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Nets with collisions (unstable nets) and crystal chemistry

Olaf Delgado-Friedrichs,[a] Stephen T. Hyde,[a] Shin-Won Mun,[b] Michael O'Keeffe[b,c]* and Davide M. Proserpio[d,e]

[a]Department of Applied Mathematics, Research School of Physics, Australian National University, Canberra, ACT 0200, Australia, [b]Graduate School of EEWS(WCU), KAIST, 373-1, Guseng Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea, [c]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA, [d]Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi, 19, 20133 Milano, Italy, and [e]Samara Center for Theoretical Materials Science (SCTMS), Samara State University, Ac. Pavlov St 1, Samara 443011, Russia. Correspondence e-mail: mokeeffe@asu.edu

Nets in which different vertices have identical barycentric coordinates (*i.e.* have collisions) are called unstable. Some such nets have automorphisms that do not correspond to crystallographic symmetries and are called non-crystallographic. Examples are given of nets taken from real crystal structures which have embeddings with crystallographic symmetry in which colliding nodes either are, or are not, topological neighbors (linked) and in which some links coincide. An example is also given of a crystallographic net of exceptional girth (16), which has collisions in barycentric coordinates but which also has embeddings without collisions with the same symmetry. In this last case the collisions are termed *unforced*.

1. Introduction

In this paper we are concerned with periodic nets which are simple connected periodic graphs [see *e.g.* Delgado-Friedrichs & O'Keeffe (2005) for terminology and definitions] often encountered in the analysis of the topology of crystal structures. It is convenient at the outset to distinguish between abstract nets and their Euclidean embeddings (Chung *et al.*, 1984). Specifically in this paper the vertices and edges of the graph correspond to nodes and links in an embedding. One reason for doing this is that we want to refer to the length of a link, whereas the 'length' of a single edge of a graph has no meaning.

The classical nets of crystal chemistry are mostly the nets of sphere packings, *i.e.* they have embeddings in which all links are of equal length and are the shortest distances between nodes. The net of diamond is a familiar example. The taxonomy of such nets and their relevance to materials design are now reasonably well established (Delgado-Friedrichs *et al.*, 2007) at least for those nets which admit tilings. However, particularly as the synthesis of metal–organic frameworks (MOFs) has developed, many nets have been discovered that do not admit tilings because many of the strong rings (cycles that are not the sum of smaller cycles) are catenated with other rings (Delgado-Friedrichs *et al.*, 2005). A recent example of a crystal structure based on a net in which *every* ring is catenated with another is provided by Yu *et al.* (2012). In the present paper we call attention to another class of nets, so far little discussed, in which different nodes are at the same site in high-symmetry embeddings. Some of these are also nets with entangled strong rings.

A very useful approach to analysis of periodic nets is to first compute a *placement* in which one vertex is arbitrarily assigned coordinates (*e.g.* 0, 0, 0) and the rest then assigned *barycentric coordinates* that are the average of those of their neighbors. It is easy to show that this results in a unique set of coordinates (Delgado-Friedrichs, 2005). These are unit-cell coordinates in the usual crystallographic sense and are independent of any metric associated with the size and shape of the unit cell; for this reason one refers to a *placement* rather than an *embedding*. The idea appeared early in the work of Tutte (1960, 1963) on finite graphs. The resulting set of coordinates for periodic graphs has been called a *standard realization* by Kotani & Sunada (2000) and an *equilibrium placement* by Delgado-Friedrichs (2004, 2005). These authors show that the coordinates are those that would result at equilibrium (minimum energy) for any finite fixed unit-cell volume if the links of the net were replaced by uniform harmonic springs. As discussed below, for certain graphs two or more nodes have identical barycentric coordinates and we say that such a graph has *collisions*. Graphs without collisions were called *stable* by Delgado-Friedrichs (2005). Barycentric coordinates are central to the algorithms of *Systre*, a computer program for determining the symmetry and identity of periodic nets (Delgado-Friedrichs & O'Keeffe, 2003) and which was used to determine symmetries in this work.

Recently we have called attention to a class of nets with collisions that nevertheless have crystallographic symmetry (de Campo *et al.*, 2013; see also Eon, 2011). This raises the questions as to what are the requirements for a graph with collisions to be crystallographic and whether such nets are relevant to crystal chemistry. The latter question is addressed in this paper. We do not discuss nets known to have non-crystallographic symmetry ('NC nets') which have been the topic of several recent publications (Moreira de Oliveira Jr & Eon, 2011, 2013). Nor do we discuss the possible symmetries of embeddings with all finite links of unstable graphs; that topic has also recently been addressed by Thimm (2009) and by Eon (2011).

We have occasion below to refer to the *quotient graph* of a net. This is the finite graph with all translationally equivalent points merged into one, and the edges labeled to indicate the adjacencies of vertices (Chung *et al.*, 1984).

We will find examples of different graphs that have embeddings with identical arrays of nodes and links (*i.e.* they coincide as sets of points and lines). Following a suggestion of Grünbaum (2003) we refer to such structures as *isomeghethic*.

Net symbols of the sort **abc** or **abc-d** are RCSR (Reticular Chemistry Structure Resource) symbols (O'Keeffe *et al.*, 2008) and data for them are available at the RCSR web site (http://rcsr.anu.edu.au/). That site also reports vertex symbols (Blatov *et al.*, 2010). The nets discussed here generally have very high topological density (O'Keeffe, 1991). The RCSR reports TD_{10} which is the average over all vertices of the number of vertices reachable from each vertex in paths of 0 to 10 edges. Some also have exceptional girth (called 'smallest ring' in the RCSR). Nets for which the shortest rings at every angle are equal are called *uniform* by Wells (1977), who attached special importance to them in crystal chemistry. Several of the nets in this paper are uniform.

2. Polygons and polyhedra with collisions

It is instructive to first consider some finite structures with collisions between vertices. Specifically an abstract *p*-gon (a polygon with *p* vertices) is a simple cycle with *p* vertices and *p* edges. The regular polygons were long ago generalized from those with embeddings as a convex figure with symbol {*p*} to include the star polygons {*p*/*n*} (illustrated in Fig. 1 for *p* = 8). Usually *p* and *n* are considered co-prime but, as Grünbaum (2003, 2007) points out, for complete generality one should really take all cases of $n \leq p/2$ even though nodes become coincident when *p* and *n* are not co-prime.

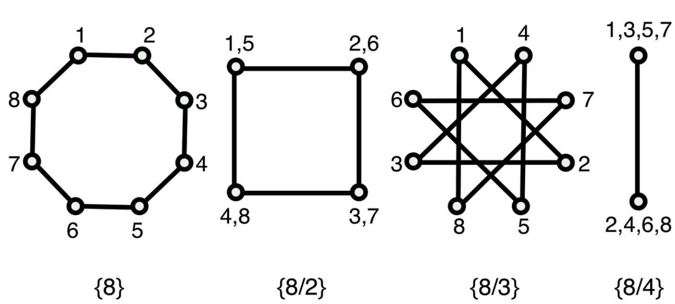

Figure 1
The regular octagons. In each case the edges are 12 23 34 45 56 67 78 81.

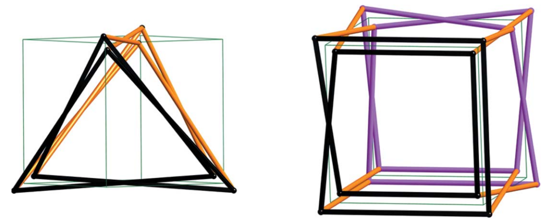

Figure 2
Left, the polyhedron {6/2,3}. One hexagonal face is in black. Right, the polyhedron {8/2,3}. Two octagonal faces are shown in black and magenta, respectively.

These generalized polygons can serve as the faces or vertex figures of regular polyhedra with Schläfli symbol {*h*, *k*} in which faces are {*h*} and the vertex figures are {*k*}. The Platonic solids are {3,3}, {3,4}, {4,3}, {3,5} and {5,3}. Adding star polygons one gets the regular icosahedral Kepler–Poinsot polyhedra {5/2,3}, {3,5/2}, {5/2,5} and {5,5/2}. Grünbaum adds to these regular polyhedra such as {6/2,3} and {8/2,3} (see Fig. 2), {12/3,3} and so on indefinitely. {6/2,3} is the same combinatorially as the cube {4,3}, a fact that emphasizes that the cube can also be considered as having intersecting faces that are skew hexagons (Petrie polygons, see *e.g.* O'Keeffe, 2008) so {6/2,3} does not have a maximum-symmetry embedding with coincident nodes.

3. Non-crystallographic and crystallographic nets with collisions

Perhaps the simplest case of occurrence of collisions in nets is when two vertices have the same neighbors (Moreira de Oliveira Jr & Eon, 2013). Clearly there is a net automorphism that simply involves interchanging those two vertices leaving the rest fixed. This cannot correspond to a crystallographic symmetry operation which acts on rigid bodies. Such non-rigid-body symmetries can lead to complicated automorphism groups, as is well documented for non-rigid molecules (Longuet-Higgins, 1963). They are sometimes called 'local symmetries' but this term is also used to refer to short-range spatial arrangements in crystals. Moreira de Oliveira Jr & Eon (2013) call them 'bounded automorphisms'. A common occurrence of such collisions in the graph of a chemical structure is found in the familiar copper carboxylate paddle-wheel shown in Fig. 3. Usually in determining the underlying

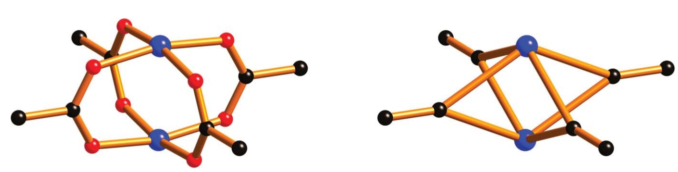

Figure 3
Left, part of a structure with the paddlewheel secondary building unit. Carbon atoms black, oxygen red and copper blue. On the right the –O– links shown as single links and the two Cu atoms linked to the same four C atoms.

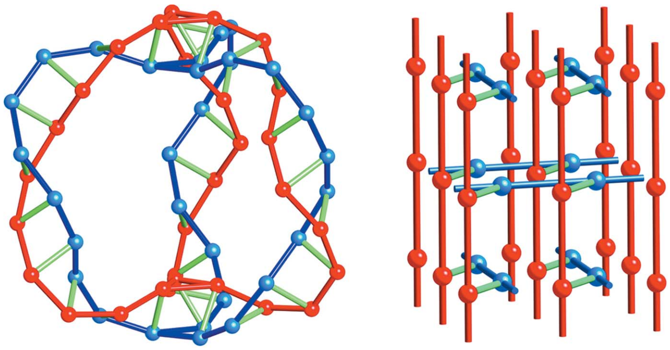

Figure 4
Left, a fragment of a 3-periodic ladder structure (the 'rungs' are green). Nodes are all 4-coordinated as shown near the top and bottom. Right, an 'antiladder' structure from de Campo *et al.* (2013). Rungs are again green. Red and blue nodes collide and the resulting structure is tetragonal ($P4_2/mmc$) isomeghethic with **cds**.

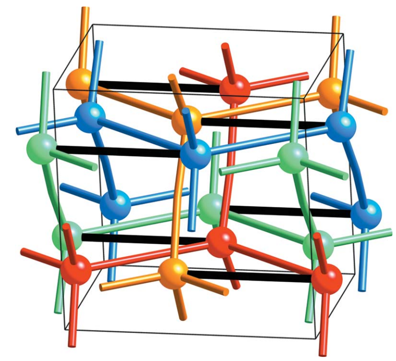

Figure 5
Four interpenetrating diamond nets joined by a fifth link, black. Note that the red and blue nets are not directly linked, nor are the yellow and green ones. This is net **rld-z**.

topology of a molecule or crystal, 2-coordinated (2-c) nodes such as a linking –O– atom are subsumed into edges so that both Cu atoms are considered directly linked to the same four carboxylate C atoms (the *points of extension* of the copper *secondary building unit*). The usual procedure at this point in determining a net is simply to replace the two Cu atoms with one 4-c node.

A generalized *ladder* is obtained when a finite number (two or more) of identical interpenetrating nets are joined by extra links in such a way that the nodes connected by the extra links are in identical orientation. In such a situation there are automorphisms of the whole structure that map any copy of the component nets to any other copy while not changing their orientation in space. If these automorphisms were to be taken as crystallographic operations they would have to be translations, but because they are a finite set that is clearly impossible. An example of a 3-periodic ladder is shown in Fig. 4. The embedding comes from a sphere packing with an embedding in $I4_132$. This is the sphere packing 4/3/*c*26 of Fischer (1974) with RCSR symbol **uld-z**.[1]

On the other hand if all colliding nodes were linked to different nodes, that did not themselves collide with each other, they can be distinguished and symmetry determined. Thus two or more component subnets could come together without links superimposing. We call these *antiladders*. A simple example is shown in Fig. 4 in which the components are rods running in orthogonal directions. This example is in fact the net called 4(3)5, one of the crystallographic minimal nets with collisions discussed by de Campo *et al.* (2013) and Eon (2011).

The process of distinction of nodes by their neighbors can be extended to further neighbors, but after next-nearest neighbors the procedure becomes rather complex to implement in practice. Indeed, the computer program *Systre*, which is the major source of symmetry information for periodic graphs, gives up at the point where next-nearest neighbors have collisions. In all the unstable nets discussed in this paper colliding vertices are distinguishable as described above, and *Systre* reports a crystallographic symmetry and an embedding in that symmetry which is used in this work.

It should be remarked that *Systre* only looks for automorphisms of the net that are consistent with the given periodic structure, *i.e.* a translation group *T*. In principle it is still possible that other automorphisms could occur as described by Moreira de Oliveira Jr & Eon (2011) and we cannot at present prove their absence mathematically. To allow for this eventuality we say that our nets are *T-crystallographic* and refer to the symmetry determined by *Systre* as the *Systre symmetry*. However our main purpose is simply to get a crystallographic symmetry so we can present an embedding with collisions required by that symmetry.

4. Nets with zero-length links in maximum-symmetry embeddings

4.1. A net based on interpenetrating diamond nets

We (de Campo *et al.*, 2013) earlier called attention to the fact that, although all the minimal (genus 3) nets had crystallographic symmetry (Eon, 2007), seven of them had collisions in their maximum-symmetry embeddings. In those embeddings they were isomeghethic to one of the minimal nets without collisions. We have not yet identified any of these minimal nets with collisions as the topologies of real crystal structures. However, an interesting structure reported by Montney *et al.* (2007) does have an underlying topology of this type. In the structure (2) of those authors, four interpenetrating 4-c **dia** (diamond) nets are joined into one continuous network by a fifth link between pairs of nodes. An illustration with symmetry *Pbcn* (the same as the observed crystal structure) is in Fig. 5. The net has the interesting property that each **dia** subnet is directly joined to only two of the three others and in fact can also be drawn as *two* interpenetrating **dia** nets joined by a fifth link as shown in Fig. 6. In that drawing links partly overlap; however, in the limit of a full symmetry embedding, one link has zero length and nodes

[1] The net of this sphere packing is the same graph as that of sphere packing 4/3/*c*25 but the two embeddings (**uld** and **uld-z** in the RCSR) are not ambient isotopic (cannot be transformed from one to the other without breaking and reforming links) (see Moreira de Oliveira Jr & Eon, 2013).

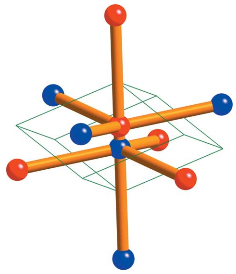

Figure 6
A fragment of two interpenetrating **dia** nets linked by a short fifth link. Note that the only links are between nodes colored red and blue.

coincide in pairs. The *Systre* symmetry is $Im\bar{3}m$ with both vertices at 0, 0, 0 so it is in fact isomeghethic with the net of the nodes of the body-centered lattice with shortest lattice vectors as links, RCSR symbol **bcu**. Another notable feature of the structure is that all the rings are 6-rings with three at each angle so 30 meeting at each vertex (compare 12 meeting at each vertex for **dia**). In the RCSR the *Pbcn* embedding is given with the symbol **rld-z**. The extension **-z** indicates that the embedding is not a maximum-symmetry one. In that embedding all links are equal length and do not intersect or overlap; it is an interesting question whether this is the highest-symmetry embedding with this property.

4.2. Other nets derived from linked interpenetrating pairs of diamond nets

Linked pairs of diamond nets give rise to a number of other interesting topologies. Fig. 7 illustrates the most symmetrical ($Pn\bar{3}m$) embedding of a pair of interpenetrating diamond nets. This has been known in crystal chemistry for 100 years as the structure of the O atoms of cuprite, Cu_2O, with –Cu– acting as links (Bragg & Bragg, 1915). Connecting the two vertices in the unit cell gives a 5-c stable net with symmetry $R\bar{3}m$ with RCSR symbol **fnu** (Fig. 7). This net also has all 6-rings, now with 48 meeting at each vertex. It might be noted that, although many of those rings are catenated with other rings as they come from catenated **dia** nets, not all are catenated and this net does admit a tiling (Blatov *et al.*, 2007).

If only half the vertices were linked to produce a (4,5)-c net as shown in Fig. 8, then one gets again a net with collisions (data given in the RCSR as **sld-z**). The pairs of newly linked

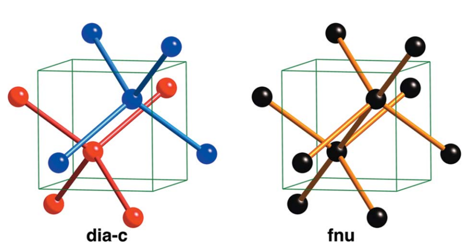

Figure 7
Left, the cubic ($Pn\bar{3}m$) cell of two interpenetrating **dia** nets. Right, a primitive rhombohedral ($R\bar{3}m$) cell of **fnu**. The extra link is along [111] of that cell.

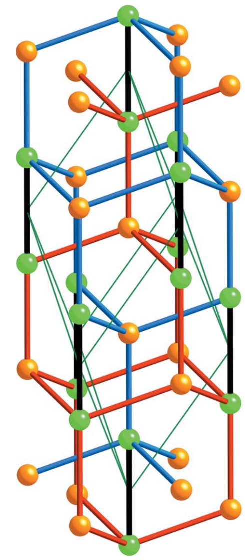

Figure 8
An equal-link embedding (**sld-z**) of a (4,5)-c net with collisions. Red and blue links outline **dia** nets.

vertices collide and now one gets a structure isomeghethic with the fluorite net, **flu**, and with symmetry $Fm\bar{3}m$, pairs of 5-c vertices at 0, 0, 0 and single 4-c vertices at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. A double interpenetrated **sld-z** is observed for a viologen Zn complex (Tan *et al.*, 2012), although the authors did not discuss it in these terms.

If, alternatively, nodes of pairs of diamond nets were linked so that previously unlinked nodes in the same orientation are linked, then in barycentric coordinates two copies of the same structure, including links, are superimposed. Accordingly the structure is a (non-crystallographic) ladder.

Fig. 9 shows quotient graphs for the diamond-related nets.

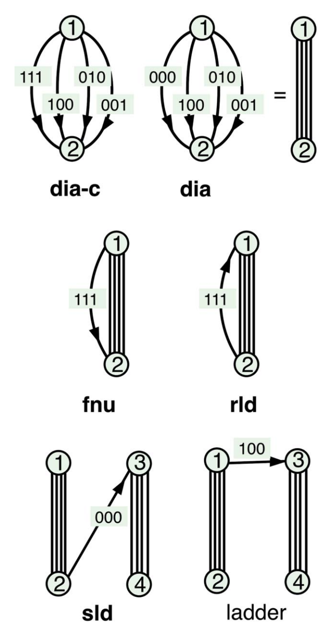

Figure 9
Quotient graphs for nets with **dia** nets as sub-graphs.

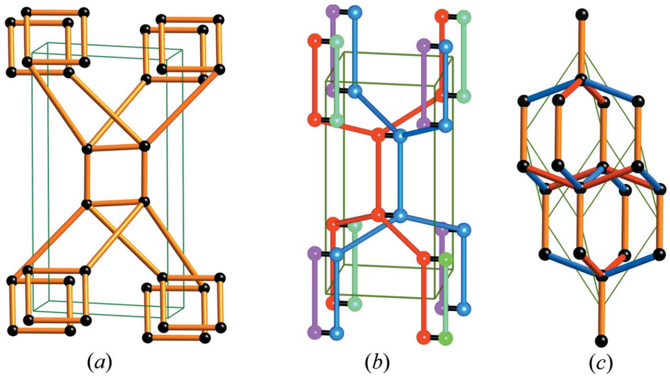

Figure 10
(*a*) An embedding of the net **hxc** using the coordinates of the nodes in the crystal structure. (*b*) An embedding with short links (black). In the maximum-symmetry embedding those links have zero length. Different color links belong to separate **ths** nets. (*c*) A primitive cell of the **sqp** net isomeghethic with the maximum-symmetry embedding of **hxc**.

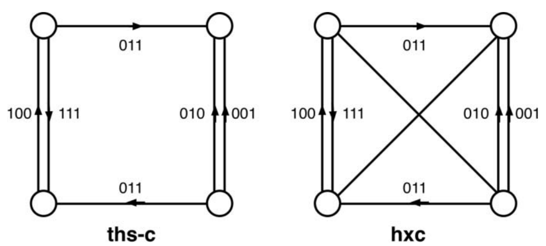

Figure 11
Quotient graphs for **ths-c4** and **hxc**. The graph on the right has the same labeling as that on the left but with two extra edges (shown as diagonal lines with labels 000).

4.3. A net with collisions related to the ths net

Our next net, RCSR symbol **hxc**, was found in a copper imidazolate MOF by Huang *et al.* (2004). Long and shorter ditopic linkers combine to link Cu atoms into a uninodal 4-c net as shown for the real structure with symmetry $P2_1/n$ in Fig. 10. This net has vertex symbol $4.8_4.8_4.8_6.8_4.8_6$, *i.e.* 24 8-rings meeting at each vertex, and is rather dense (TD_{10} = 1918, compare 981 for **dia**). The structure has collisions in the *Systre* symmetry of $I4/mmm$ and pairs of nodes in 0, 0, z with $z \sim 0.18$. Now 4-rings collapse so both links and nodes collide as shown in the figure. The figure also illustrates that again the net can be considered as four linked subnets, that are now the 3-c minimal net **ths** (rather than the 4-c **dia** in the previous example), joined by zero-length links. There are just four nodes in the primitive cell – the same as for **ths** and **ths-c4** (four interpenetrating **ths** nets) and the structure is isomeghethic with the 5-c net **sqp**, also shown in Fig. 10.

It is interesting that the quotient graph for four interpenetrating **ths** nets can be labeled in such a way that additionally linking two pairs of vertices with edges labeled 0, 0, 0 produces the quotient graph for **hxc** (Fig. 11).

4.4. A net with collisions related to the srs net

A structure of two linked **srs** nets was recently reported by Wang *et al.* (2013). In that work it was found that a copper cyanide MOF formed two interpenetrating 3-c nets with the **srs** topology with opposite hand. **srs**, like **ths** of the previous example, is a minimal net as it has the minimal number (four) of 3-c vertices in the repeat unit. One fourth of the nodes in the nets are Cu atoms which form Cu–Cu links between the two nets. In barycentric coordinates these pairs of vertices collide and the *Systre* symmetry becomes $R\overline{3}m$. For the two nets to have the exact shape of the cubic **srs** net the 3-c vertices are at $\frac{1}{4}$, 0, 0 and the 4-c vertices collide in linked pairs at 0, 0, 0. For unit link length the unit-cell parameters are $a = 4$, $c = 6^{1/2}$. This structure is illustrated in Fig. 12. The net has an embedding as a sphere packing (links equal and the shortest distance between nodes) in $R\overline{3}$ with a = 4.000, c = 2.4495, 4-c nodes at 0, 0.0, 0.2041 and 3-c nodes at 0.0000, 0.2500, 0.2041. The vertex symbol is $(8.8.10_6)_3(8_2.10_5.8_2.10_5.8_2.10_5.)$. This is assigned RCSR symbol **llw-z**.

The quotient graph is just a linked pair of graphs K_4 (the complete graph with four vertices) as shown in Fig. 13.

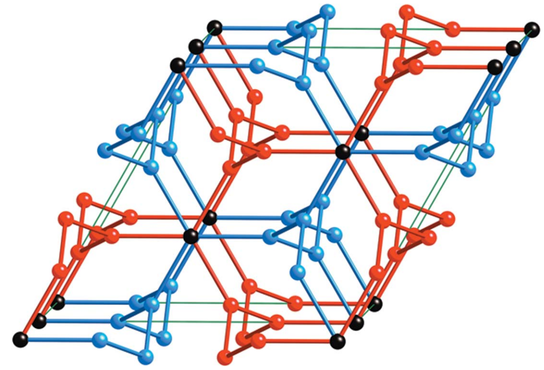

Figure 12
Two **srs** nets (red and blue) of opposite hand colliding at the nodes shown in black.

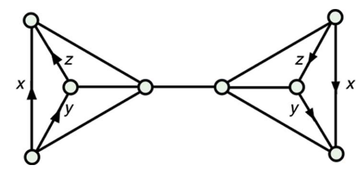

Figure 13
The quotient graph of the net shown in Fig. 12.

5. A net with collisions but with all links of non-zero length

A less common occurrence is that of nets in which at maximum-symmetry embedding nodes collide but all links have finite length. Indeed we are aware of just one example from a crystal structure (Ma *et al.*, 2013). Linking $Cu_2(-CO_2)_4$ paddlewheels with a very non-planar tritopic carboxylate linker gave a new edge-transitive (3,4)-c net with RCSR symbol **mhq**. The structure is uniform of girth 12 – the vertex symbol is $(12_{15}.12_{15}12_{15})_4(12_6.12_6.12_{12}.12_{12}.12_{12}.12_{12})_3$. As Ma *et al.* discuss, the structure is topologically very dense and the 12-rings catenated to a remarkable degree.

The crystal structure has symmetry $F432$ and an embedding of the net in that symmetry is obtained with the 4-c vertex at $x_1, 0, 0$ and the 3-c vertex at x_2, x_2, x_2 with links from $x_1, 0, 0$ to $\frac{1}{2} - x_2, x_2, \frac{1}{2} + x_2$ as shown in Fig. 14 (drawn with $x_1 = 0.25$ and $x_2 = 0.3$). However the *Systre* symmetry is the supergroup $P432$ with $\mathbf{a}' = \mathbf{a}/2$ and the 3-c vertices merge in groups of four to a common coordinate set as suggested in the figure. The structure specification in $P432$ is 4-c vertex at $\frac{1}{2}, 0, 0$ and four 3-c vertices at 0, 0, 0 with edges from 0, 0, 0 to $\frac{1}{2}, \frac{1}{2}, 0$; note however the ambiguity in this description – a point at 0, 0, 0 has 12 neighbors symmetry-related to $\frac{1}{2}, \frac{1}{2}, 0$ and is isomeghethic to the (4,12)-c net **ftw**. Accordingly the net topology is best specified either by its lower-symmetry embedding or its quotient graph (see below).

The net is interesting in that there are embeddings in $F432$ with links of arbitrarily large length (measured in units of the unit-cell edge length a). Thus links from $\frac{1}{2} - x_2, x_2, \frac{1}{2} + x_2$ to $i + x_1, j, k$ with i, j and k integers, together with symmetry-related links, are always embeddings of the same graph. So are links from the same reference node ($\frac{1}{2} - x_2, x_2, \frac{1}{2} + x_2$) to $i, j, k + x_1$. However links, again from the same reference node, to $i, j + x_1, k$ generally produce multiple copies of the same net in a complicated way. For example a link to $0, x_1, k$ produces $2^3.(k-1)^3$ interpenetrating **mhq** nets.[2]

We call attention to yet another aspect in which the **mhq** net is special. It and the edge-transitive (3,4)-c net **bor** are the only two such nets known that have as quotient graph the complete bipartite graph $K_{3,4}$. These two quotient graphs are shown in Fig. 15.

Finally we note that **mhq** has the largest girth (12) of any known edge-transitive 3-periodic graph without 2-c vertices.

6. A second net with collisions and no zero-length links

Here we discuss another net that describes a crystal structure (Volkringer *et al.*, 2009).[3] The structure contains $Mg_2O_3(CO_2)_4$ secondary building units (SBUs), joined to four tritopic linkers and further linked to two other SBUs by a second ditopic linker. Accordingly we abstract the topology as a (3,6)-c net known as 3,3,6T26 in the *TOPOS* database (Blatov, 2006). In barycentric coordinates unlinked nodes collide in pairs. Another pair come close to colliding in barycentric coordinates but if an equal link-length constraint is applied to the embedding they also come together in pairs. In the crystal with symmetry $R\bar{3}$ there are two distinct SBU centers (6-coordinated) at nodes 1 and 2 in general positions $18f$ (36 nodes). The linkers are of four topological types with 3-c nodes 3 and 4 in position $18f$ (36 nodes) and 5 and 6 at positions $6c$: 0, 0, z (12 nodes) as shown in Fig. 16. In the *Systre* symmetry, $R\bar{3}m$, embedding nodes 1 and 2 jointly occupy general positions $36i$ and so do nodes 3 and 4. However, nodes 5 and 6 doubly occupy $6c$: 0, 0, z. The site symmetry is $3m$ and links to the 6-c node in general positions must be sixfold [*i.e.* two sets of three from identical positions in a (001) plane related by vertical mirrors].

In the equal-link embedding nodes 3 and 4 come together at $18h$: $x, 2x, z$. But this last is not a collision in the sense used in this paper as the coordinates are not now barycentric.

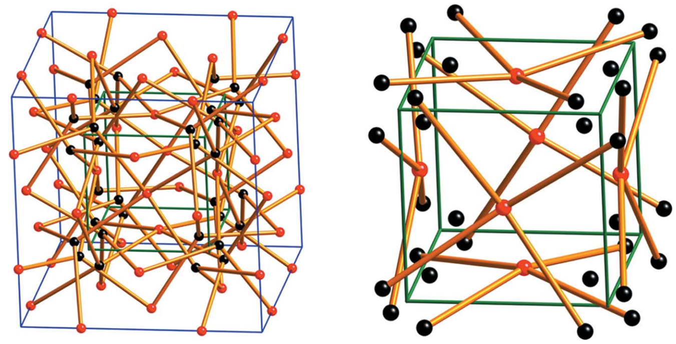

Figure 14
Left, the net **mhq** in an $F432$ embedding. The unit cell is outlined in blue. Right, an enlargement of the center of the figure on the left. At maximum symmetry ($P432$) groups of four black nodes collide and the new unit cell is that shown with green lines.

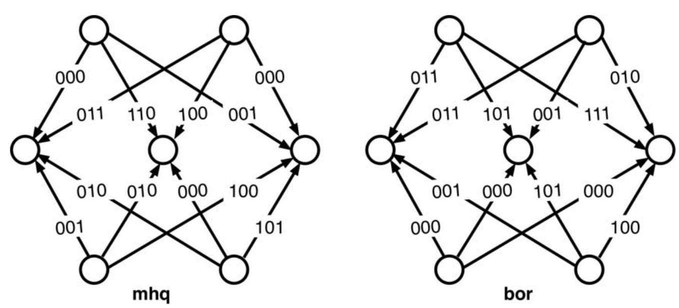

Figure 15
Quotient graphs for two edge-transitive (3,4)-c nets. The graphs are the complete bipartite graph $K_{3,4}$.

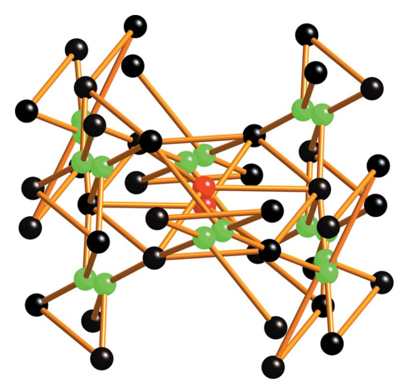

Figure 16
An embedding in $R\bar{3}$ of the (3,6)-coordinated net of the crystal structure of Volkringer *et al.* (2009). The structure illustrated is close to equal links. In barycentric coordinates the red nodes collide in pairs. In an equal-link embedding both the red and green nodes collide in pairs.

7. A net of exceptional girth and unforced collisions

The question of the largest girth for periodic nets with a given number of vertices in the quotient graph appears to be an

[2] *Systre* can be used to determine the number of interpenetrating nets. To give a somewhat extreme example: using the operations of $F432$ a link from 0.2, 0.3, 0.8 to 100.25, 100.0, 100.0 produces a single copy of **mhq**; if the link is instead to 100.0, 100.25, 100.0 the number of copies of **mhq** is 63 044 792 (= $2^3.199^3$).
[3] Our analysis differs from that of the original authors.

interesting one that has not yet received much attention. We know of only one net of girth >13 that has been found in crystal structures. This is **oft** – a uniform binodal 3-c net with vertex symbol $(14_8.14_8.14_8)_3(14_4.14_8.14_8)$ which has been found in several materials (Liu *et al.*, 2008, 2010).

The largest girth periodic net we are aware of is a uninodal, edge-2-transitive, 3-c one of girth 16.[4] This was generated from the uniform large-girth 4-c net **ten** (Delgado-Friedrichs *et al.*, 2005) which has vertex symbol $10_7.10_7.10_9.10_{13}.10_{12}.10_{12}$ (60 10-rings at each vertex). Deletion of one edge (edge E2 in RCSR) produces a new 3-c net (Blatov, 2007). This net, with RCSR symbol **sxt**, has vertex symbol $16_8.16_8.16_8$. Interestingly the stable net **ten** has symmetry $I23$ with nodes in general positions $24f$ with only trivial site symmetry. On the other hand **sxt** has the *Systre* supergroup symmetry $I432$ with vertices now in $24i$: $\frac{1}{4}$, y, $\frac{1}{2} - y$ and point symmetry 2. In barycentric coordinates $y = \frac{1}{4}$ and nodes collide in groups of three at $8c$: $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. That site has symmetry 32 but the individual nodes only have symmetry 2. We call these *unforced* collisions because there are embeddings without collisions in the same symmetry but with $y \neq \frac{1}{4}$. An embedding with $y = 0.292$, a value that makes all links equal in length, is shown in Fig. 17. We remark that, unless forced by symmetry, barycentric coordinates are rarely used for embeddings of nets. In the RCSR for example, the embeddings are, when possible, for equal links, and then subject to that restraint, for minimal density.

8. Concluding remarks

We have shown by example that T-crystallographic nets with collisions in barycentric coordinates indeed occur in crystal structures. In some cases these collisions are unforced (not required by symmetry) and full symmetry embeddings are possible without coincident nodes or zero-length links. In other cases full (*Systre*) symmetry embeddings are only possible with more than one node at the same point and possibly also links of zero length.

The quotient graphs presented herein were all verified by *Systre* (available at http://gavrog.org). The nets in *Systre*-readable format are available as supplementary information.[5]

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[4] This graph has just 12 vertices in the quotient graph. In contrast the smallest finite graph with 3-coordinated nodes of girth 16 has 960 vertices (Biggs, 1989).
[5] Supplementary material for this paper is available from the IUCr electronic archives (Reference: EO5027). Services for accessing these data are described at the back of the journal.

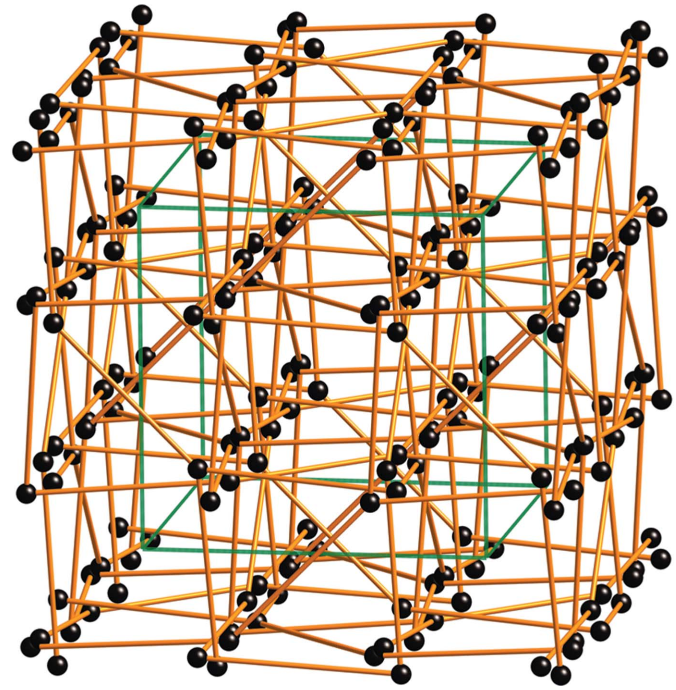

Figure 17
An embedding of the net **sxt** with equal links.

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