# 18

# Topology

## 18.1 Introduction

Describing and understanding matter is at the heart of the chemical sciences. For finite units such as molecules this is generally trivial; however, the description of structures of (crystalline) solid-state materials is significantly more challenging and several methods can be used to describe such structures. The crystal structure is the most detailed description and includes information about the atomic composition, connectivity, spatial arrangement, and symmetry of the overall structure. This description can be very complicated and therefore, in the field of inorganic solid-state chemistry, a concept of describing crystal structures as a packing of one type of atom where other atoms occupy the voids of the structure is common practice. While this works well for ionic solids, this is less helpful for extended solids such as metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and covalent organic frameworks (COFs). The description of extended structures in terms of topology (from the Greek τόπος meaning "place," and λόγος meaning "study") is more frequently used [1]. This concept allows to simplify structures by only considering the connections between constituents, not their chemical nature. The differences in structure description are illustrated in Figure 18.1.

This approach significantly reduces the complexity of a given structure description [2]. Aside from the simplified description of crystal structures, this concept also allows for reverse engineering of crystal structures, or simply put, "to design solid-state materials" [3]. Before we consider different topologies we need to understand what "topology" is, how to determine the topology of a given structure, and introduce the terminology required for its description.

## 18.2 Graphs, Symmetry, and Topology

### 18.2.1 Graphs and Nets

Nets are a collection of nodes that are linked by connections (edges). They are a special kind of graph, an abstract mathematical object. For mathematical graphs we distinguish between infinite and finite graphs and classify them based on

*Introduction to Reticular Chemistry: Metal-Organic Frameworks and Covalent Organic Frameworks,*
First Edition. Omar M. Yaghi, Markus J. Kalmutzki, and Christian S. Diercks.

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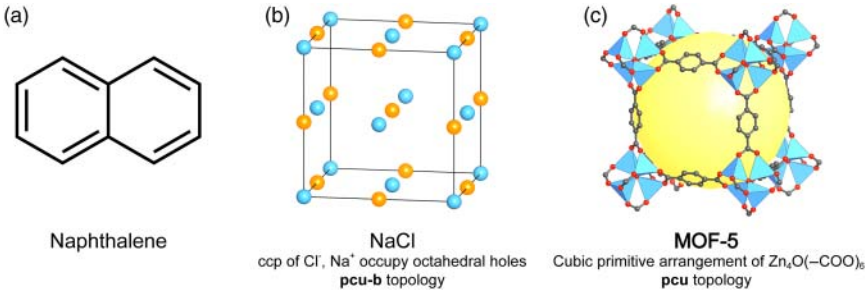



**Figure 18.1** Comparison of different structure descriptions. (a) Molecular compounds are defined by the type of atoms and the chemical bonds between them, where specific units are given trivial names. (b) Ionic structures can be described by a packing of one type of ion (here cubic closest packing of $Cl^-$) where the other ions occupy the voids (here $Na^+$ occupies all octahedral holes). Alternatively, this arrangement can be described as a **pcu-b** net. (c) The crystal structure of MOF-5 can be simplified to a primitive cubic packing of $Zn_4O(–COO)_6$ SBUs that are connected by linear ditopic BDC linkers or as a **pcu** net.

their properties into (i) graphs that have loops, meaning vertices connected to themselves, (ii) graphs containing vertices that are connected by multiple links, (iii) graphs that are directional, and (iv) graphs that have loose ends.

With respect to the description of the crystal structures of MOFs in terms of nets there are only infinite 2- and 3-periodic graphs, meaning they do not possess any of the abovementioned properties (loops, multiple connections, directionality, and loose ends). It is important to note that periodicity is not synonymous with dimensionality. While every polyhedron is a 3D object, it is not periodic.

To understand these concepts and their applicability to the description of framework structures we consider a problem described by Leonhard Euler in 1735: "The seven bridges of Koenigsberg." A river flows through the city of Königsberg creating a central island and three riverbanks (bank A, B, and C) that are connected by seven bridges (Figure 18.2). Euler showed that to find

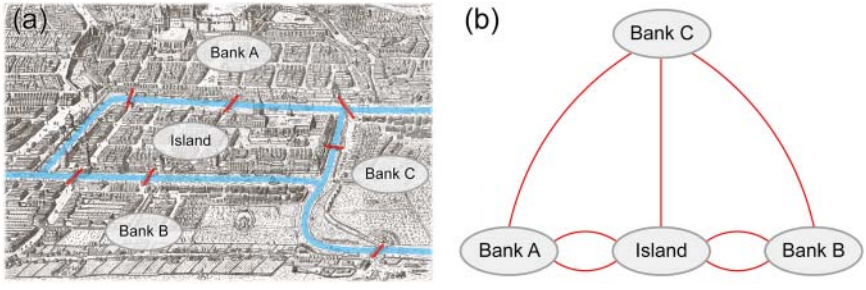



**Figure 18.2** (a) The old city of Koenigsberg with the seven bridges highlighted in red. (b) Illustration of the graph describing this problem. Here, the riverbanks and the islands represent the nodes and the bridges represent the edges (red lines). From the analysis of this graph it becomes clear that it is impossible to walk through the city of Koenigsberg while passing every bridge only once.

out whether it is possible to cross the city while only crossing every bridge exactly once, neither the length of the bridges nor the distances between them is relevant. Solving this question only requires the knowledge over which bridges are connected to which islands or riverbanks.

### 18.2.2 Deconstruction of Crystal Structures into Their Underlying Nets

The above example highlights the need to identify the nodes and edges making up a crystal structure to establish a graph that describes it. This is referred to as the deconstruction of a crystal structure [4]. We will illustrate this process for a MOF but a similar procedure can be applied to other extended frameworks. The first step involves defining the building units that represent nodes and edges in the corresponding topology. For MOFs the building units are typically the inorganic secondary building units (SBUs) and the organic linkers. In special cases larger structural fragments can be chosen as the building units (see Section 5.2.3). To decide which building units are edges and which are nodes we need to define the number of "points of extensions" for each of them. The points of extension represent the number of connections a specific building unit makes to other building units in the structure. As an example, for carboxylate-based MOFs these points of extension are typically placed on the carboxylate carbon. Building units making only two connections represent edges, whereas all building units making three or more connections are nodes. In this chapter, we will refer to the connectivity using the abbreviation "*X*-c," indicating an *X*-connected vertex. To illustrate this process, we consider the structure of HKUST-1 and deconstruct it into its building units to derive the underlying topology. HKUST-1 is built from $Cu_2L_2(-COO)_4$ paddle wheel SBUs that are connected through BTC linkers (Figure 18.4). We separate the SBUs and the linker at the carboxylate carbon and are left with a paddle wheel, which can be reduced to a 4-c node, and the BTC linker, which can be reduced to a 3-c node. To derive the net formed by linking these nodes it is not sufficient to know their number of points of extension (here, three and four) and local symmetry (here, triangle and square) but also the connections between them and the spatial arrangement of the nodes with respect to each other. A net of nodes and edges is only unique if it cannot be transformed into another net by bending or stretching but only by breaking and making connections. This is illustrated in Figure 18.3. Connecting 3-c nodes to form 2D layers can lead to different structures, depending on the geometry of the 3-c nodes but all three structures have the same topology (Figure 18.3a). Figure 18.3b shows another case where even though all points are only connected to two other points and the order is identical, all three arrangements represent different topologies since they cannot be transformed into one another without breaking and making connections.

In our example, deconstructing the structure of HKUST-1 leads to a "twisted boracite" or **tbo** net (Figure 18.4). We will use the net identifiers of the reticular chemistry structure resource (RCSR) database [5]. According to the RCSR, topologies are denoted by three-letter identifiers (lower case, bold). These identifiers allow for the unambiguous naming of unique nets and we discuss the nomenclature of net topologies later in more detail.

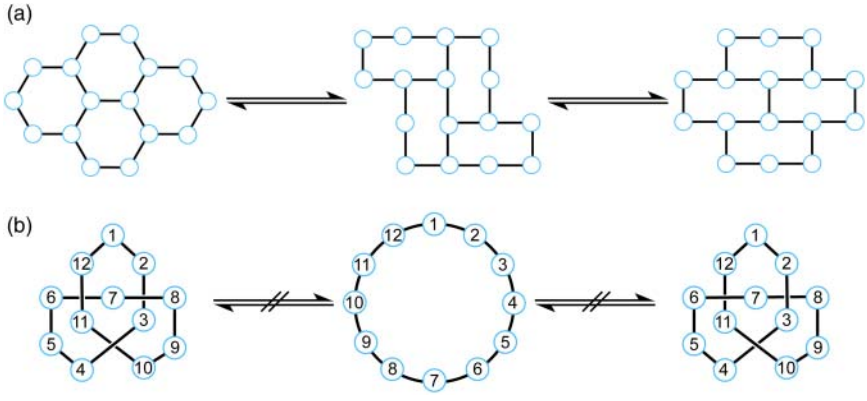



**Figure 18.3** (a) Hexagonal layers of 3-c vertices can be distorted to form "brick-wall"-like layers. Since all three arrangements can be transformed into each other without the need to break and make connections they are "topologically identical" (**hcb**, honeycomb). (b) While the connectivity of all units is identical for all three arrangements, they cannot be transformed into one another without breaking and making of connections. Thus, they are topologically distinct even though the graphs are "isomorphic."

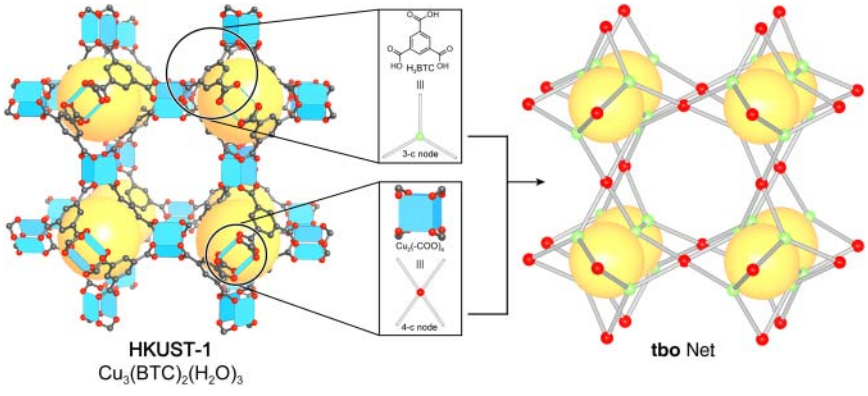



**Figure 18.4** Deconstruction of the structure of HKUST-1 into its underlying building units to derive the topology. Dissecting the structure at the points of extension (here the carboxylate carbons) gives two different building units: the trigonal BTC linker and the square paddle wheel SBU. These units are connected to give an overall "twisted boracite" or **tbo** net (shown on the right).

Using this approach, crystal structures can be simplified and classified. The general principle used to deconstruct the structure of HKUST-1 can be transferred to other extended frameworks. For MOFs built from other constituents, appropriate points of extension must be chosen and for COF structures generally the structure is dissected into building units at the linkage (see Chapter 9). The simple net derived in this way is abstract and does not contain chemical information. Since chemists commonly use polyhedra to represent the shape of molecules, adding vertex figures to the vertices provides us with a more helpful

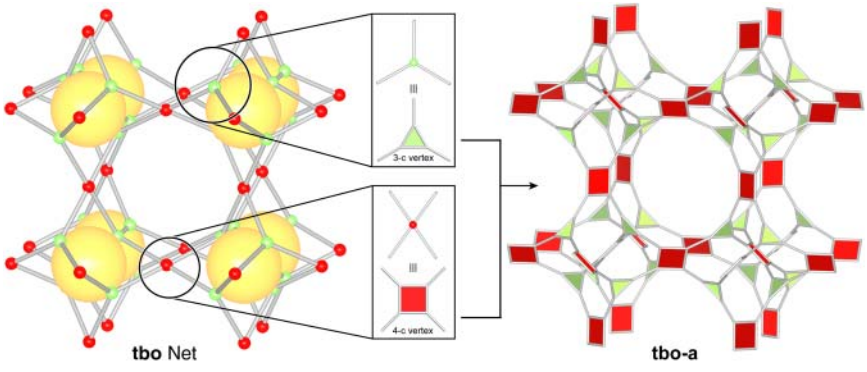



**Figure 18.5** The simple net of HKUST-1 is transferred into its augmented form by replacing the nodes with their respective vertex figures. The augmented net is denoted by appending "**-a**" to the topology symbol. In comparison to the simple **tbo** net, the augmented **tbo-a** net shows more resemblance to the crystal structure of HKUST-1. Consequently, the augmented representation is more frequently used.

representation and we call this the augmented net, which is denoted by adding "**-a**" to the topology symbol. This process is illustrated in Figure 18.5 for the **tbo** net of HKUST-1.

### 18.2.3 Embeddings of Net Topologies

The previous discussion pointed out that a net is merely an arrangement of nodes that are connected by edges and does not include information about the specific symmetry of the structure it represents. However, the illustrations of the **tbo** and **tbo-a** net in Figure 18.5 are of high symmetry and resemble the structure of HKUST-1, which has that particular topology. This is because the location of the vertices and edges is typically chosen in such a way that the smallest number of different vertices and edges is required to realize the net while the connection scheme remains unaltered. Here, "different" means they are not related by symmetry. To do this the vertices and midpoints of the edges are positioned on coordinates with maximum site symmetry. This permits to create a real and simple representation of an abstract mathematical object and we refer to this as the embedding. In the embedding the abstract nodes and edges become real vertices and links and we will use this nomenclature when talking about the embedding of nets.

### 18.2.4 The Influence of Local Symmetry

As illustrated in Figure 18.3a, in terms of net topology we do not differentiate between vertices based on their geometry but rather on their connectivity. This means that both tetrahedra and squares are 4-c vertices regardless of the difference in their geometry. It is however possible that different arrangements of vertices of the same connectivity have different topologies. While the local

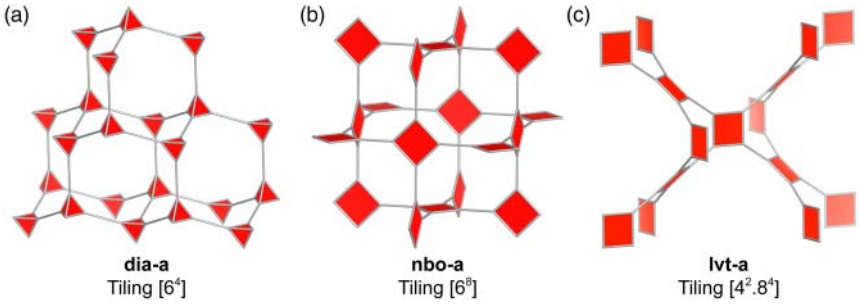



**Figure 18.6** Augmented nets of (a) **dia**, (b) **nbo**, and (c) **lvt**. All three nets are 3-periodic and 4-c but differ in the local geometry of the vertices. These differences result in different arrangements of the vertices with respect to each other and thus different topologies. The three nets have different tilings that make their description unambiguous.

geometry of the building units is not a topological feature, it results in different arrangements in space when connecting these vertices. To illustrate this, we consider three 3-periodic 4-c uninodal nets: **dia**, **nbo**, and **lvt** (Figure 18.6). It is clear that linking tetrahedra or squares results in two different arrangements and thus two different topologies. Smaller changes in the local symmetry of the vertex or more precisely the angles between them when they are linked into an extended structure can also lead to different arrangements. The influence of the angles between square vertices on the resulting topology and ways to influence them have been discussed in Section 4.2.2 and we showed that it is not only possible to form different 3-periodic 4-c nets but also 0-periodic, 1-periodic, and 2-periodic nets (see Figure 4.3). This highlights that the local symmetry of the vertices is an important factor for both the design of new materials based on topological considerations and the deduction of topologies. To render the assignment of topologies unambiguous, further parameters are needed to characterize nets. Unfortunately, many different terms or symbols are used to characterize nets and their constituents. Here, we will discuss the concepts of tilings, transitivity, and the face symbols as these are most frequently used in the context of reticular materials [6]. Further methods are discussed in the literature [7].

### 18.2.5 Vertex Symbols

2-periodic nets consist of cycles and the vertex symbols of 2-periodic nets give all possible "strong rings" within the net. Only those cycles of a graph that are not the sum of smaller cycles are strong rings. This is illustrated in Figure 18.7 for an **fxt** net. The strong rings in an **fxt** net are 4-, 6-, and 12-membered (in blue, red, and yellow respectively, Figure 18.7a), whereas the 8-membered cycle (green, Figure 18.7b) is the sum of the 4- and 6-membered ring and therefore does not constitute a strong ring. The vertex symbol of a 2-periodic net is denoted as $[q]$, where $q$ is the size of the strong ring. The **fxt** net is consequently denoted as [4.6.12].

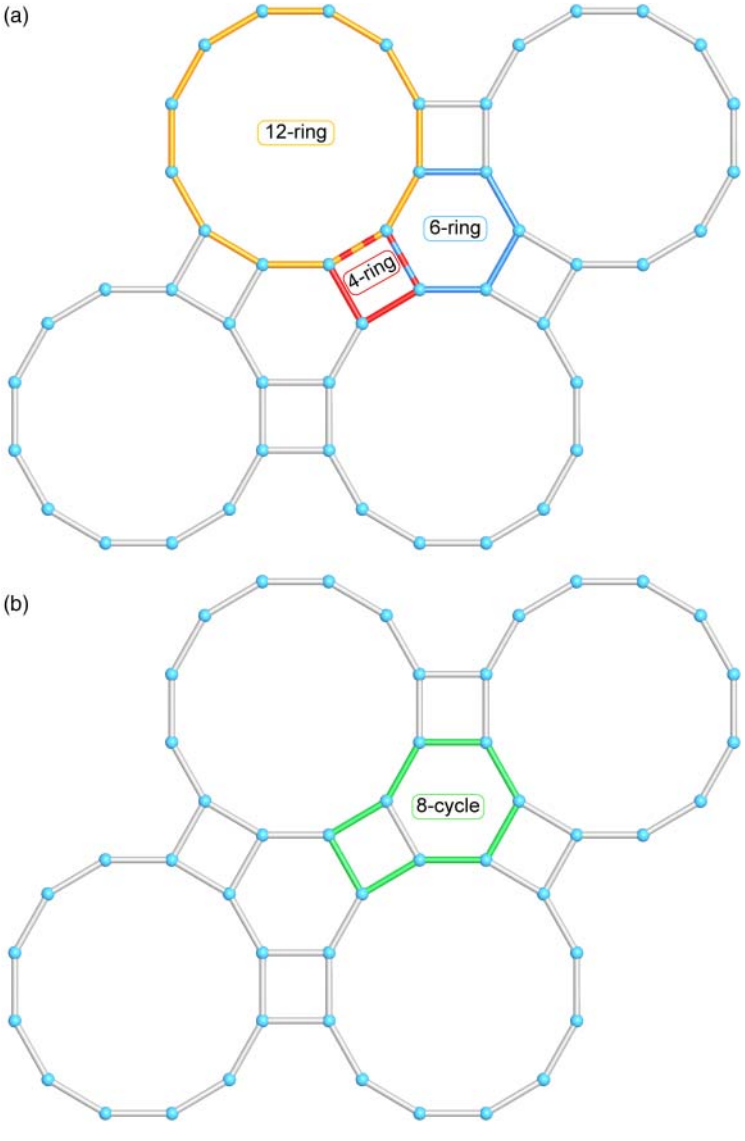



**Figure 18.7** Illustration of a fragment of the **fxt** net. (a) The smallest possible rings are strong rings. The **fxt** net has three different types of strong ring: 12-, 6-, and 4-membered (yellow, blue, and red, respectively). (b) Closed cycles that are a combination of smaller rings (8-membered ring, green) are not strong rings. Here the ring could be closed by taking a shortcut.

### 18.2.6 Tilings and Face Symbols

In a tiling, the space is divided into generalized face-sharing polyhedra or polygons for 3-periodic or 2-periodic nets, respectively. These geometric constructs fill the open space encompassed by the net. Tilings may have curved faces and are

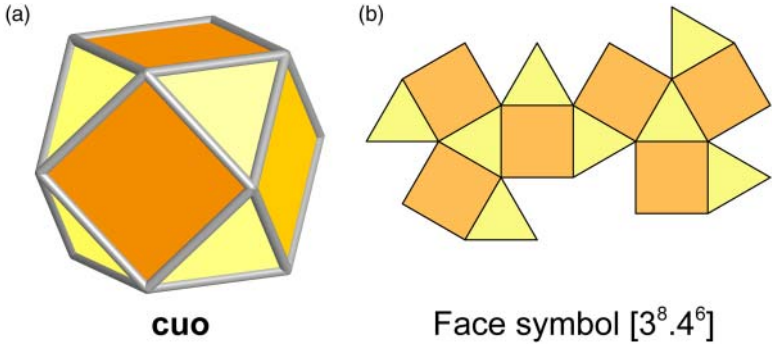



**Figure 18.8** Determination of the face symbol of a polyhedron of **cuo** topology (cuboctahedron). (a) The polyhedron is composed of eight 3-membered rings and six 4-membered rings. (b) This is more easily seen by unfolding the polyhedron. Counting the number of faces facilitates the deduction of the face symbol $[3^8.4^6]$.

not necessarily convex but are completely space filling. In terms of porous frameworks, tilings are an idealized representation of the pores of the open extended structures, which renders this approach particularly useful for the description of porous materials.

Before we discuss tilings of 3-periodic nets we will consider a 0-periodic net: the **cuo** (cuboctahedron). The cuboctahedron has 3- and 4-membered rings, and again the same rules apply; only those rings that are not the sum of shorter rings are counted. The polyhedron consists of eight 3-membered and six 4-membered rings. In a tiling, we define the individual tiles with their face symbol $[p^q]$, where $q$ is the number of $p$-sided faces. Accordingly, the face symbol of the cuboctahedron is $[3^8.4^6]$ (Figure 18.8).

The tiling of 3-periodic structures is determined in a similar way and we will show this for the **dia** and the **lon** net. Both nets are composed of 4-c vertices that are connected by edges. The **dia** net has one kind of tile with four identical faces of 6-membered rings. The natural tiling of the diamond net is the adamantane polyhedron with the face symbol $[6^4]$. In contrast, the **lon** net, often referred to as hexagonal diamond, has a natural tiling with equal numbers of two distinct tiles – one with three identical faces of 6-membered rings and one with five identical faces of 6-membered rings. The face symbols of 3-periodic structures with multiple tiles are denoted as $[q_1{}^p.q_2{}^p\ldots]$; therefore the face symbol of **lon** is $[6^3.6^5]$ [3a] (Figure 18.9).

The vertices of the net constitute the vertices of the tiles and the edges of the net constitute their borders – we say the tiling carries the net. The concept of tilings is not only important for the unambiguous assignment of a net topology but is also a helpful tool in reticular chemistry because they allow for the facile deduction and visualization of the different pores present in framework structures. For example, when comparing the tilings of the **dia** and the **lon** net it is immediately evident that there is just one kind of cage in frameworks with **dia** topology but two distinct cages in frameworks with **lon** topology.

Tilings can further be used to derive the transitivity of a net, which is helpful in enumerating and classifying them. The transitivity is described by a set of

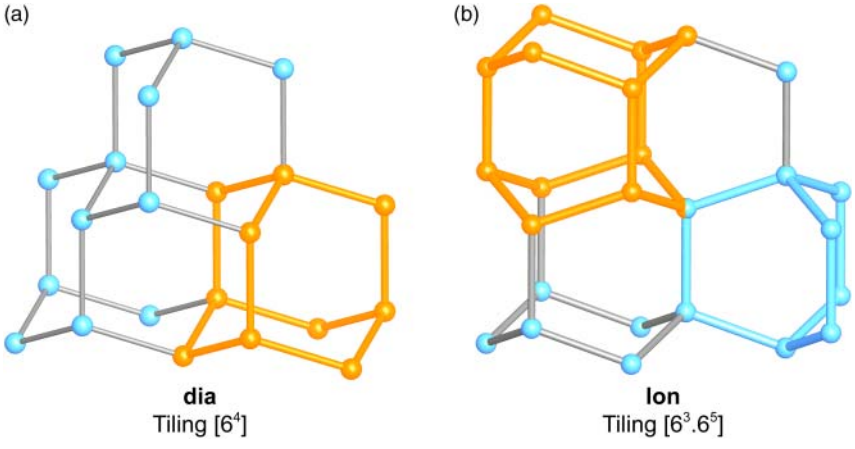



**Figure 18.9** Comparison of the simple nets of (a) **dia** and (b) **lon**. Both nets are built from 4-c tetrahedral vertices but they differ in their tiling. (a) While **dia** has only one kind of tile with the face symbol $[6^4]$, (b) **lon** has two types of tile and the face symbol $[6^3.6^5]$.

four parameters, *pqrs* [8]. These four parameters represent the number of topologically distinct vertices (*p*), the number of topologically distinct edges (*q*), the number of distinct faces (or rings) (*r*), and the number of different types of tiles (*s*). We will use the transitivity of nets later when we consider specific 3-, 2-, and 0- periodic nets (polyhedra).

## 18.3 Nomenclature

In the context of reticular chemistry net topologies are denoted by three-letter (lower case, bold) identifiers as specified in the RCSR database [5]. Every net topology in the RCSR database is assigned a unique symbol. Many net topologies are named after minerals or other naturally occurring compounds such as sodalite (**sod**), a naturally occurring zeolitic mineral, or diamond (**dia**). New topologies are assigned new 3-letter acronyms that may be related to the name of a compound or a specific connectivity but can generally be chosen arbitrarily.

We already discussed the simple and augmented nets earlier in this chapter. There are further derived nets that are signified by a suffix appended to the basic symbol. In the following, derived nets that are of relevance in the context of this book will be introduced. These are (i) augmented nets (suffix "**-a**"), (ii) binary nets (suffix "**-b**"), (iii) dual nets (suffix "**-d**"), (iv) interpenetrated/catenated nets (suffix "**-c**"), (v) cross-linked, (vi) weaving (suffix "-**w**"), and (vii) interlocking (suffix "-**y**").

### 18.3.1 Augmented Nets

Replacing the nodes in a net with the corresponding polygons or polyhedra, which we refer to as vertex figures, gives the augmented net. The process of

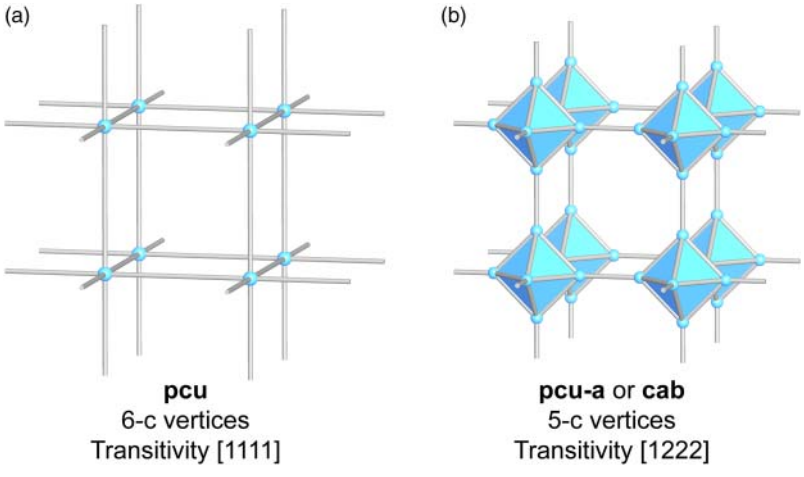



**Figure 18.10** Comparison of the **pcu** and the augmented **pcu** (**pcu-a** or **cab**) net. (a) In the **pcu** net all vertices are 6-connected and the transitivity is [1111]. (b) In contrast, the new vertices in the **pcu-a** (**cab**) net are 5-connected and the transitivity is [1222].

augmentation is not based on graph theory and the new set of vertices and edges created in this process do not necessarily form a closed graph. In the augmented net the connectivity of the nodes as a whole does not change, but since each node is composed of multiple new vertices the connectivity of those fragments changes. The augmented representation of a net is helpful in that is includes the local geometry of the vertices, which makes it easier to design building units of a specific geometry to target a framework of a particular topology. Augmented nets are denoted with a suffix "**-a**." In special cases, the augmented net has its own name since the arrangement and connectivity of the new vertices are identical to another simple net. The augmented net of **pcu** (primitive cubic) is not termed **pcu-a** but **cab** (calcium boride, $CaB_6$) to reflect that the connectivity and arrangement of new vertices is identical to that in the **cab** net (Figure 18.10).

### 18.3.2 Binary Nets

In the topological description only the connectivity of the vertices, their spatial arrangement, and the connections between them are taken into account but not their chemical nature. In reticular chemistry, however, structures can be composed of two different building units of the same connectivity and coordination geometry, such as two chemically distinct tetrahedral building units within one framework of **dia** topology. This aspect can be added to the three-letter identifier of the net by appending the suffix "**-b**", as in "binary net." An example for a binary net is sphalerite, ZnS (**dia-b**), the binary version of diamond (**dia**) (Figure 18.11).

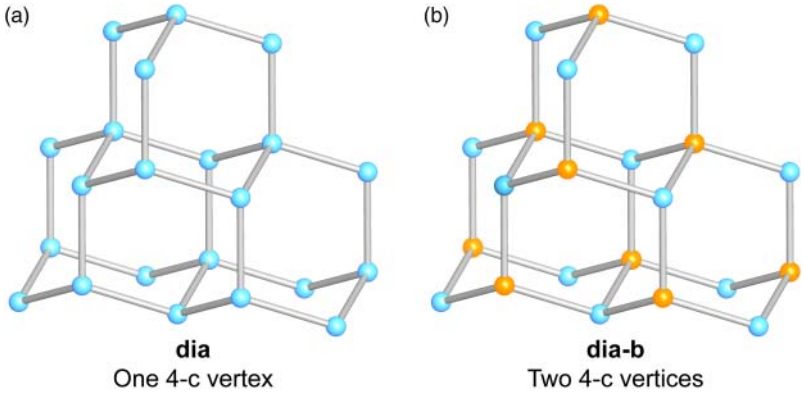



**Figure 18.11** Comparison of the uninodal **dia** net and its derived binary **dia-b** net. (a) In the **dia** net all vertices are not only topologically but also chemically identical, whereas in (b) the binary **dia-b** net chemically distinct vertices are arranged in an alternating manner.

### 18.3.3 Dual Nets

In porous framework structures, the open space encompassed by the framework is not necessarily empty but it can be occupied by guest molecules or even a second framework structure. Such frameworks that extend throughout the pore system of another framework are described by "dual nets." In Section 18.2.5 we illustrated an approach to creating a tiling for a given net. The tiling can be used to derive the dual net for a given net topology. To do so a new vertex is placed at the center of each tile and these new vertices are consequently connected though new edges that pass through the faces of the tiles. This gives a new net within the first net, termed the dual net, and the suffix "**-d**" is appended to the RCSR identifier. There are two scenarios regarding the nature of the dual net. (i) The dual net is of a different topology than the first net and is therefore referred to as a "hetero-dual." (ii) The dual net has the same topology as the first net and is thus referred to as a "self-dual" [8]. The concept of the dual net is illustrated in Figure 18.12 for the **dia** net (a self-dual net) and the **lon** net (a hetero-dual net).

The first net and its dual net are connected by mechanical, not chemical bonds. This type of entanglement is also referred to as "interpenetration." Owing to the difference in topology between the original net and its hetero-dual, interpenetration is commonly not observed for these nets.

### 18.3.4 Interpenetrated/Catenated Nets

Open space is energetically not favored and therefore it is not surprising that open framework structures that encompass a large amount of open space tend to interpenetrate. In such structures, the empty space is partially occupied by one or more additional frameworks. These additional frameworks are not connected among each other by chemical bonds but are mechanically entangled.

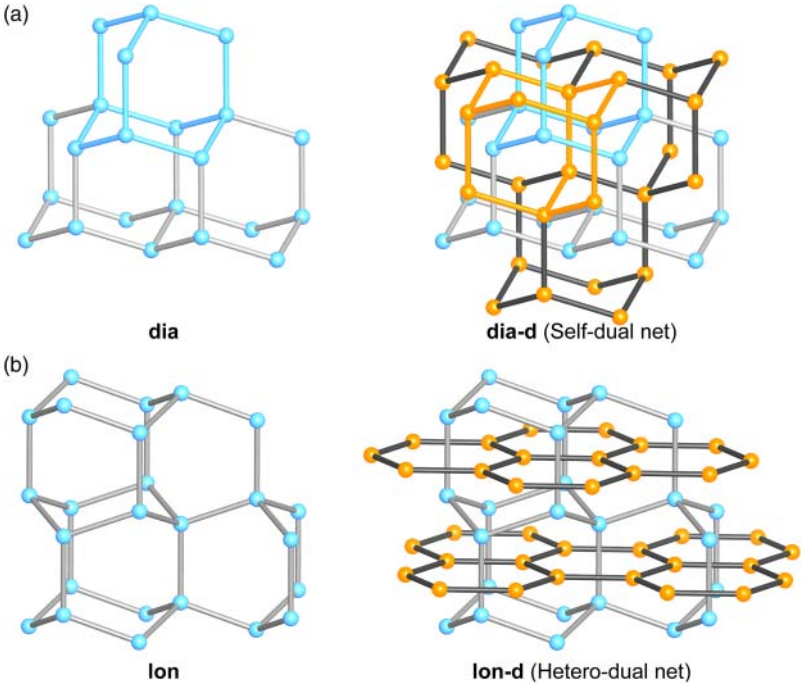



**Figure 18.12** (a) Comparison of the simple **dia** net (left) and its dual **dia-d** (right). The dual net of **dia** is also a **dia** net, and thus it is self-dual. Self-dual nets are also often highlighted by a suffix "**-c**" (for catenated). One cage of the simple net (blue) and the self-dual net (orange) are highlighted for clarity. (b) Comparison of the simple **lon** net (left) and its dual **lon-d** (right). The dual of the **lon** net is a **gra** net (offset **hcb** layers); thus, it is a hetero-dual.

Interpenetrated structures are given the suffix "**-c**," for "catenated." The presence of multiple interpenetrating frameworks is highlighted by adding their number to the suffix "**-c**" (e.g. a triply interpenetrated **dia** net is denoted as **dia-c3**). The example in Figure 18.13 shows the non-interpenetrated and interpenetrated **pcu** net. This example highlights that in general, MOFs with self-dual nets, large pores, and large pore apertures are likely to form interpenetrated structures to avoid the unfavorable open space. This concept is helpful in the design of MOFs since it allows to target structures that are unlikely to interpenetrate (hetero-dual nets).

### 18.3.5 Cross-Linked Nets

Since nets cannot contain multiple connections between the same vertices as in "double bonds," the term "cross-linking" of nets is used to describe structures where the same vertices are connected by more than one edge. One example of a structure is bio-MOF-100. The structure has an **lcs** net; however, every vertex is connected to each adjacent vertex by three linkers, and thus the structure is referred to as a "triply cross-linked **lcs** net" (Figure 18.14).

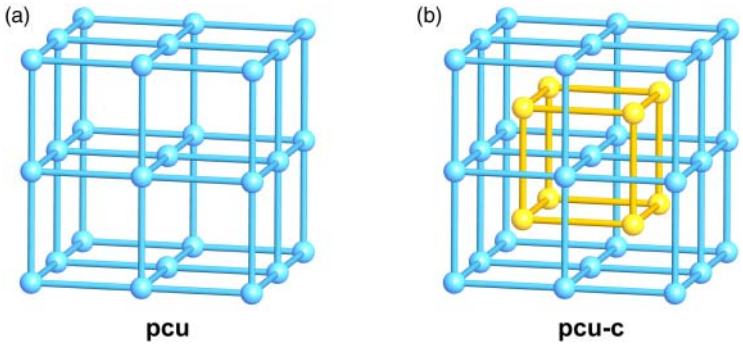



**Figure 18.13** (a) Non-interpenetrated and (b) interpenetrated **pcu** net. Depending on the pore size it is possible that more than one interpenetrating framework forms. The vertices that mark the origin of the interpenetrating frameworks lie along the diagonal of the cubic unit cell.

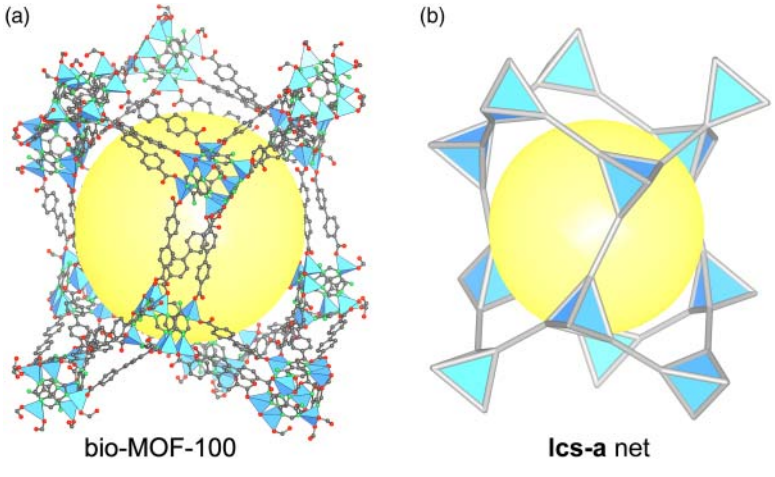



**Figure 18.14** (a) One cage in the structure of bio-MOF-100 and (b) the corresponding topology representation as an **lcs-a** net. Since the tetrahedral nodes are connected to each other by three linkers, this is referred to as triply cross-linked. In the augmented net each link represents three linkers in the crystal structure and therefore, the **lcs** net remains unaltered.

### 18.3.6 Weaving and Interlocking Nets

In addition to the nets discussed thus far, recently structures with weaving topologies have been reported. In such structures infinite elements are entangled into extended structures in a manner akin to the weaving of fabrics from threads. The identifier of woven nets is denoted by appending the suffix "**-w**." A COF that has such a woven net (**dia-w**) is described in more detail in 21.3.2 (see Figure 21.9). It is also possible (even though thus far not reported) to form nets of interlocked rings, which is highlighted by appending the suffix "**-y**" to the RCSR identifier. Figure 18.15 shows an example of a woven (**dia-w**) and an interlocking (**sod-y**) net.

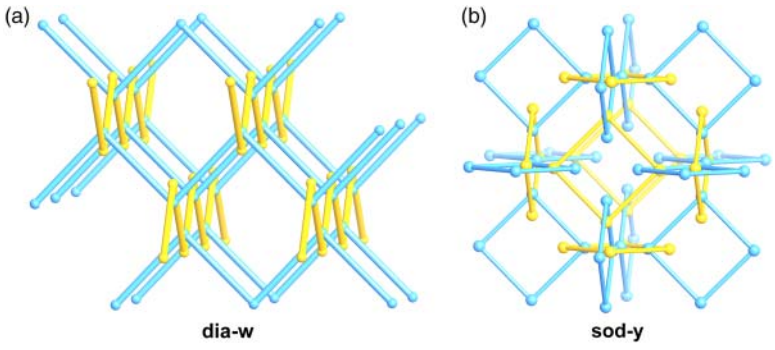


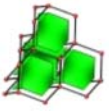

**Figure 18.15** (a) Woven diamond net (**dia-w**). In the woven **dia-w** net independent 1D struts are woven in an up–down–up pattern. The points at which the struts cross (points of registry) correspond to the tetrahedral nodes in the **dia** net. (b) Interlocking sodalite net (**sod-y**). The interlocking **sod-y** net consists of 4-membered ring that are interlocking at each corner of the ring. The points at which the rings cross (points of registry) correspond to the tetrahedral nodes in the **sod** net.

## 18.4 The Reticular Chemistry Structure Resource (RCSR) Database

We have already referred to the RCSR database earlier in this chapter and have used the three-letter identifiers to name topologies [5]. Today, this database comprises 2803 3-periodic, 300 2-periodic, and 78 0-periodic nets (polyhedral), each of which is assigned a unique identifier. These identifiers are sufficient to define a certain net unambiguously. The database lists attributes for every net entry such as the topological density, the number of distinct vertices and edges, the tiling, the topology of the dual net, and the transitivity (Figure 18.16) [6]. The transitivity and the topological density can be used to predict thermodynamic and kinetic products of reactions. Nature prefers the formation of highly symmetric and dense structures, and consequently those are thermodynamically favored. To illustrate this, we consider the **ctn** and the **bor** net. Both consist of square 4-c and trigonal 3-c vertices and in both arrangements each 4-c vertex is connected to four 3-c vertices, and each 3-c vertex is connected to three 4-c vertices. Both nets have the transitivity [2122] but due to a difference in their tiling, they differ in their topological density. The **ctn** net has a higher topological density ($d_{\text{top}} = 0.5513$) than the **bor** net ($d_{\text{top}} = 0.4763$), and this is reflected in the finding that in COF chemistry the **ctn** net is more likely to be formed from the combination of square 4-c and trigonal 3-c building units than the **bor** net.

To allow for the visualization of the nets in the RCSR database structural data (space groups and fractional coordinates of all vertices and edges) for their highest symmetry embedding are given. In the highest symmetry embedding, where the vertices and centers of the edges occupy positions of maximum site symmetry, the lengths of the edges are constrained to be equal to unity, and the volume is subject to that constraint.

Dia



RCSR reference: http://rcsr.net/nets/dia

Names: diamond, sqc6, 4/6/c1
Keywords: regular net, uniform net, self dual net, quasisimple tiling, good
References: Acta Cryst. A59, 22-27 (2003), Acta Cryst. A60, 517-520 (2004)

| Embed type | Space group | Volume | Density | Genus | td10 | Deg freedom |
|---|---|---|---|---|---|---|
| 1a | Fd-3m | 12.3168 | 0.6495 | 3 | 981 | 1 |

| A | B | C | α | β | γ |
|---|---|---|---|---|---|
| 2.3094 | 2.3094 | 2.3094 | 90.0 | 90.0 | 90.0 |

Vertices: 1

| Vertex | cn | *x* | *y* | *z* | Symbolic | Wyckoff | Symmetry | Order |
|---|---|---|---|---|---|---|---|---|
| V1 | 4 | 0.1250 | 0.1250 | 0.1250 | 1/8, 1/8, 1/8 | 8 a | –43m | 24 |

| Vertex | $cs_1$ | $cs_2$ | $cs_3$ | $cs_4$ | $cs_5$ | $cs_6$ | $cs_7$ | $cs_8$ | $cs_9$ | $cs_{10}$ | $cum_{10}$ | Vertex symbol |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V1 | 4 | 12 | 24 | 42 | 64 | 92 | 124 | 162 | 204 | 252 | 981 | 6(2).6(2).6(2).6(2).6(2).6(2) |

Edges: 1

| Edge | *x* | *y* | *z* | Symbolic | Wyckoff | Symmetry |
|---|---|---|---|---|---|---|
| E1 | 0.0000 | 0.0000 | 0.0000 | 0, 0, 0 | 16 c | –3m |

Tiling:

| Tiling | Dual | Vertices | Edges | Faces | Tiles | *D*-symbol |
|---|---|---|---|---|---|---|
| [6^4] | dia | 1 | 1 | 1 | 1 | 2 |

**Figure 18.16** Entry for the **dia** net in the RCSR database. A representation of the topology is given at the top (here, the tiling is also shown). The space group, unit cell parameters, and fractional coordinates for the vertices and edges represent the highest symmetry embedding of the net and give information about their local site symmetry. The transitivity (see tiling: vertices, edges, faces, tiles) and the topological density can help to predict the outcome of a reticulation.

## 18.5 Important 3-Periodic Nets

We discussed the concept of transitivity in Section 18.2.5. The transitivity is described by the four parameter "*pqrs*" of the tiling carrying that particular net where $p$ is the number of topologically distinct vertices, $q$ is the number of topologically distinct edges, $r$ is the number of distinct faces or rings in the tiling, and $s$ is the number of different types of tiles [8]. 3-periodic nets with transitivity 1111 are referred to as "regular nets" (**bcu**, **dia**, **nbo**, **pcu**, and **srs**), 3-periodic nets with transitivity 1112 are referred to as "quasiregular nets" (**fcu**), and those

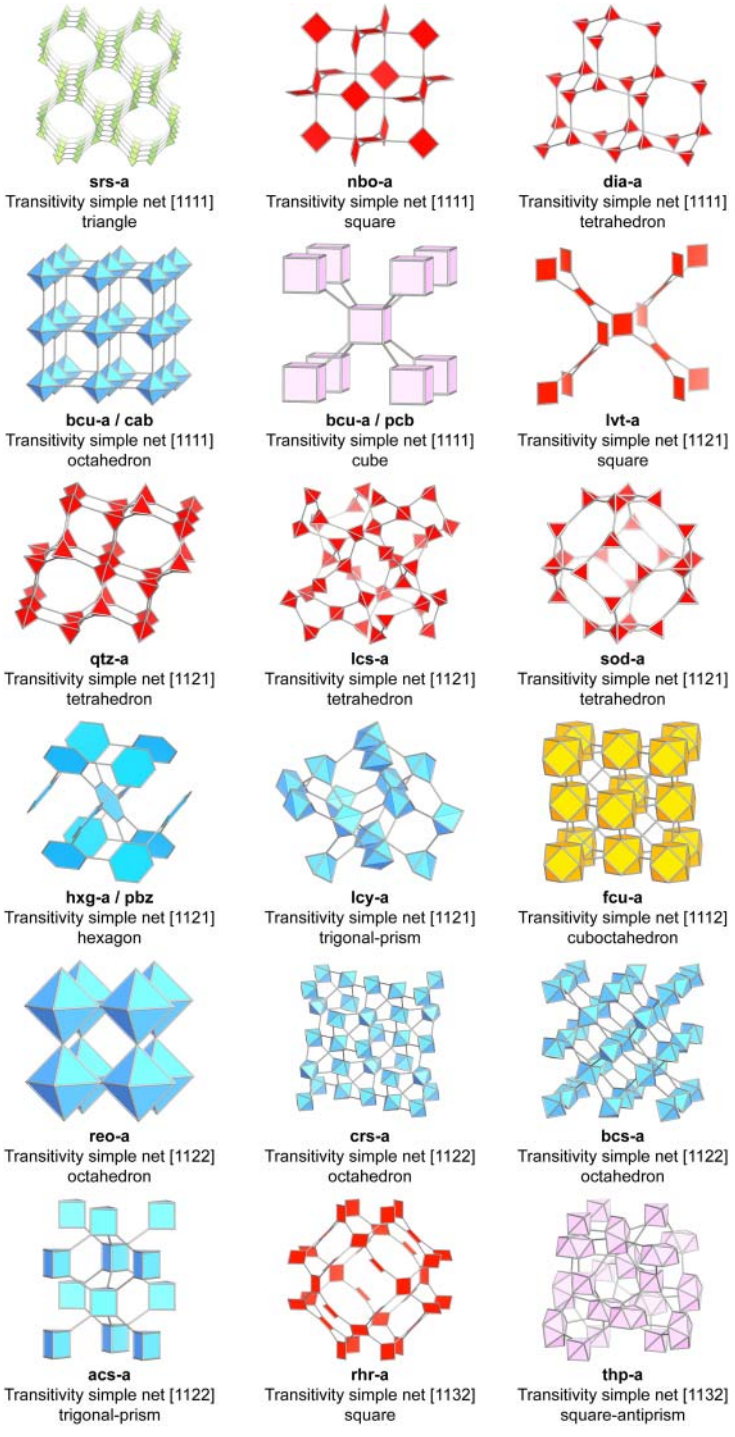



**Figure 18.17** 3-periodic "regular," "quasiregular," and "semiregular" nets sorted by the digit sum of the transitivity for the corresponding simple net. All nets are shown in their augmented form, with their respective RCSR identifier, and the transitivity of the corresponding simple net. 3-c vertices are shown in green, 4-c vertices in red, 6-c vertices in blue, 8-c vertices in pink, and 12-c vertices in orange.

with transitivity 11*rs* are referred to as "semiregular" (**lvt**, **sod**, **lcs**, **lcv**, **qtz**, **hxq**, **lcy**, **crs**, **bcs**, **acs**, **reo**, **thp**, **rhr**, and **ana**). These three groups of 3-periodic nets are the ones that are most likely to form when one type of vertex is linked by one type of edge, or in terms of MOF chemistry, one type of SBU is reticulated with a ditopic linker [3c, 6]. All regular, quasiregular, and semiregular nets are shown in Figure 18.17 in their augmented form. As outlined before, for the combination of two building units of similar (or identical) geometry, those nets with the lowest transitivity, the most symmetric highest symmetry embedding, and the highest topological density are the most likely to form. This holds especially true for combinations of single metal ions linked by flexible linkers. We refer to these topologies as the default topologies for a given combination of vertex geometries. In reticular chemistry, geometrically well-defined, rigid building units are used to form extended framework structures, and by their judicious choice and under appropriate reaction conditions, topologies other than the default ones can be targeted.

All nets shown in Figure 18.17 consists of one type of vertex and one type of edge and are thus referred to as "uninodal edge-transitive nets." Edge-transitive nets are the most likely products of reticular synthesis. Therefore, nets that are edge-transitive but built from two different types of vertices ("binodal"), where each type of vertex is only connected to the second type of vertex ("bipartite"), are of great importance for reticular chemistry. All binodal, bipartite edge-transitive nets are given in Figure 18.18.

Aside from the nets discussed above, where discrete vertices are connected by edges, 1D vertices can be linked into nets. Such structures are found in MOF chemistry, where rod-like SBUs can form to give 3D frameworks. These structures are not as common as those discussed above and for a more detail discussion of rod-MOFs and their topological description, the reader is referred elsewhere [9].

## 18.6 Important 2-Periodic Nets

Many frameworks have 2D layered structures. This is especially true for COFs. Such structures can either be described as 3-periodic (stacked 2-periodic nets) or 2-periodic nets. An example for this is the description of staggered **hcb** layers by the **gra** net (see Figure 18.12). This description is confusing since the 2D layers are only held together by weak interactions rather than actual "links," which makes the definition of edges between vertices of neighboring layers difficult. Consequently, the description of such structures as 3-periodic nets is generally not helpful for the overall understanding and the topological description of layered structures as 2-periodic nets is preferred. In analogy to the transitivity of 3-periodic nets, the transitivity of the tiling of a plane with $p$ kinds of vertex, $q$ kinds of edge, and $r$ kinds of ring is given as [$pqr$] [6]. There are a total of five possible edge-transitive 2-periodic nets: (i) three "regular nets" with transitivity 111 (**hcb**, **sql**, and **hxl**), (ii) one "quasiregular net" with transitivity 112 (**kgm**), and (iii) and one binodal net with transitivity 211 (**kgd**). These nets are shown in Figure 18.19 alongside their augmented versions.

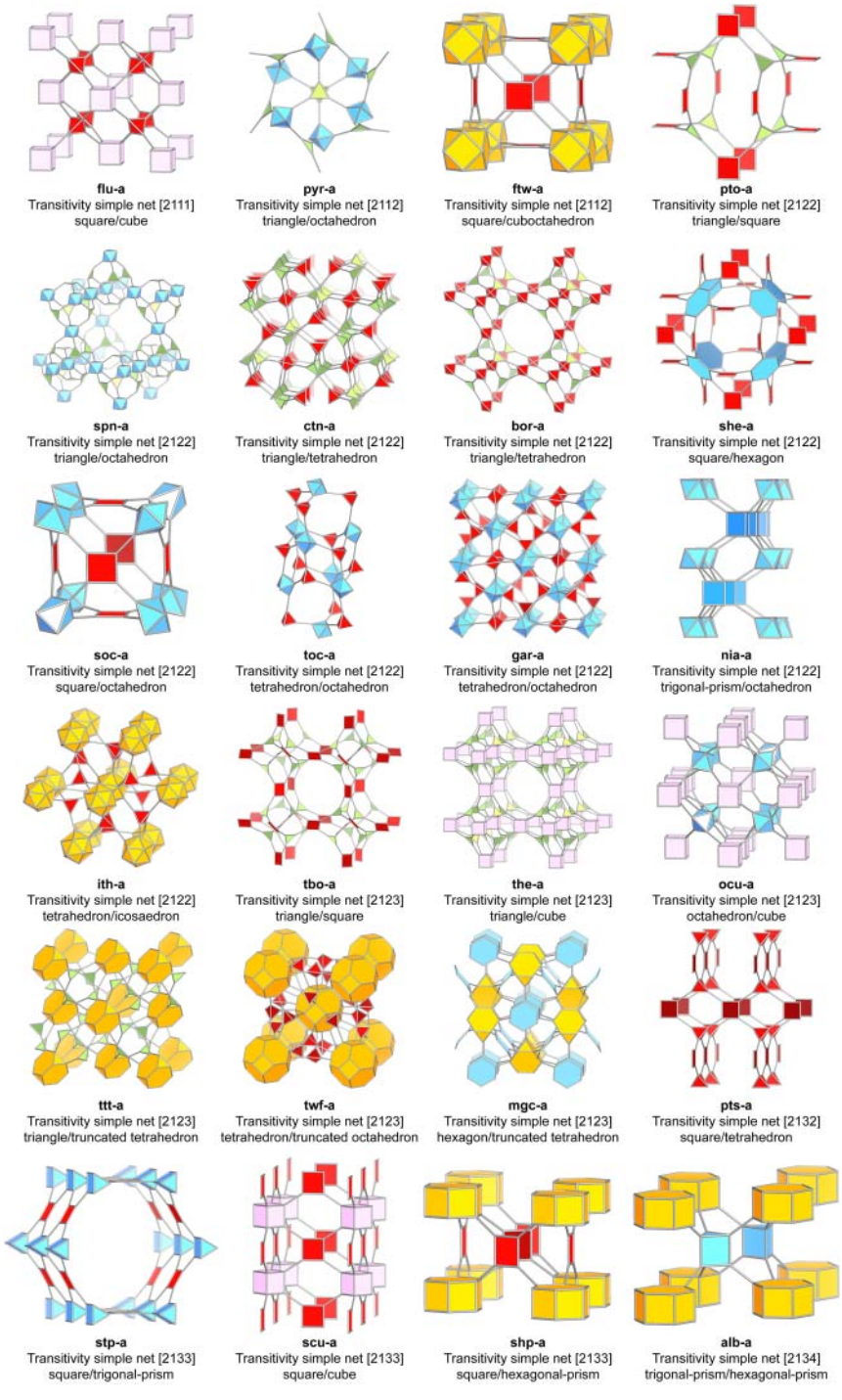



**Figure 18.18** 3-periodic binodal edge-transitive nets sorted by the digit sum of the transitivity for the corresponding simple net. All nets are shown in their augmented form, with their respective RCSR identifier and the transitivity of the corresponding simple net. 3-c vertices are shown in green, 4-c vertices in red, 6-c vertices in blue, 8-c vertices in pink, and 12-c as well as 24-c vertices in orange.

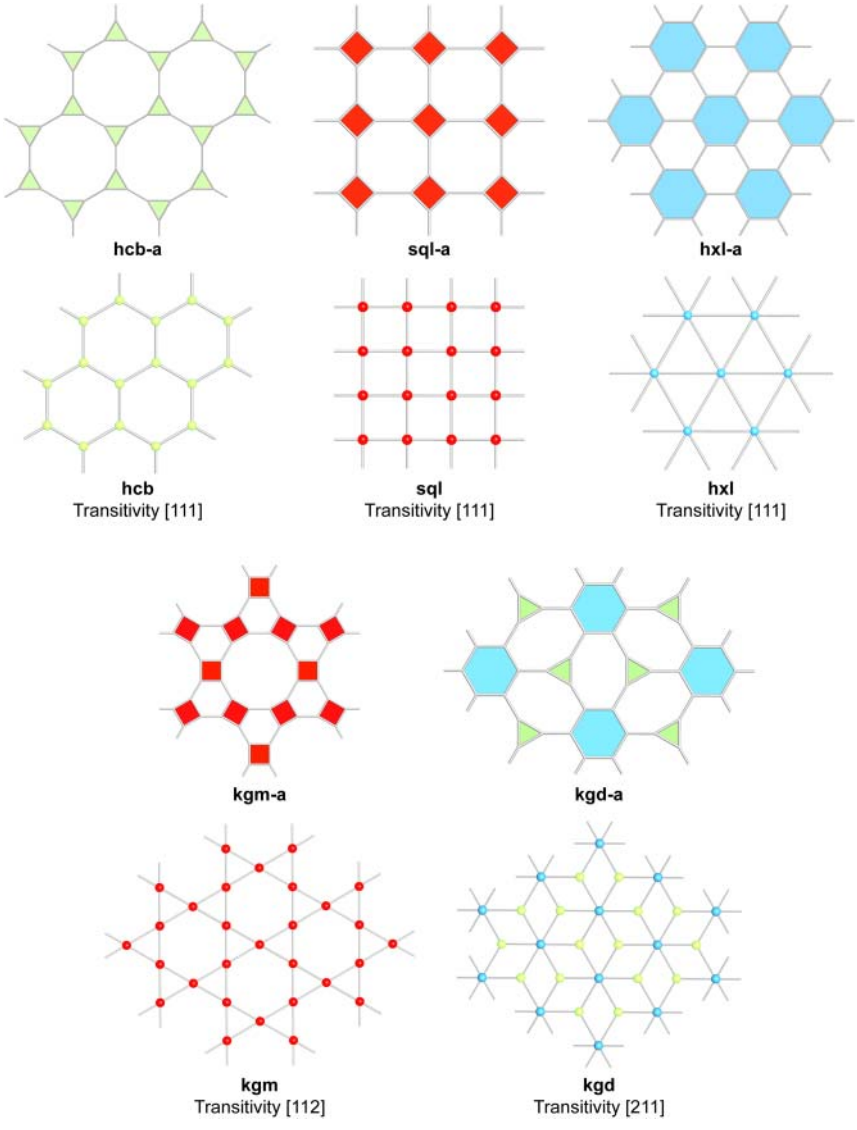



**Figure 18.19** The five edge-transitive 2-periodic nets. Both the simple and augmented nets are shown and the transitivity for the simple net is given. 3-c vertices are shown in green, 4-c vertices in red, 6-c vertices in blue.

## 18.7 Important 0-Periodic Nets/Polyhedra

Reticular chemistry does not only involve the making of 2D and 3D extended structures but also that of complex molecular moieties (see Chapter 19). So far, we discussed the topological description of framework structures (e.g. MOFs, ZIFs, and COFs) as 2- or 3-periodic nets, and discrete polyhedra are described in

a similar way. This is important not only for the description of molecular entities such as metal-organic and covalent organic polyhedra (MOPs and COPs), but also for the topological description of individual cages within framework structures [10]. As in the case of 3-periodic and 2-periodic nets, the most frequently encountered 0-periodic polyhedra in reticular chemistry are edge transitive and among these, the most commonly observed ones are "regular convex polyhedra" or "Platonic solids." Such polyhedra have one kind of vertex, one kind of edge, and one kind of face and consequently have a transitivity of [111] (**tet**, **oct**, **cub**, **ico**, and **dod**). The second most common polyhedra are "quasiregular" polyhedra, which have one kind of vertex and edge, but two kinds of face and therefore a transitivity of [112] (**rdo** and **cuo**). There are two more edge-transitive polyhedra with a transitivity [211], meaning they have two kinds of vertex, one kind

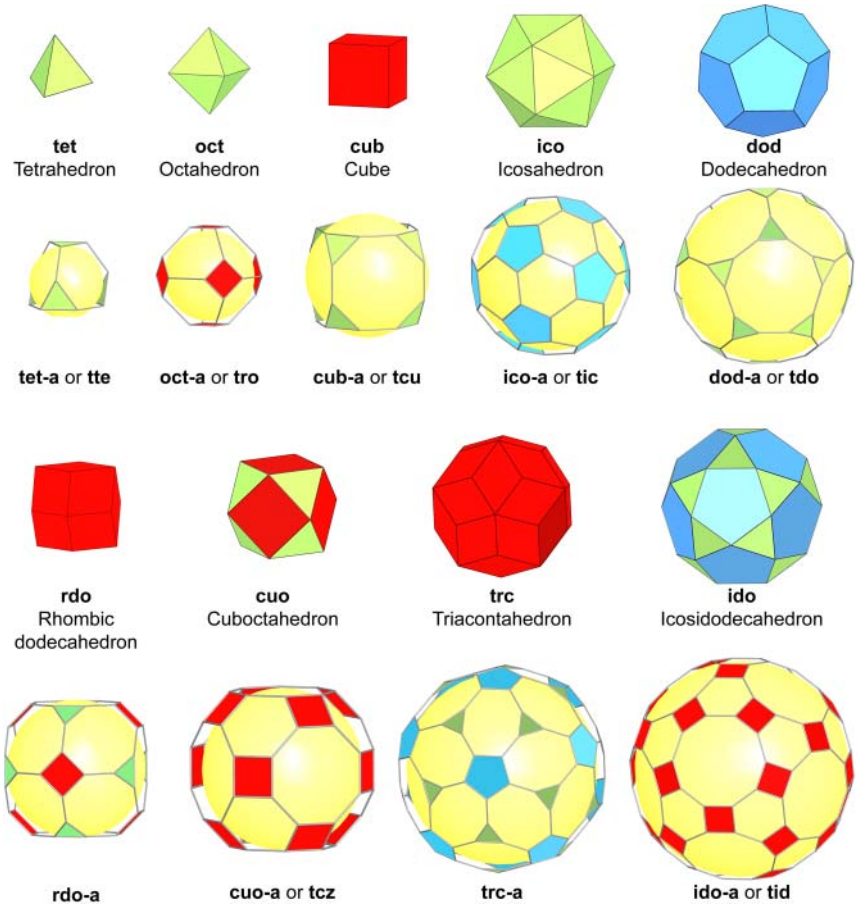



**Figure 18.20** 0-periodic "regular," "quasiregular," and "semiregular" tilings. Both the Platonic solids and their augmented counterparts are shown. 3-c vertices and trigonal faces are shown in green, 4-c vertices and quadrangular faces in red, and 5-c vertices and pentagonal faces in blue. The yellow sphere in the augmented representation is added for clarity and represents the potential voids within compounds of this topology.

of edge, and one kind of face (**trc** and **ido**). These polyhedra are the duals of the "quasiregular" polyhedra.

Edge transitive polyhedra are the most common polyhedra in reticular chemistry. The reason therefore is that the vertex figure of their augmented versions (in their highest symmetry embedding) are regular polygons (e.g. triangle, square, and pentagon), shapes that are synthetically accessible molecular building units [6] (Figure 18.20).

## 18.8 Summary

In this chapter, we introduced the concept of "topology" as a way to describe, simplify, and classify structures of extended solids based on the connectivity of their building units, their spatial arrangement, and the resulting pattern of connections arising therefrom. We introduced the nomenclature used by the RCSR to unambiguously identify net topologies. After introducing the concept of transitivity, we took a closer look at 3-periodic, 2-periodic, and 0-periodic edge-transitive nets, which are the most frequently encountered nets in reticular chemistry. The concept of topology is not only helpful in simplifying crystal structures and classifying them, but also for the deliberate and rational design of new materials, and this aspect is discussed in more detail in other chapters of this book (for MOFs (Chapters 1–6), ZIFs (Chapter 20), COFs (Chapters 7–11), and MOPs and COPs (Chapter 19)).

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