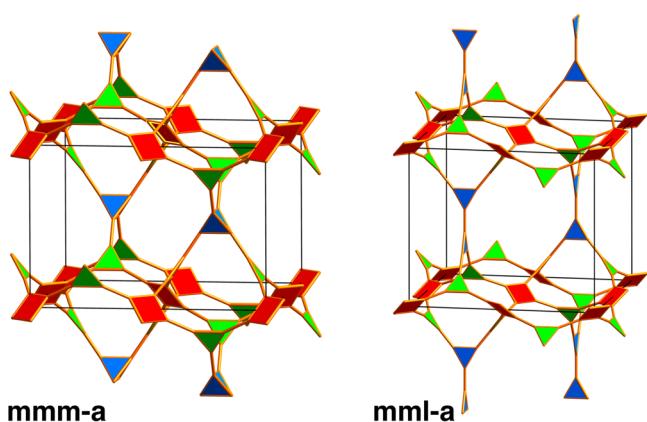


Figure 73. The relationship between mmm and mml. The latter is derived from the former by splitting tetrahedral nodes into two triangular ones.

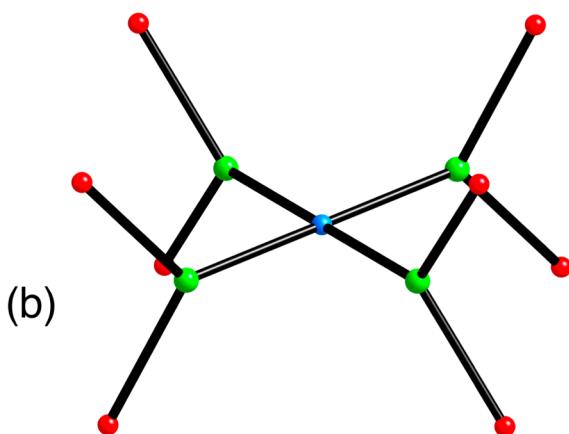
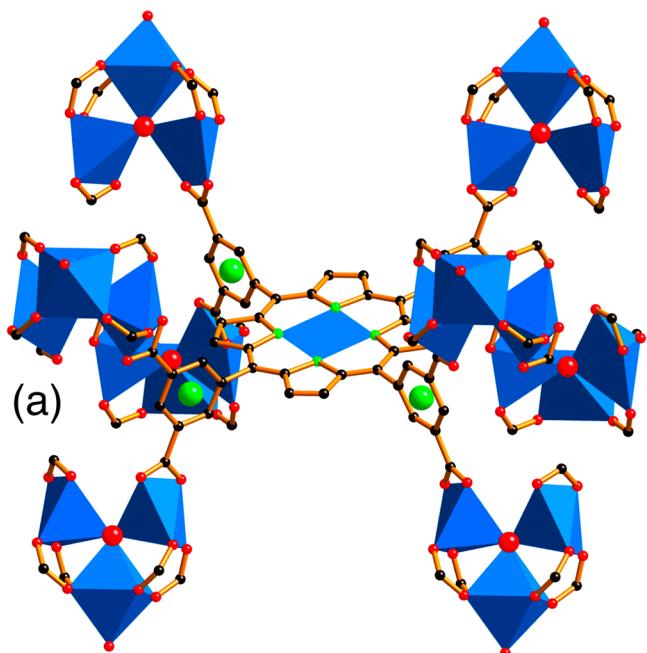


Figure 74. (a) The linker and SBUs in the MOF MMPF-2 (section 6).⁷⁴ (b) In the skeleton, red balls are 6-c nodes with trigonal prismatic geometry.

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 know¹² 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, IFMC-200, contains an unprecedented 24-c metal SBU with composition $Zn_{16}(HPO_3)_4(-CO_2)_{24}$ 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

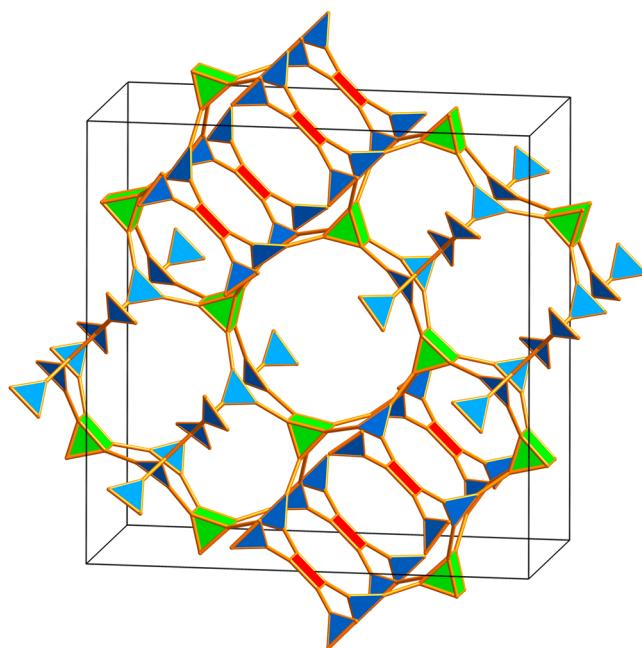


Figure 75. The net **wxs** shown in augmented form **wxs-a**. The view direction is close to the tetragonal *c* axis.

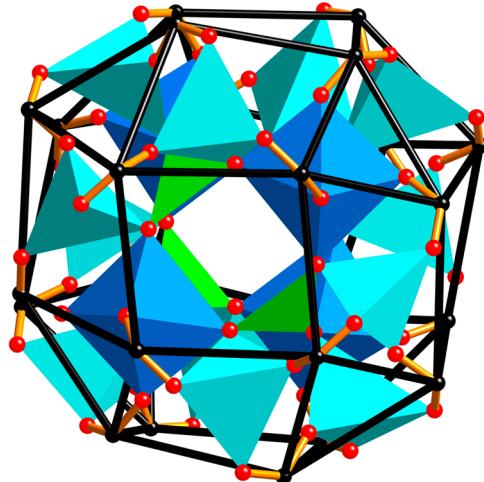


Figure 76. The Zn- and P-containing SBU in IFMC-200 (section 6).⁷⁵ PO₃, green; ZnO₄, light blue; ZnO₆, darker blue. Black spheres are carboxylate C atoms (points of extension) and red ones are O. The black lines linking points of extension outline a distorted rhombicuboctahedron.

(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)-c **ddy**, 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-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

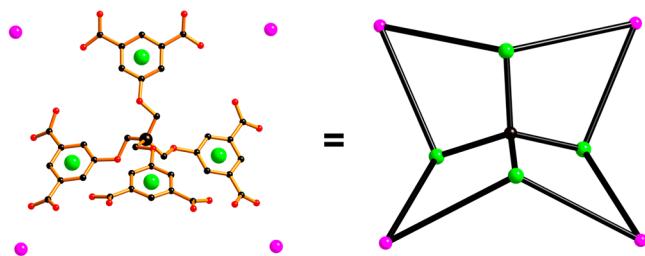


Figure 77. The linker in IFMC-2000 (section 6).⁷⁵ The large black ball (carbon) is the 4-c branch point, and the green balls are at 3-c branch points. Magenta balls are at the centers of 24-c SBUs.

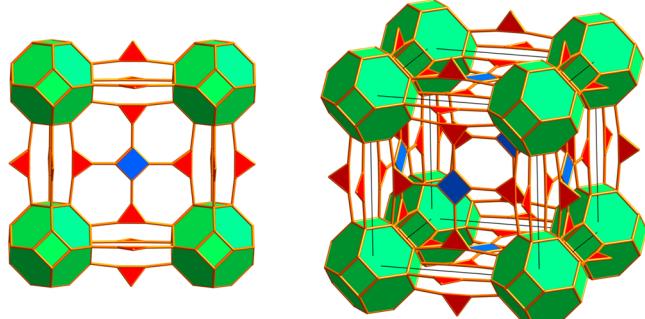


Figure 78. (Left) A fragment of the augmented ddy net. (Right) A unit cell of the same.

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) edge-transitive nets with transitivity 1 1 and 2 1, 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 A–C and B–C and so minimal possible transitivity 3 2.

In all the other MOFs there is generally one kind of metal-containing SBU (we do not count metal atoms in a porphyrin-based organic linker³⁹ 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 (A–B and B–B) in the graph and transitivity 2 2 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 (MT = minimal transitivity).

- (i) A with links A–A (ditopic linker), MT 1 1: **nbo**, **pcu**
- (ii) AB with links A–B, MT 2 1: **csq**, **pth**, **pts**, **pyr**, **scu**, **soc**, **tbo**, **the**
- (iii) AB with links A–B and B–B, MT 2 2: **act**, **dmd**, **edq**, **fof**, **fog**, **lil**, **lim**, **phw**, **stu**, **stx**, **sty**, **sur**, **tfb**, **tfi**, **xly**

- (iv) ABC with links A–B and B–C, MT 3 2: **agw**, **asc**, **ddy**, **fsn**, **hey**, **idp**, **jjt**, **mmm**, **ntt**, **tfe**, **zxc**, **zyg**
- (v) ABC with links A–B, B–C, and C–C, MT 3 3: **lwg**, **mml**
- (vi) ABC with links A–B, A–C, and B–C, MT 3 3: **pzh**
- (vii) ABC with links A–B, A–C, and C–C, MT 3 3: **ttz**
- (viii) ABC with links A–B, A–C, B–B, and C–C, MT 3 4: **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 2 1), are not really minimal because there are nets (**nbo** is one) in which all square nodes are equivalent and have transitivity 1 1. 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)-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 1 1 and the minimal transitivity is 1 2, as in the commonly found 5-c nets **ubt**, **bnn**, and **sqp**.^{13,16} Likewise, the (3,9)-c nets **xmz** and **gfy** found in MOFs¹⁶ with transitivity 2 2 (rather than 2 1) 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 2 2 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**.^{40c} However, it has an isomeric form, PCN-12', of considerable complexity, most unusual for a MOF, with eight vertices and 10 edges (transitivity 8 10, section 3.1). IZE-1 and IZE-2 are isomers of MOFs with chemically identical frameworks, both with minimal transitivity (2 2) nets, but there is a third isomer, IZE-3, with net **hyx** that has transitivity 3 3.^{40k} 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 (2 1) **tbo** or **pto** topology.¹⁸ We know of only one exception, a MOF with the **fmj** topology with transitivity 5 4.⁷⁸

One of the most striking exceptions to the minimal transitivity principle is MOF-177 and the isoreticular MOF-180 and MOF-200.⁷⁹ These have structures in which octahedral

$\text{Zn}_4(-\text{CO}_2)_6$ 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 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 **pts**-derived 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 3 2 (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, MgAl_2O_4 (**spl**) and of cubic perovskite, e.g. 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”.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mokeeffe@asu.edu.

Notes

The authors declare no competing financial interest.

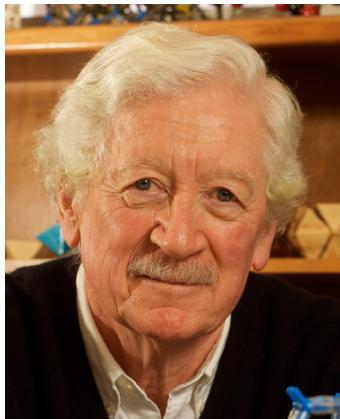
Biographies



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 Fund 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 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).

REFERENCES

- (1) Delgado-Friedrichs, O.; O'Keeffe, M. *J. Solid State Chem.* **2005**, *178*, 2480.
- (2) (a) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977. (b) Wells, A. F. *Further Studies of Three-Dimensional Nets*; Monograph 9; Am. Cryst. Assoc.: Littleton, CO, 1979.
- (3) (a) Iwamoto, T. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: London, 1991; Chapter 6. (b) Kitazawa, T.; Nishikiori, S.-i.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3695. (c) Iwamoto, T.; Nishikiori, S.-i.; Kitazawa, T.; Yuge, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4127. These papers give references to the extensive earlier work of this group.
- (4) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735.
- (5) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13.
- (6) Schindler, M.; Hawthorne, F. C.; Baur, W. H. *Acta Crystallogr. B* **1999**, *55*, 811.
- (7) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.
- (8) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257.
- (9) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- (10) Delgado-Friedrichs, O.; Huson, D. H. *Discrete Comput. Geom.* **2000**, *24*, 279.
- (11) Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr. A* **2003**, *59*, 22.
- (12) (a) Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr. A* **2006**, *62*, 350. (b) Delgado-Friedrichs, O.; O'Keeffe, M. *Acta Crystallogr. A* **2007**, *63*, 344. These are essentially those nets that have embeddings (realizations in space) in which the links correspond to shortest distances between nodes. Without some such restriction, the number of edge transitive nets is easily shown to be infinite: (c) Delgado-Friedrichs, O.; O'Keeffe, M. *Acta Crystallogr. A* **2009**, *65*, 360.
- (13) Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1035.
- (14) Bureekaew, S.; Schmid, R. *CrystEngComm* **2013**, *15*, 1551.
- (15) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782 (The RCSR database is available at rcsr.anu.edu.au).
- (16) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 675.
- (17) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (c) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (d) Yang, J.; Grzech, A.; Mulder, F. M.; Dingemans, T. J. *Microporous Mesoporous Mater.* **2013**, *171*, 65.
- (18) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (b) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474. (c) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (d) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858. (e) Wang, X.-S.; Ma, S.; Yuan, D.; Yoon, J. W.; Hwang, Y. K.; Chang, J.-S.; Wang, X.; Jørgensen, M. R.; Chen, Y.-S.; Zhou, H.-C. *Inorg. Chem.* **2009**, *48*, 7519. (f) Furukawa, H.; Go, Y. B.; Ko, N.; Park, Y. K.; Uribe-Romo, F. J.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Inorg. Chem.* **2011**, *50*, 9147. (g) Peikert, K.; Hoffmann, F.; Fröba, M. *Chem. Commun.* **2012**, *48*, 11196. (h) Yao, Q.; Su, J.; Zou, X. Z. *Kristallogr.* **2013**, *228*, 323.
- (19) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3.
- (20) Buerger, M. *J. J. Chem. Phys.* **1947**, *15*, 1.
- (21) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.

- (22) Abu-Youssef, M. A. M.; Langer, V.; Öhrström, L. *Chem. Commun.* **2006**, 1082.
- (23) Brunner, G. O. Z. *Kristallogr.* **1981**, 156, 295.
- (24) (a) Yang, Q.; Zhong, C.; Chen, J.-F. *J. Phys. Chem. C* **2008**, 112, 1562. (b) Babarao, R.; Jiang, J. *Langmuir* **2008**, 24, 6270. (c) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, 49, 6058. (d) Getman, R. B.; Bae, Y.-S.; Wilmer, C. E.; Snurr, R. Q. *Chem. Rev.* **2012**, 112, 703. (e) Wilmer, C. E.; Farha, O. K.; Bae, Y.-S.; Hupp, J. T.; Snurr, R. Q. *Energy Environ. Sci.* **2012**, 5, 9849. (f) Mendoza-Cortés, J. L.; Goddard, W. A., III; Furukawa, H.; Yaghi, O. M. *J. Phys. Chem. Lett.* **2012**, 3, 2671. (g) Dzubak, A. L.; Lin, L.-C.; Kim, J.; Swisher, J. A.; Poloni, R.; Maximoff, S. N.; Smit, B.; Gagliardi, L. *Nat. Chem.* **2012**, 4, 810. (h) Kim, K. C.; Yu, D.; Snurr, R. Q. *Langmuir* **2013**, 29, 1446. (i) Martin, R. L.; Haranczyk, M. *Chem. Sci.* **2013**, 4, 1781. (j) Martin, R. L.; Haranczyk, M. *J. Chem. Theory Comput.* **2013**, 9, 2816. (k) Martin, R. L.; Lin, L.-C.; Jariwala, K.; Smit, B.; Haranczyk, M. *J. Phys. Chem. C* **2013**, 117, 12159.
- (25) Li, M.; Mun, S. W.; Li, D.; O'Keeffe, M.; Yaghi, O. M. Manuscript to be published.
- (26) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, 130, 1833.
- (27) (a) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, 123, 4368. (b) Moulton, B.; Lu, J.; Mondal, A.; Zaworotko, M. *J. Chem. Commun.* **2001**, 863.
- (28) Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. *Angew. Chem., Int. Ed.* **2001**, 40, 2113.
- (29) Hao, X.-R.; Wang, X.-L.; Shao, K.-Z.; Yang, G.-S.; Su, Z.-M.; Yuan, G. *CrystEngComm* **2012**, 14, 5596 (tfe, structures 2 and 3; idp, structure 6).
- (30) Zhao, X.; Wang, X.; Wang, S.; Dou, J.; Cui, P.; Chen, Z.; Sun, D.; Wang, X.; Sun, D. *Cryst. Growth Des.* **2012**, 12, 2736.
- (31) Wang, Z.; Kravtsov, V. Ch.; Zaworotko, M. *J. Angew. Chem., Int. Ed.* **2005**, 44, 2877.
- (32) Fang, Q.; Zhu, G.; Xue, M.; Wang, Z.; Sun, J.; Qiu, S. *Cryst. Growth Des.* **2008**, 8, 319.
- (33) Luo, F.; Che, Y.-x.; Zheng, J.-m. *Cryst. Growth Des.* **2008**, 8, 176.
- (34) Wong-Foy, A. G.; Lebel, O.; Matzger, A. *J. Am. Chem. Soc.* **2007**, 129, 15740.
- (35) Duan, J.; Yang, Z.; Bai, J.; Zheng, B.; Li, Y.; Li, S. *Chem. Commun.* **2012**, 48, 3058.
- (36) Yang, H.; Wang, F.; Kang, Y.; Li, T.-H.; Zhang, J. *Chem. Commun.* **2012**, 48, 9424.
- (37) Schoedel, A.; Cairns, A. J.; Belmabkhout, Y.; Wojtas, L.; Mohamed, M.; Zhang, Z.; Proserpio, D. M.; Eddaoudi, M.; Zaworotko, M. *J. Angew. Chem., Int. Ed.* **2013**, 52, 2902.
- (38) Lian, T.-T.; Chen, S.-M.; Wang, F.; Zhang, J. *CrystEngComm* **2013**, 15, 1036.
- (39) Morris, W.; Volosky, B.; Demir, S.; Gándara, F.; McGrier, P. L.; Furukawa, H.; Cascio, D.; Stoddart, J. F.; Yaghi, O. M. *Inorg. Chem.* **2012**, 51, 6443.
- (40) (a) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, 44, 4745. (b) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem., Int. Ed.* **2006**, 45, 7358. (c) Wang, X.-S.; Ma, S.; Forster, P. M.; Yuan, D.; Eckert, J.; López, J. J.; Murphy, B. J.; Parise, J. B.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, 47, 7263. (d) Wang, X.-S.; Ma, S.; Rauch, K.; Simmons, J. M.; Yuan, D.; Wang, X.; Yildirim, T.; Cole, W. C.; López, J. J.; Meijere, A.; de Zhou, H.-C. *Chem. Mater.* **2008**, 20, 3145. (e) Xue, M.; Zhu, G.; Li, Y.; Zhao, X.; Kang, E.; Qiu, S. *Cryst. Growth Des.* **2008**, 8, 2478. (f) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, 130, 1012. (g) Lee, Y.-G.; Moon, H. R.; Cheon, Y. E.; Suh, M. P. *Angew. Chem., Int. Ed.* **2008**, 47, 7741. (h) Lin, X.; Telepeni, I.; Blake, A. J.; Dailly, A.; Brown, C. M.; Simmons, J. M.; Zoppi, M.; Walker, G. S.; Thomas, K. M.; Mays, T. J.; Hubberstey, P.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2009**, 131, 2159. (i) Hu, Y.; Xiang, S.; Zhang, W.; Zhang, Z.; Wang, L.; Bai, J.; Chen, B. *Chem. Commun.* **2009**, 7551. (j) Zhao, D.; Yuan, D.; Yakovenko, A.; Zhou, H.-C. *Chem. Commun.* **2010**, 46, 4196. (k) Hu, Y.-X.; Ma, H.-B.; Zheng, B.; Zhang, W.-W.; Xiang, S.; Zhai, L.; Wang, L.-F.; Chen, B.; Ren, X.-M.; Bai, J. *Inorg. Chem.* **2012**, 51, 7066. (l) Vukotic, V. N.; Harris, K. J.; Zhu, K.; Schurko, R. W.; Loeb, S. J. *Nat. Chem.* **2012**, 4, 456. (m) Zheng, B.; Liu, H.; Wang, Z.; Yu, X.; Yi, P.; Bai, J. *CrystEngComm* **2013**, 15, 3517. (n) Duan, X.; Yu, J.; Cai, J.; He, Y.; Wu, C.; Zhou, W.; Yildirim, T.; Zhang, Z.; Xiang, S.; O'Keeffe, M.; Chen, B.; Qian, G. *Chem. Commun.* **2013**, 49, 2043. (o) Grünker, R.; Senkovska, I.; Biedermann, R.; Klein, N.; Klausch, A.; Baburin, I. A.; Mueller, U.; Kaskel, S. *Eur. J. Inorg. Chem.* **2010**, 3835. (p) Cai, J.; Yu, J.; Xu, H.; He, Y.; Duan, X.; Cui, Y.; Wu, C.; Chen, B.; Qian, G. *Cryst. Growth Des.* **2013**, 13, 2094. (q) Zheng, B.; Luo, J.; Wang, F.; Peng, Y.; Li, G.; Huo, Q.; Liu, Y. *Cryst. Growth Des.* **2013**, 13, 1033 (fof, structure 2; tfl, structure 4).
- (41) (a) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. Ch.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. *J. Am. Chem. Soc.* **2008**, 130, 1560. (b) Meng, L.; Cheng, Q.; Kim, C.; Gao, W.-Y.; Wojtas, L.; Chen, Y.-S.; Zaworotko, M. J.; Zhang, X. P.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, 51, 10082. (c) Stoeck, U.; Krause, S.; Bon, V.; Senkovska, I.; Kaskel, S. *Chem. Commun.* **2012**, 48, 10841.
- (42) There are two other edge-transitive nets compatible with those of linking square nodes, viz., rhr and ssc. We have not found examples of their occurrence in this context.
- (43) (a) Eddaoudi, N.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, 124, 376. (b) Furukawa, H.; Kim, J.; Ockwig, N. W.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2008**, 130, 11650. (c) Jeung, K. S.; Go, Y. B.; Shin, S. M.; Lee, S. J.; Kim, J.; Yaghi, O. M.; Jeong, N. *Chem. Sci.* **2011**, 2, 877.
- (44) Li, Z.; Li, M.; Zhan, S.-Z.; Huang, X.-C.; Ng, S. W.; Li, D. *CrystEngComm* **2008**, 10, 978.
- (45) Cheon, Y. E.; Park, J.; Suh, M. P. *Chem. Commun.* **2009**, 5436.
- (46) (a) Gao, T.; Wang, X.-Z.; Gu, H.-X.; Xu, Y.; Shen, X.; Zhu, D.-R. *CrystEngComm* **2012**, 14, 5905. (b) Li, R.-J.; Li, M.; Zhou, X.-P.; Li, D. Manuscript to be published.
- (47) (a) Wu, S.; Ma, L.; Long, L. S.; Zheng, L.-S.; Lin, W. *Inorg. Chem.* **2009**, 48, 2436. (b) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. *Nat. Chem.* **2010**, 2, 838.
- (48) Zheng, M.; Liu, Y.; Wang, C.; Liu, S.; Lin, W. *Chem. Sci.* **2012**, 3, 2623.
- (49) Zou, Y.; Yu, C.; Li, Y.; Lah, M. S. *CrystEngComm* **2012**, 14, 7174.
- (50) Wang, F.-K.; Song, X.-X.; Yang, S.-Y.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem. Commun.* **2007**, 10, 1198.
- (51) (a) Shields, L. *J. Chem. Soc., Faraday Trans. 2* **1985**, 81, 1. (b) Heintz, R. A.; Zhao, H.; Ouyang, X.; Grandineti, G.; Cowen, J.; Dunbar, K. R. *Inorg. Chem.* **1999**, 38, 144. (c) O'Kane, S. A.; Clérac, R.; Zhao, H.; Ouyang, X.; Galán-Mascarós, J. R.; Heintz, R.; Dunbar, K. R. *J. Solid State Chem.* **2000**, 152, 159. (d) Lopez, N.; Zhao, H.; Ota, A.; Prosvirin, A. V.; Reinheimer, E. W.; Dunbar, K. R. *Adv. Mater.* **2010**, 22, 986. (e) Dunbar, K. R. *Private communication.* (f) Abrahams, B. F.; Elliott, R.; Hudson, T.; Robson, R. *Cryst. Growth Des.* **2013**, 13, 3018.
- (52) Natarajan, R.; Savitha, G.; Dominiak, P.; Wozniak, K.; Moorthy, J. N. *Angew. Chem., Int. Ed.* **2005**, 44, 2115.
- (53) Sun, D.; Collins, D. J.; Ke, Y.; Zuo, J.-L.; Zhou, H.-C. *Chem.—Eur. J.* **2006**, 12, 3768.
- (54) Grünker, R.; Senkovska, I.; Biedermann, R.; Klein, N.; Lohe, M. R.; Müller, P.; Kaskel, S. *Chem. Commun.* **2011**, 47, 490.
- (55) Liu, Y.; Eubank, J. F.; Cairns, A. J.; Eckert, J.; Kravtsov, V. Ch.; Luebke, R.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2007**, 46, 3278.
- (56) Naumov, N. G.; Virovets, A. V.; Sokolov, M. N.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed.* **1998**, 37, 1943.
- (57) Grünker, R.; Bon, V.; Heerwig, A.; Klein, N.; Müller, P.; Stoeck, U.; Baburin, I. A.; Mueller, U.; Senkovska, I.; Kaskel, S. *Chem.—Eur. J.* **2012**, 18, 13299.
- (58) (a) Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wei, Z.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, 51, 10307. (b) Mondloch, J. E.; Bury, W.; Fairen-Jiminez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, 135, 10294.

- (59) (a) Zhang, P.; Li, B.; Zhao, Y.; Meng, X.; Zhang, T. *Chem. Commun.* **2011**, *47*, 7722. (b) Park, J.; Li, J.-R.; Chen, Y.-P.; Yu, J.; Yakovenko, A. A.; Wang, Z. U.; Sun, L.-B.; Balbuena, P. B.; Zhou, H.-C. *Chem. Commun.* **2012**, *48*, 9995.
- (60) (a) Chae, H. K.; Eddaoudi, M.; Kim, J.; Hauck, S. I.; Hartwig, J. F.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 11482. (b) Chen, Z.; Xiang, S.; Liao, T.; Yang, Y.; Chen, Y.-S.; Zhou, Y.; Zhao, D.; Chen, B. *Cryst. Growth Des.* **2010**, *10*, 2775. (c) Jia, J.; Sun, F.; Fang, Q.; Liang, X.; Cai, K.; Bian, Z.; Zhao, H.; Gao, L.; Zhu, G. *Chem. Commun.* **2011**, *47*, 9167.
- (61) Eryazici, I.; Farha, O. K.; Hauser, B. G.; Yazaydin, A. Ö.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *Cryst. Growth Des.* **2012**, *12*, 1075.
- (62) (a) Jia, J.; Sun, F.; Borjigin, T.; Ren, H.; Zhang, T.; Bian, Z.; Gao, L.; Zhu, G. *Chem. Commun.* **2012**, *48*, 6010. (b) He, Y.; Furukawa, H.; Wu, C.; O'Keeffe, M.; Krishna, R.; Chen, B. *Chem. Commun.* **2013**, *49*, 6773.
- (63) Davies, R. P.; Lickiss, P. D.; Robertson, K.; White, A. J. P. *CrystEngComm* **2012**, *14*, 758.
- (64) RCSR calls the (3,6)-c net of the bonds other than the S–S bond in FeS₂ the pyrite net (pyr) after the following: Chae, H. K.; Kim, J.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3907 (The (4,6)-c net fsn includes the S–S bond. We note the interesting fact that SiP₂ and SiP₂O₇ share the same net).
- (65) (a) Zou, Y.; Park, M.; Hong, S.; Lah, M. S. *Chem. Commun.* **2008**, 2340. (b) Yan, Y.; Lin, X.; Yang, S.; Blake, A. J.; Dailly, A.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Chem. Commun.* **2009**, 1025. (c) Yan, Y.; Telepeni, I.; Yang, S.; Lin, X.; Kockelmann, W.; Dailly, A.; Blake, A. J.; Lewis, W.; Walker, G. S.; Allan, D. R.; Barnett, S. A.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2010**, *132*, 4092. (d) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357. (e) Farha, O. K.; Yazaydin, A. Ö.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2*, 944. (f) Yan, Y.; Yang, S.; Blake, A. J.; Lewis, W.; Poirier, E.; Barnett, S. A.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2011**, *47*, 9995. (g) Yuan, D.; Zhao, D.; Zhou, H.-C. *Inorg. Chem.* **2011**, *50*, 10528. (h) Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 748. (i) Luebke, R.; Eubank, J. F.; Cairns, A. J.; Belmabkhout, Y.; Wojtas, L.; Eddaoudi, M. *Chem. Commun.* **2012**, *48*, 1455. (j) Li, B.; Zhang, Z.; Li, Y.; Yao, K.; Zhu, Y.; Deng, Z.; Yang, F.; Zhou, X.; Li, G.; Wu, H.; Nijem, N.; Chabal, Y. J.; Lai, Z.; Han, Y.; Shi, Z.; Feng, S.; Li, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 1412. (k) Farha, O. K.; Wilmer, C. E.; Eryazici, I.; Hauser, B. G.; Parilla, P. A.; O'Neill, K.; Sarjeant, A. A.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 9860. (l) Farha, O. K.; Eryazici, I.; Jeong, N. C.; Hauser, B. G.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Nguyen, S. T.; Yazaydin, A. Ö.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 15016. (m) Eubank, J. F.; Nouar, F.; Luebke, R.; Cairns, A. J.; Wojtas, L.; Alkordi, M.; Bousquet, T.; Hight, M. R.; Eckert, J.; Emba, J. P.; Georgiev, P. A.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 10099. (n) Zhao, X.; Sun, D.; Yuan, S.; Feng, S.; Cao, R.; Yuan, D.; Wang, S.; Dou, J.; Sun, D. *Inorg. Chem.* **2012**, *51*, 10350. (o) Zheng, B.; Yang, Z.; Bai, J.; Li, Y.; Li, S. *Chem. Commun.* **2012**, *48*, 7025. (p) Wilmer, C. E.; Farha, O. K.; Yildirim, T.; Eryazici, I.; Krungleviciute, V.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T. *Energy Environ. Sci.* **2013**, *6*, 1158.
- (66) (a) Thimm, G. *Acta Crystallogr. A* **2009**, *65*, 213. (b) Eon, J.-G. *Acta Crystallogr. A* **2007**, *63*, 53. (c) Eon, J.-G. *Acta Crystallogr. A* **2011**, *67*, 68. (d) Moreira de Oliveira, M., Jr.; Eon, J.-G. *Acta Crystallogr. A* **2011**, *67*, 240. (e) Moreira de Oliveira, M., Jr.; Eon, J.-G. *Acta Crystallogr. A* **2013**, *69*, 276. (f) Delgado-Friedrichs, O.; Hyde, S. T.; Mun, S. W.; O'Keeffe, M.; Proserpio, D. M. *Acta Crystallogr. A* **2013**, *69*, 535.
- (67) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O'Keeffe, M.; Chen, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 3178.
- (68) He, Y.; Furukawa, H.; Wu, C.; O'Keeffe, M.; Chen, B. *CrystEngComm* **2013**, *15*, 9328.
- (69) Wang, X.-S.; Chrzanowski, M.; Gao, W.-Y.; Wojtas, L.; Chen, Y.-S.; Zaworotko, M. J.; Ma, S. *Chem. Sci.* **2012**, *3*, 2823.
- (70) Yang, X.-L.; Xie, M.-H.; Zou, C.; He, Y.; Chen, B.; O'Keeffe, M.; Wu, C.-D. *J. Am. Chem. Soc.* **2012**, *134*, 10638.
- (71) (a) Lu, W.; Yuan, D.; Makal, T. A.; Li, J.-R.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, *51*, 1580. (b) Wei, Z.; Lu, W.; Jiang, H.-L.; Zhou, H.-C. *Inorg. Chem.* **2013**, *52*, 1164.
- (72) (a) Tan, C.; Yang, S.; Champness, N. R.; Lin, X.; Blake, A. J.; Lewis, W.; Schröder, M. *Chem. Commun.* **2011**, *47*, 4487. (b) Zhuang, W.; Yuan, D.; Liu, D.; Zhong, C.; Li, J.-R.; Zhou, H.-C. *Chem. Mater.* **2012**, *24*, 18. (c) Xue, Y.-S.; Jin, F.-Y.; Zhou, L.; Liu, M.-P.; Xu, Y.; Du, H.-B.; Fang, M.; You, X.-Z. *Cryst. Growth Des.* **2012**, *12*, 6158.
- (73) Ma, L. Q.; Mihalcik, D. J.; Lin, W. *J. Am. Chem. Soc.* **2009**, *131*, 4610.
- (74) Wang, X.-S.; Chrzanowski, M.; Kim, C.; Gao, W.-Y.; Wojtas, L.; Chen, Y.-S.; Zhang, X. P.; Ma, S. *Chem. Commun.* **2012**, *48*, 7173.
- (75) Du, D.-Y.; Qin, J.-S.; Sun, Z.; Yan, L.-K.; O'Keeffe, M.; Su, Z.-M.; Li, S.-L.; Wang, X.-H.; Wang, X.-L.; Lan, Y.-Q. *Sci. Rep.* **2013**, *3*, 2616.
- (76) Pauling, L. *J. Am. Chem. Soc.* **1929**, *51*, 1010.
- (77) For example: (a) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239 (MOF-38). (b) Zang, S.-Q.; Cao, L.-H.; Liang, R.; Hou, H.-W.; Mak, T. C. W. *Cryst. Growth Des.* **2012**, *12*, 1830.
- (78) Cai, Y.; Zhang, Y.; Huang, Y.; Marder, S. R.; Walton, K. S. *Cryst. Growth Des.* **2012**, *12*, 3709.
- (79) (a) Chae, H. K.; Silberio-Pérez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523. (b) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. Ö.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, *329*, 424.
- (80) For example: (a) Chae, H. K.; Kim, J.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3907. (b) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607.
- (81) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58.
- (82) Delgado-Friedrichs, O.; O'Keeffe, M. *Acta Crystallogr. A* **2003**, *59*, 351.
- (83) Alexandrov, E. V.; Blatov, V. A.; Kochetkov, A. V.; Proserpio, D. M. *CrystEngComm* **2011**, *13*, 3947.