Taxonomy of periodic nets and the design of materials

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The concept of a natural tiling for a periodic net is introduced and used to derive a *transitivity* associated with the structure. It is accordingly shown that the transitivity provides a useful method of classifying polyhedra and nets. For design of materials to serve as targets for synthesis, structures with one kind of edge (*edge transitive*) are particularly important. Edge-transitive polyhedra, layers and 3-periodic nets are then described. Some other nets of special importance in crystal chemistry are also identified.

1. Introduction

Particularly in the case of porous materials based on metal–organic frameworks (MOFs), it has proved possible to synthesize a targeted composition and structure with the topology of a specific periodic net.[1] The process occurs by linking together molecular secondary building units (SBUs). This is often, correctly in our view, referred to *design* of materials. The possibility of materials (crystal) design has been questioned;[2] however, the objections depend mainly on interpretation of the word 'design' itself. English and American dictionaries generally agree that the primary meaning is that of a *purposive plan*[3] and this is the sense that we and, we suspect, many of our colleagues, use the term in a chemical context, and it is the sense that is used here. Of course in the world of *haute couture* for example, 'design' has a rather different connotation.

In design of crystalline materials one must know the "principal topological possibilities"[4] and a major problem has been that of deciding which of the infinite number of possibilities[5] present feasible targets. It has been argued[1,6] that only a small number of special, high-symmetry nets will be of overwhelming importance in this connection, and indeed this hypothesis is verified by analysis of data for existing materials.[7] In this review we give an informal account of our work towards a method of systematic classification (taxonomy) of polyhedra and periodic nets that is appropriate for identifying the structures of special interest as feasible targets of synthesis. For a general account of the different kinds of net and methods for their enumeration see ref. 5.

A generally useful method of proceeding is to consider the patterns formed by *tilings*. The tilings we will be interested are coverings of a surface (a 2-D space) with polygonal tiles or of 3-D Euclidean space by generalized polyhedra or *cages*. 2-D tilings may be the familiar coverings of the plane by squares, hexagons *etc*., or tilings of a sphere in which case the structure corresponds to a convex polyhedron. The filling of space with cubes is a familiar example of a 3-D tiling. In 2-D tilings, the edges of the tiles are common to exactly two tiles, the tilings are *edge-to-edge*. In the 3-D case the faces of tiles are common to exactly two tiles and the tilings are *face-to-face*. The set of vertices and edges of the tilings (the *1-skeleton*) are a net (a simple, connected graph) and we say that the tiling *carries* a net. A review of basic terms and definitions relevant to the description of crystal nets as graphs has been given recently.[8]

Every tiling carries a unique net, and indeed the systematic enumeration of tilings is a very powerful way of enumeration of 3-periodic nets of a desired type.[9,10] On the other hand a given net may have more than one, indeed even an infinite number, of possible tilings. However there is usually a unique special tiling that we call the *natural* tiling; this is described next.

We like to think of nets as topological constructs, however in the discussion below when we refer to symmetries of the structure, we refer to the most symmetrical embedding in Euclidean space. For all the structures we mention here the automorphism group of the net is isomorphic to the symmetry group of the most-symmetrical embedding.

2. Natural tilings, transitivity and symbols for nets

In tilings of 2-D surfaces, we consider only as tiles, the cycles of the graph that are *strong rings*, *i.e.* cycles that are not the sum of smaller cycles.[8] This condition is necessary as in for example a cube, as well as the 'obvious' 4-sided faces, we could use 6-cycles as faces.[11]

In the 3-D (better *3-periodic*) case we always use *natural* tilings that obey the conditions that the tiling (a) conserves the symmetry of the net (tilings that do this are termed *proper*). For many high-symmetry structures this already leads to a unique tiling, but sometimes we need to add: (b) tiles cannot have non-face strong rings the same size as or smaller than the smallest face and (c) all the faces of tiles are strong rings (this means that a tile cannot have one face bigger than all the rest). For some complex low-symmetry nets it is necessary to add further conditions[12] to lead to a unique tiling but these will not concern us here.

Tilings for some 3-periodic nets are shown in Fig. 1. In the first, the net is that of the –T–O–T– (here T is a tetrahedrally-coordinated atom—Si or Al) framework of the mineral sodalite. The intrinsic (maximum) symmetry of this net is

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$Im\bar{3}m$. The only possible tiling with the same symmetry (including preserving all translations) is the one shown-a space filling by truncated octahedra. The second example is provided by the tiling of the net of the invariant lattice complex with symbol Y. The natural tiling uses 3-rings and 5-rings, but, as shown, we could use double tiles with faces that are all 5-rings and still conserve the symmetry ($P4_132$) so now we need rule (b) above to give a natural tiling. A third example (also in Fig. 1) is provided by the net of the *hc* closest sphere packing. In closest packing of spheres the holes are at the centers of octahedra and tetrahedra and a natural tiling for the net of a closest packing should always reflect this. However in *hc* octahedra and one set of tetrahedra comes in face-sharing pairs and a tiling with these pairs fused would conserve the symmetry ($P6_3/mmc$) so again rule (b) is required to ensure a unique natural tiling by octahedra and tetrahedra. Notice that an octahedron is a 'natural' tile so it is never split into *e.g.* two square pyramids ('half octahedra'); rule (c) ensures this.

It may be noticed in Fig. 1 that we have used 3-letter symbols for nets; **sod** for the sodalite net, **lcy** for lattice complex Y, *etc*. A database of basic nets and their crystallographic properties (symmetry, coordinates, *etc*.) is under construction and nets can be retrieved under these symbols. A preliminary version of this database is to be found at http://okeeffe-ws1.la.asu.edu/RCSR/home.htm. When the new version is ready that address will direct to the new location.

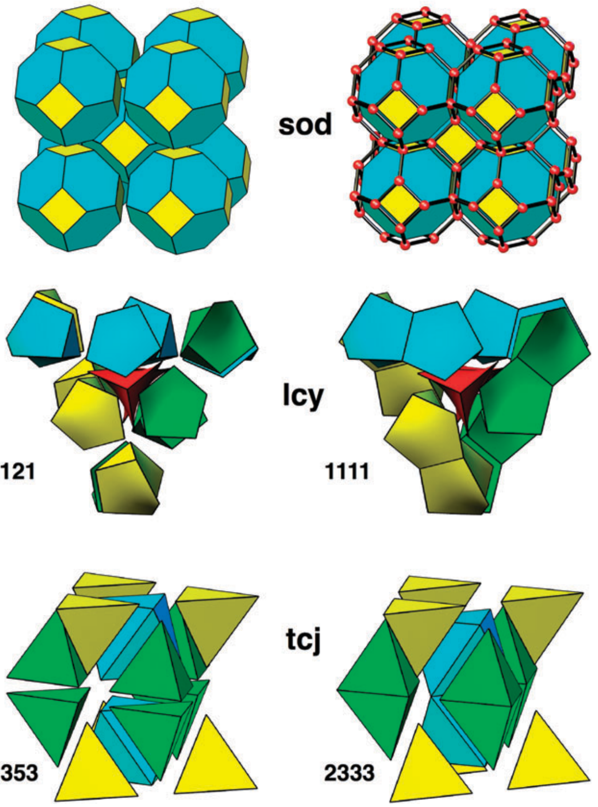

Fig. 1 Examples of natural tilings for nets. For **sod** the net is indicated on the right. For **lcy** and **tcj** the tilings on the right are not natural as explained in the text. The sets of four digits are the transitivities.

A useful property characterizing a tiling is the *transitivity*, defined as follows. Let there be p kinds of vertex, q kinds of edge, r kinds of face and s kinds of tile. Then the transitivity is the array of four integers $pqrs$. Here by *kind* we mean that vertices of one kind are all related by a symmetry of the tiling and if there are more than one kind there is no symmetry operation relating vertices of one kind to those of another. If there is just one kind of vertex (edge, *etc*.) we say that the structure is vertex- (edge-, *etc*.) transitive. In the discussion below, transitivity will be treated as if the array were a single number and used as a measure of regularity. Thus the most regular structures have transitivity 1111, next 1112 and so on. Transitivity is given for some tilings in Fig. 1; notice that it is a property of the tiling, not of the net the tiling carries.

For structures derived by tiling two-dimensional surfaces (polyhedra *etc*.) there are p kinds of vertex, q kinds of edge, r kinds of face and the transitivity is pqr.

3. Dual tilings

The concept of a polyhedron dual to an original one should be familiar. Informally it is the polyhedron obtained by putting a vertex in the middle of each face and joining it by edges to the new vertices in adjacent faces. The dual of a dual is the original polyhedron. The octahedron and cube are an example of a mutually dual pair, as are the cuboctahedron and rhombic dodecahedron (illustrated below), and the tetrahedron is an example of a self-dual polyhedron. It should be clear that the dual of a polyhedron with transitivity pqr has transitivity rqp.

The concept of duality readily transfers to 3-D tilings. Now the vertices of the dual structure are placed inside the old tiles and joined by edges to vertices in adjacent (face-sharing) tiles. A number of examples of dual pairs and self-dual tilings will be adduced later. The dual of a tiling with transitivity $pqrs$ has transitivity $srqp$. For a tiling to be self-dual it is necessary, but not sufficient, that the transitivity be palindromic. Only in the case of the most-symmetric nets (but these are our main concern here) is it generally true that the dual tiling is natural. The dual tiling always has the same symmetry as the original of course.

It is often convenient to refer to a 'dual' of a net. What we mean by this is the net carried by the tiling dual to the natural tiling of the original net. Similarly a 'self-dual' net is one that has a natural tiling that is self-dual. A self-dual net can readily accommodate a second copy of itself in the dual position, and it has been observed that in the great majority of crystal structures based on pairs of interpenetrating nets, the nets are simple self-dual nets.[5]

4. Edge-transitive polyhedra

In the subsequent discussion we will use the concept of *coordination figure* of a vertex. This is the figure formed by the neighbors of a vertex (more strictly the convex hull of those neighbors) and will be a polygon or polyhedron.

The familiar *regular* convex polyhedra (the Platonic solids) have one kind of face, one kind of edge and one kind of vertex, *i.e.* transitivity 111 (more generally a more restrictive definition of regularity is necessary[11]). Notice that in the maximum

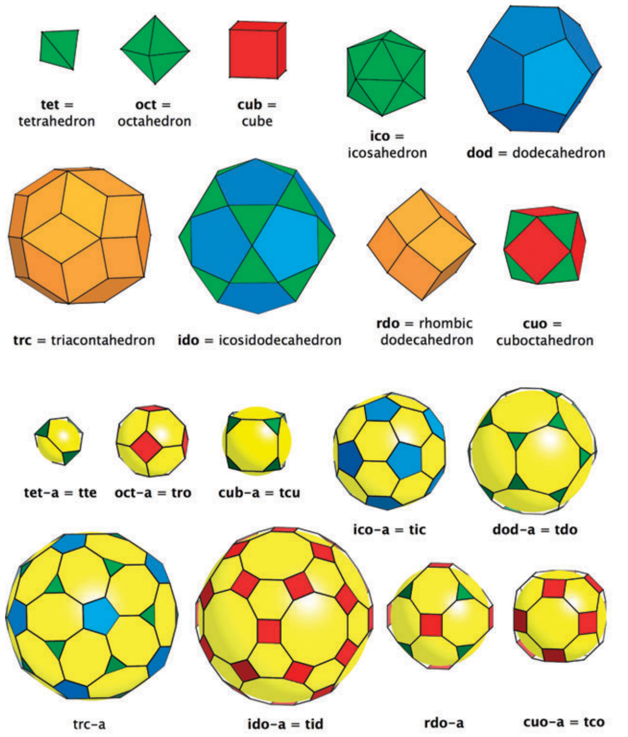

Fig. 2 Top two rows: the edge-transitive polyhedra. Bottom two rows: the augmented versions.

symmetry realization (embedding), the coordination figure of a vertex of a regular polyhedron is a regular polygon (triangle, square or pentagon). As the regular polyhedra are the only polyhedra with transitivity 111, it follows that the dual of a regular polyhedron is also a regular polyhedron.

There are also two *quasiregular* polyhedra with one kind of vertex and edge, but two kinds of face, *i.e*. transitivity 112. The duals of these two have transitivity 211 and complete the list of edge-transitive polyhedra which are shown in Fig. 2.

To see why we have selected these polyhedra as of special interest, consider what we call the *augmented* structures in which the vertices of the original polyhedra are replaced by a group of vertices with the shape of the coordination figure. This process of augmentation is usually called *truncation* in the case of polyhedra, but we prefer 'augmentation' as we wish to extend the concept to infinite structures where truncation is not possible. The net of the augmented polyhedra consists of polygons linked by edges, and in the case of augmented edge-transitive polyhedra, the structure consists of polygons linked by equal edges as illustrated in Fig. 2. If one wants to make a polyhedral molecule using molecular building blocks,[13] these are the prime targets for synthesis by design. Notice that these are the only possibilities with at most one link joining any given pair of polygons. Prisms and antiprisms are examples of structures containing multiple links of the same kind between a pair of faces.

5. Edge-transitive layers and rods (cylinder tilings)

In a similar fashion we can identify the edge-transitive layers (tilings of the plane). There are three regular structures with transitivity 111, a quasiregular structure (*kagome*) with transitivity 112 and the dual of the last with transitivity 211. These are illustrated in Fig. 3. Again we show also the augmented structures which represent the possible ways of linking polygons with one kind of link to form layers, and again these are prime targets for synthesis by design.

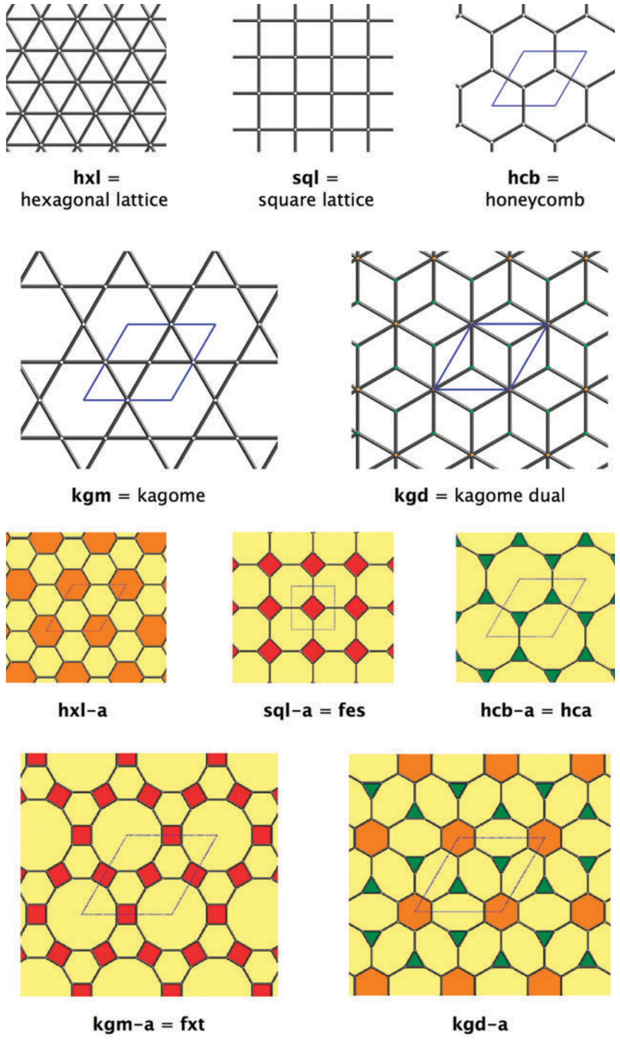

Fig. 3 Top two rows, the edge-transitive 2-periodic nets. Bottom two rows, the augmented version.

For completeness we should consider also the case of tilings of a cylinder. There is only one family of edge transitive structures (with transitivity 111) that is obtained by tiling the surface of a cylinder with squares. See Fig. 4.

6. Regular and quasiregular three-periodic nets

Following a hint given earlier in discussing regular polyhedra and layers, we define a regular net as one with one kind of vertex that in its most symmetric embedding has a coordination figure that is *required* by symmetry to be a regular polygon or regular polyhedron—specifically a triangle, square, hexagon, tetrahedron, octahedron or cube (these are the only

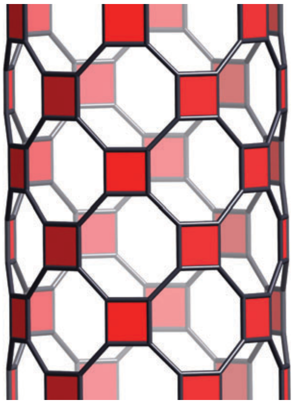

Fig. 4 The augmented version of a tiling of a cylinder by squares. This is the only one-periodic way of linking polygons by one kind of edge.

possibilities compatible with crystallographic symmetry). A quasiregular net has a vertex figure that is a quasiregular polyhedron, namely a cuboctahedron. It is straightforward to show these are the only possibilities and that there is just one 3-periodic net for each case, except for the case of the hexagon which can only lead to a 2-periodic structure.[14] In Fig. 5 we show these nets and their augmented forms and some of their properties are listed in Table 1. They are:

srs. 3-coordinated, vertex figure triangle. The net has the same topology as the –Si–Si– net in $SrSi_2$, hence the symbol. It has some special properties: it is the only chiral (symmetry $I4_132$) regular net and it is the only 3-coordinated 3-periodic net with 3-fold symmetry axis at the site of the vertex (actual symmetry $32 = D_3$), and thus the only 3-coordinated net with one kind of edge.

nbo. 4-coordinated, vertex figure square. This is the net of the atoms in NbO, hence the symbol.

dia. 4-coordinated, vertex figure tetrahedron. This is the net of the diamond structure met above and, we hope, familiar.

pcu. 6-coordinated, vertex figure octahedron. The augmented net (linked octahedra) is the –B–B– net in CaB_6 and is given symbol **cab. pcu** is special in the sense that it is the net of the only regular *tiling* of Euclidean space (a tiling of space by just one kind of regular polyhedron).

bcu. 8-coordinated, vertex figure cube. This is the net of the body-centered cubic lattice, considered as 8-coordinated (we also like on occasion to include second-nearest neighbors to then consider body-centered cubic as 14-coordinated, but then the net is different and we use symbol **bcu-x**). The augmented net (symbol **pcb**) is made up of linked cubes and sometimes called polycubane.

fcu. 12-coordinated, vertex figure cuboctahedron. This is the net of the face-centered cubic lattice and well known as the structure of cubic closest sphere packing. Also familiar is the fact that there are two kinds of hole in the structure corresponding to the centers of the two kinds of tile. The tiles are regular tetrahedra and octahedra which occur in the ration 2:1. The augmented net (symbol **ubt**) is the –B–B– net of UB_{12}.

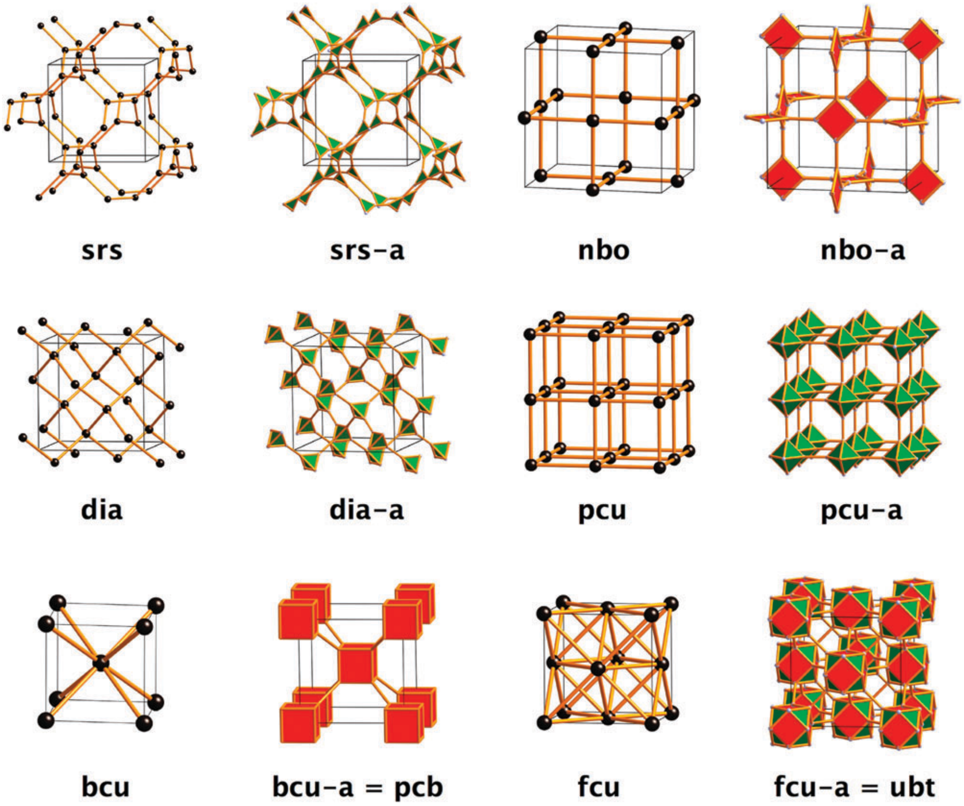

Fig. 5 The regular and quasiregular (**fcu**) nets in their normal and augmented conformations.

Table 1 Some properties of the regular, quasiregular and known semiregular nets. 'CN' is coordination number and 'CF' is short for coordination figure. The symmetry is the point symmetry at a vertex, and 'order' refers to the order of that symmetry group

net	Transitivity	CN	CF	Symmetry	Order
srs	1111	3	Triangle	$32\ (D_3)$	6
nbo	1111	4	Square	$4/mmm\ (D_{4h})$	16
dia	1111	4	Tetrahedron	$\bar{4}3m\ (T_d)$	24
pcu	1111	6	Octahedron	$m\bar{3}m\ (O_h)$	48
bcu	1111	8	Cube	$m\bar{3}m\ (O_h)$	48
fcu	1112	12	Cuboctahedron	$m\bar{3}m\ (O_h)$	48
lvt	1121	4	Rectangle	$2/m\ (C_{2h})$	4
sod	1121	4	Tetrahedron	$\bar{4}2m\ (D_{2d})$	8
lcs	1121	4	Tetrahedron	$\bar{4}\ (S_4)$	4
lcv	1121	4	Tetrahedron	$222\ (D_2)$	4
qtz	1121	4	Tetrahedron	$222\ (D_2)$	4
hxg	1121	6	Hexagon	$\bar{3}m\ (D_{3d})$	12
lcy	1121	6	Trigonal Metaprism	$32\ (D_3)$	6
crs	1122	6	Octahedron	$\bar{3}m\ (D_{3d})$	12
bcs	1122	6	Octahedron	$\bar{4}\ (C_{3i})$	6
acs	1122	6	Trigonal prism	$\bar{6}m2\ (D_{3h})$	12
reo	1122	8	Tetragonal prism	$4/mmm\ (D_{4h})$	16
thp	1122	8	Bisdisphenoid	$\bar{4}\ (S_4)$	4
rhr	1132	4	Rectangle	$mm2\ (C_{2v})$	4
ana	1132	4	Tetrahedron	$2\ (C_2)$	2

In deriving these nets we have made no reference to their tilings. In fact the natural tilings have the property that those of the regular nets have transitivity 1111 and that of the quasiregular net has transitivity 1112. Furthermore we believe that these are the only natural tilings of nets that have these properties. The non-natural tiling of **lcy** shown in Fig. 1 has transitivity 1111 (the natural tiling has transitivity 1121).

Fig. 6 illustrates natural tilings for the regular and quasiregular nets. Notice that the dual of a tiling with transitivity 1111 also has transitivity 1111. The pair **nbo** and **bcu** form a mutually dual pair and **srs**, **dia** and **pcu** are self-dual (the dual of **srs** is actually the opposite enantiomorph). The cubic periodic minimal surfaces of lowest genus are known as *G*, *D*, and *D* and are of considerable importance in many contexts such liquid crystals and mesoporous materials. They divide space into two equal parts that have a system of pores (labyrinths) that have the structure of intergrown pairs of **srs**, **dia** and **pcu** nets, respectively.

7. Semiregular three-periodic nets

Semiregular nets are defined as nets that are vertex- and edge-transitive—*i.e.* that have natural tilings with transitivity 11*rs* with $r > 1$.[15] We restrict ourselves to nets which have embeddings in which there is no intervertex distance shorter than the edge length, as without this restriction there are infinite families of high-coordination vertex- and edge-transitive nets.[5]

Table 1 lists some properties of the regular, quasiregular, and known semiregular nets, and most of the last (**lcv** and **ana** are omitted) are illustrated in augmented form in Fig. 7. Notice that sometimes the same coordination figure occurs in more than one net. Indeed there are six nets with tetrahedral coordination figure. As discussed elsewhere[7] those with the highest point symmetry at the vertex (*i.e.* **dia** and **sod**) are of the greatest importance in chemistry.

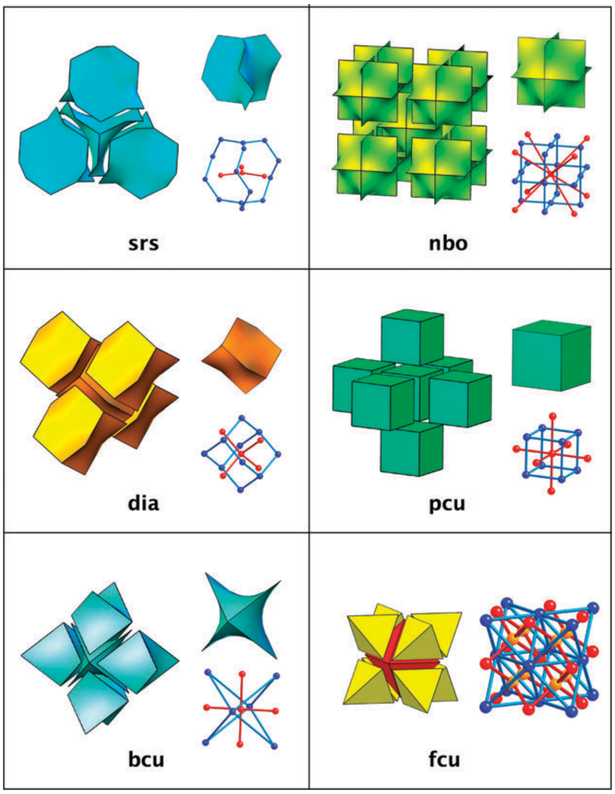

Fig. 6 Tilings for the regular and quasiregular nets. The ball-and-sick sketches show the skeleton of one tile (or group of tiles for **fcu**) in blue, with part of the dual net in red.

8. Edge-transitive binodal nets

The vertex- and edge-transitive nets are relevant to synthesis in which a molecular component of a given shape is to be linked by a ditopic linker which plays the role of edge in the net. Often, though, one is linking together components of two different shapes and the important structures are now the binodal edge transitive structures.

The structures of this sort that we have identified,[16] now with the restriction that there are no distances between unlike vertices shorter than the edge lengths, are listed in Table 2, and most (**pth**, **ifi**, **ibd**, and **iac** are omitted) are shown as augmented structures in Fig. 8. They present attractive targets for synthesis, but of course, one must first design components of the right shape to link together.[1] When there are more than one possibility, *e.g.* **pts** and **pth** for linking squares and tetrahedra, it is generally found that the one with highest point symmetry at the vertices (**pts**) dominates in observed structures, and makes the most viable target for a designed synthesis. In the case of linking triangles and octahedra, the **spn** net, although with higher point symmetry at the vertices, is generally less favorable than **pyr**, as a planar configuration at the 3-coordinated vertices in **spn** brings these vertices close together.

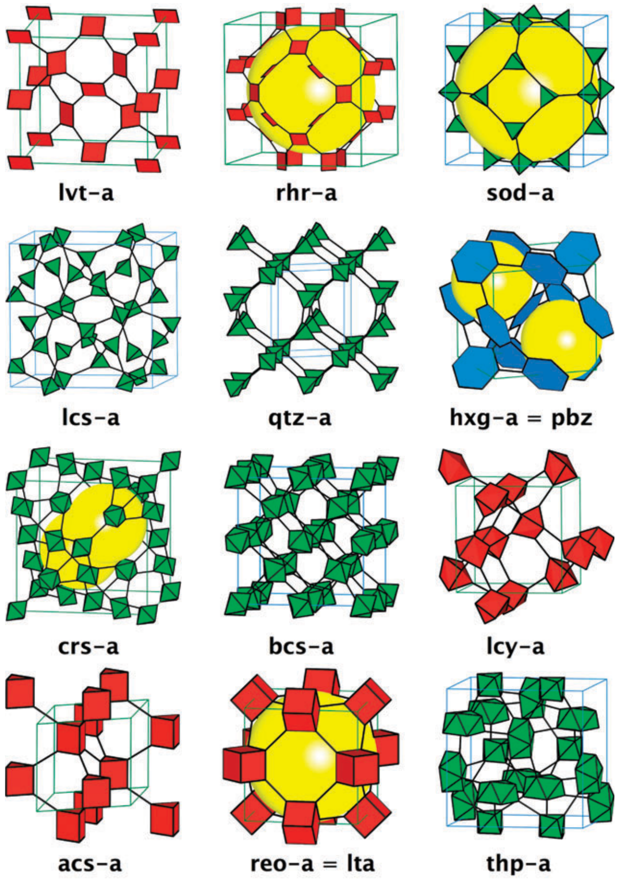

Fig. 7 Some semiregular nets shown in augmented form.

Table 2 Some properties of binodal edge-transitive nets. 'CN' is coordination number and 'CF' is short for coordination figure. 'order' refers to the order of the point symmetry at the vertices

net	Transitivity	CN	CF	Order
pto	2122	3, 4	Triangle, square	6, 8
tbo	2123	3, 4	Triangle, rectangle	6, 8
bor	2122	3, 4	Triangle, tetrahedon	6, 8
ctn	2122	3, 4	Triangle, tetrahedon	3, 4
pyr	2112	3, 6	Triangle, octahedon	3, 6
spn	2122	3, 6	Triangle, octahedon	6, 12
the	2123	3, 8	Triangle, tetragonal prism	6, 16
ttt	2123	3, 12	Triangle, truncated tetrahedron	6, 24
rht	2123	3, 24	Triangle, rhombicuboctahedron	6,48
pts	2132	4, 4	Square, tetrahedron	8, 8
pth	2132	4, 4	Square, tetrahedron	4, 4
soc	2122	4, 6	Square, octahedron	8, 12
she	2122	4, 6	Square, hexagon	8, 12
stp	2133	4, 6	Rectangle, trigonal prism	8, 24
sqc	2132	4, 8	Rectangle, tetragonal prism	4, 8
scu	2133	4, 8	Rectangle, tetragonal prism	8, 16
shp	2133	4, 12	Rectangle, hexagonal prism	8, 24
ftw	2112	4, 12	Square, cuboctahedron	16, 48
toc	2122	4, 6	Tetrahedron, octahedron	8, 12
gar	2122	4, 6	Tetrahedron, octahedron	4, 6
ibd	2122	4, 6	Tetrahedron, octahedron	4, 6
iac	2123	4, 6	Tetrahedron, octahedron	4, 6
ifi	21..	4, 6	Tetrahedron, octahedron	4, 6
flu	2111	4, 8	Tetrahedron, cube	24, 48
ith	2122	4, 12	Tetrahedron, icosahedron	8, 24
twf	2123	4, 24	Tetrahedron, truncated octahedron	8, 48
nia	2122	6, 6	Octahedron, trigonal prism	12, 12
ocu	2123	6, 8	Octahedron, tetragonal prism	12, 16
alb	2134	6, 12	Trigonal prism, hexagonal prism	12, 24
mgc	2123	6, 12	Hexagon, truncated tetrahedron	12, 24

The table has 30 entries and includes two nets, **rht** and **sqc**, that were omitted from the original paper.[16]

9. Further important three-periodic nets

9.1 Minimal nets

The primitive cell of a 3-periodic net must contain at least one 6-coordinated vertex (as in **pcu**, the net of the primitive cubic lattice) or two 4-coordinated vertices (as in diamond, **dia**) for there to be links in positive and negative senses in three different directions. (A pair of 4-coodinated vertices linked by a common edge have six remaining links). Beukemann and Klee[17] have shown that here are 15 such 3-periodic *minimal* nets. They include the regular nets (**srs**, **dia** and **pcu**) with self-dual tilings.[18] Here we call attention to two others of special interest in crystal chemistry. These are **ths** with (like **srs**) four 3-coordinated vertices per primitive unit cell and **cds** with (like **dia**) two 4-coordinated vertices per primitive unit cell. Some properties of these nets are listed in Table 3, and they are illustrated in Fig. 9. It is easy to show[18] that the dual of a minimal net must be another minimal net. Of particular interest is the fact that the **cds** net is self dual. An extended discussion of the this net has been given elsewhere.[19]

9.2 Rod nets

The two nets of the previous section can be interpreted as made up of rods running in layers with the rod directions at 90° in successive layers. In the case of **ths** the coordinates are modified to make the rods straight lines as shown in Fig. 10, and the net is symbolized **ths-z**. They are examples of nets based on *rod packings* (packings of cylinders are examples of rod packings) and in this case the rod axes are coincident with symmetry axes and have fixed coordinates. There are 14 such *invariant rod packings*.[20] Those with parallel rods are simply derived from invariant circle packings, but there are two more with rods in parallel layers that are of special interest (the rest are 3-way or 4-way cubic patterns). These are illustrated in Fig. 10 and some properties listed in Table 3. **qzd** is of some interest as the dual of the net (**qtz**) derived from the quartz structure.[19]

9.3. Five-coordinated nets

Five-coordinated structures are fairly common but it should be clear that they cannot be edge-transitive as there is no crystallographic symmetry with order that is a multiple of five. There are just two topologies for a coordination figure, *viz.* trigonal bipyramid and square prism, and simple high-symmetry nets can be constructed for both vertex figures as shown in Fig. 11. It is found that these dominate in observed structures.[7]

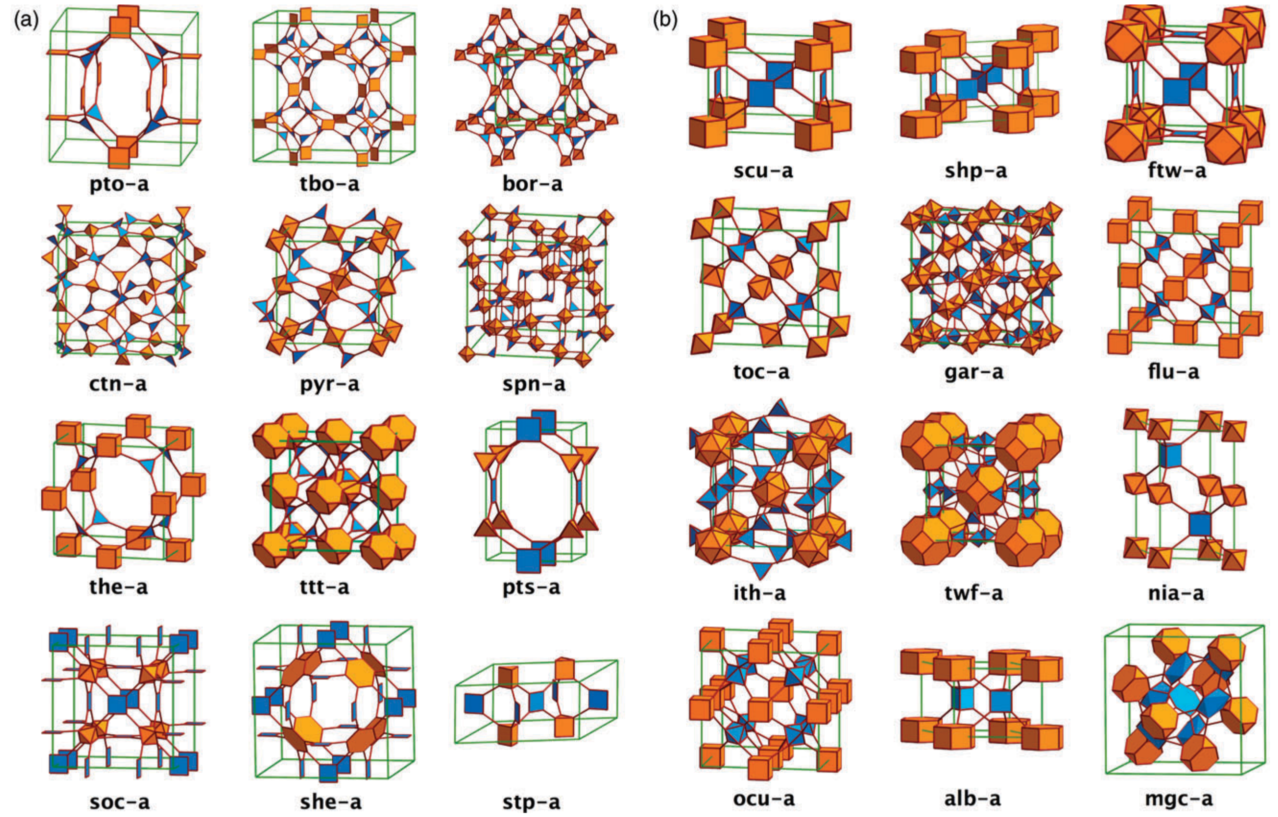

Fig. 8 (a). Twelve of the binodal edge-transitive nets in augmented form. (b) Twelve more binodal edge-transitive nets in augmeted form.

9.4. Two more 4-coordinated nets: sra and crb

There are two more nets that are not uncommon in MOFs[7] and worth mentioning here. The commonest rod-like SBU has the underlying topology of a ladder and the simplest mode of linking ladders to form a 3-periodic nets is in the net **sra** (this is the Al net of the common structure type of $SrAl_2$).[20] The other net of this section is **crb**—this is the net of the B atoms in CrB_4 but also form the basis of MOF structures and some low-density sulfides.[21] They are illustrated in Fig. 12 and some properties listed in Table 3.

10. Further considerations for designed synthesis

Here we have described the nets that we believe are some of the most important for targeted synthesis of structures. This is just the beginning of the story however. For example, we have listed nine ways of linking squares by one kind of edge. To determine which, if any, of these will be obtained in a synthesis one must not only assure that the square SBU is prepared, but design a linker of suitable shape to select one possibility. How to do this has been discussed elsewhere in a paper[22] that describes the synthesis of five of these possibilities, and a sixth has been achieved by design subsequently.[23]

In particular, once one has established the conditions to produce a certain MOF of given topology for a certain combination of shapes, it is possible then to produce a suite of materials with the same topology but different organic SBU. Such series of compounds are called *isoreticular*.[24]

However, chemistry will always be first an experimental science and surprises abound.[25] We give one example where the surprise was pleasant. A first attempt at linking octahedral and triangular SBUs resulted in a structure with the expected

Table 3 Some properties of additional uninodal nets. 'CN' is coordination number and 'CF' is short for coordination figure. The symmetry is the point symmetry at a vertex, and 'order' refers to the order of that symmetry group

net	Transitivity	CN	CF	Symmetry	Order
ths	1211	3	T or Y	*mm*2 (C_{2v})	4
cds	1221	4	Rectangle	*mmm* (D_{4h})	8
bto	1221	3	T or Y	2 (C_2)	2
qzd	1211	4	Rectangle	222 (D_2)	4
sqp	1222	5	Square pyramid	4*mm* (C_{4v})	8
bnn	1221	5	Trigonal bipyramid	$\bar{6}m2$ (D_{3h})	12
sra	1331	4	Tetrahedron	*m* (C_s)	2
crb	1232	4	Tetrahedron	*mm*2 (C_{2v})	4

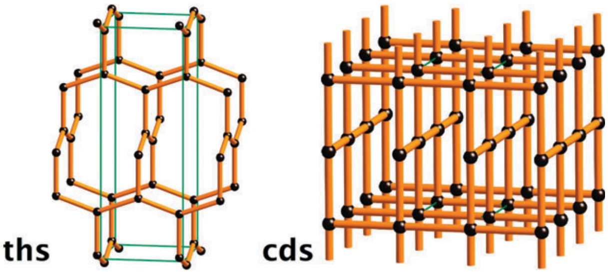

Fig. 9 The **ths** and **cds** minimal nets.

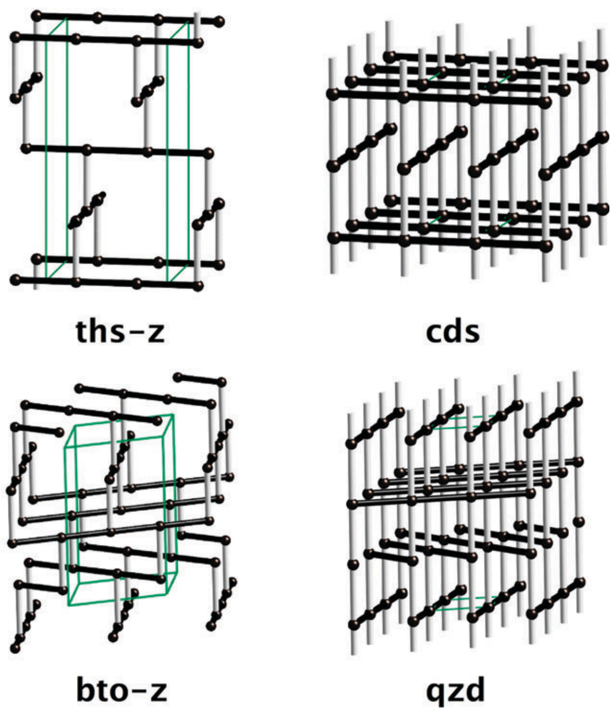

Fig. 10 Examples of rod nets.

pyr topology (there are good reasons not to expect the other 3,6-coordinated topology of Table 2, see Section 8). The pyrite net is self-dual and, also as expected, a pair of intergrown structures resulted.[26] However using a different triangular organic SBU a different, but closely related topology, was found, that could be rationalized by hindsight.[27] The nice part though is that this second structure is not self-dual and is not interpenetrated, and in fact the material was of unprecedented openness.

The considerations of this paper are of little consequence to the designed synthesis of materials such as zeolites. Indeed of the more than 150 known zeolites only **SOD** (**sod**) **BCT** (**crb**) and **ABW** (**sra**) are based on topologies mentioned in this account (here zeolite framework codes[28] are given in upper case). It is worth noting in this context that in MOFs consisting of tetrahedral cations, T, joined by imidazolate linkers, Im, many structures are observed, the majority of them having the topology of uninodal silicate zeolite frameworks.[29] This is readily understood as the T–Im–T angle is close to 145°, an angle close to that generally preferred for Si–O–Si links.

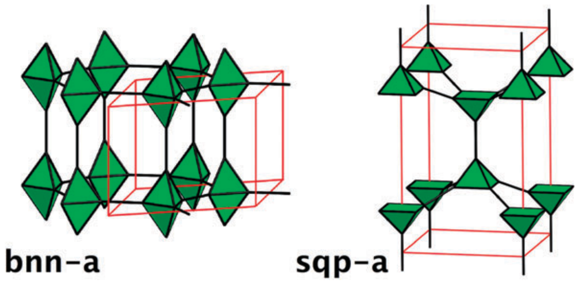

Fig. 11 Two 5-coordinated nets shown augmented.

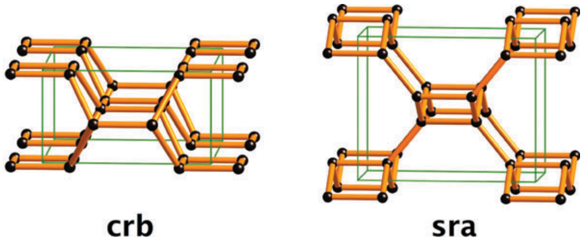

Fig. 12 The **sra** and **crb** nets.

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