Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 23 February 2005
Accepted 24 March 2005

Isohedral simple tilings: binodal and by tiles with ≤16 faces

Olaf Delgado-Friedrichs and Michael O'Keeffe*

Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA. Correspondence e-mail: mokeeffe@asu.edu

All isohedral simple tilings of 3D Euclidian space by tiles with ≤16 faces have been determined. There are no such tilings by polyhedra with less than 14 faces. For simple polyhedra with 14, 15 and 16 faces, there are respectively 10, 65 and 434 that fill space and a total of 23, 136 and 710 distinct tilings. The tilings by 14-face polyhedra are described in detail as are binodal (vertex 2-transitive) isohedral simple tilings.

1. Introduction

Simple polyhedra are those in which exactly three edges meet at each vertex.[1] In simple tilings of three-dimensional space, two such polyhedra meet in a shared face, three at each edge and four at each vertex (*i.e.* in each case the minimum number). Physical examples of such structures are provided by foams and related cellular materials such as plant cell tissue and the assembly of grains in polycrystalline materials. On the atomic level, the framework of tetrahedrally coordinated atoms in materials such as zeolites often corresponds to a simple tiling; the structure of faujasite provides a well known example. In *isohedral* tilings, all tiles are related by symmetry operations of a symmetry group, which must be a space group for tilings that fill all space. The skeleton of the tiling is the net of vertices and edges, and we say that the net is *carried* by the tiling.

In applications to crystal chemistry, we are particularly interested in the conformations of these structures in which all edges are equal and correspond to the shortest distances between vertices; *i.e.* the positions of the vertices correspond to the centers of packings of equal spheres, each of which is in contact with exactly four neighbors. We refer to these configurations as 'sphere packings' below.

In 1887, Lord Kelvin asked the question of the structure that provided the solution to 'the division of space with minimum partitional area' (Thomson, 1887). His solution was based on a tiling of space by truncated octahedra (which have six quadrilateral and eight hexagonal faces), slightly modified to have curved edges so that the angles between all pairs of the four edges meeting at each vertex are the 'tetrahedral' angle, $\cos^{-1}(-1/3) = 109.5^\circ$ (instead of 90 and 120° for the Archimedean polyhedron with plane faces). Kelvin's solution was the best known until Weaire & Phelan (1994*a*) showed an example of a subdivision into two different kinds of tile with equal volume and significantly lower surface area for a given volume of tile. Interestingly, the Weaire–Phelan structure is found in many contexts in chemistry where it is usually known as the type I clathrate structure. However, the optimum solution to the Kelvin problem remains unknown, even for isohedral tilings. For this reason, it is of interest to know what isohedral tilings exist – a question we address here. We should remark that Plateau conditions (Weaire & Hutzler, 1999) for a stable dry foam: (*a*) that the faces intersect only three at a time and at 120°, and (*b*) no more than four of the intersection lines (or six of the faces) meet at a vertex where the angles between the lines are all the tetrahedral angle $\cos^{-1}(-1/3)$ (for the proof, see Taylor, 1976), ensure that the solution to the Kelvin problem will correspond to a simple tiling.

The Kelvin structure is often referred to as the sodalite structure by crystal chemists; it occurs as the basis for a large number of oxides, sulfides, nitrides and chlorides. Surprisingly, it appears that no other simple isohedral tiling was known until 1968 when Williams (1968) described two new structures of packings of 14-face polyhedra derived from the Kelvin structure and indicated their importance as idealized models of foams. The structures have been referred to as W_1 and W_2, respectively (O'Keeffe, 1998). A fourth simple 14-face space-filling polyhedron appears to have been discovered by several groups independently. Rosa & Fortes (1986) identified this polyhedron (type II in their notation) and remarked that it filled space when combined with its enantiomorph. The same polyhedron was found in foams by Weaire & Phelan (1994*b*), who called it the 'twisted Kelvin cell', and Aste *et al.* (1996) showed that it tiled space. None of these works identified the space groups of the packings or provided explicit coordinates. However, tiling of space by the same polyhedron was also identified in the crystal structure of $BaCu_2P_4$ by O'Keeffe & Hyde (1996). O'Keeffe (1998) considered structures dual to certain high-coordination sphere packings and showed that in addition to the Kelvin structure (K) and the W_1 and W_2 structures, there were three distinct packings of the twisted Kelvin cell, and a sixth structure involving a fourth kind of 14-face polyhedron called O. The coordinates for all these structures as 4-coordinated sphere packings were given.

[1] In the present context, a polyhedron has a graph that is planar and 3-connected.

Simple isohedral tilings, which can be realized as 4-coordinated sphere packings, by polyhedra with more than 14 faces are also known. Aste *et al.* (1996) identified a 16-face tile and the tiling by this polyhedron (the *ABR* polyhedron) was described by O'Keeffe (1997). An isohedral tiling by a polyhedron (the 'β-Sn dual polyhedron') with 18 faces was described by O'Keeffe & Sullivan (1998).

Ferro & Fortes (1985) described the topology (Schlegel diagrams) of some polyhedra with up to 26 faces that filled space by translation alone. The tiles corresponding to these polyhedra are of necessity non-convex as it is well known that the Kelvin structure is the only simple tiling by convex polyhedra that fill space by translation alone (*parallelohedra*). Nevertheless, O'Keeffe (1999*a*) showed that all these tilings could be realized as 4-coordinated sphere packings. An example with 32 faces is adduced below.

All the work described above was essentially empirical discovery, and leaves many questions unanswered. There is a well known result that is a simple consequence of Euler's theorem for polyhedron packings (see *e.g.* O'Keeffe & Hyde, 1996) that for simple tilings the average number of edges per face is $n = 6 - 12/F$, where F is the average number of faces per polyhedron. It has also been established that $n > 9/2$ (Luo & Stong, 1993), which translates into $F > 8$. This limit can be rapidly approached by recursively replacing the vertices of a simple tiling by a tetrahedron of vertices (O'Keeffe, 1999*b*).

For isohedral tilings in which the polyhedra can relax to the shape of a minimal foam without combinatorial change, it has been shown that $F \geq 14$ (Kusner, 1992). In fact, exhaustive generation of all possibilities, as described below, shows that this lower limit obtains without qualification. We (Delgado Friedrichs *et al.*, 2002) have also described an isohedral simple tiling with $F = \infty$, so there is no upper limit to F. The largest known *convex* simple isohedral tile with equal edge lengths is the 18-face β-Sn dual tile (O'Keeffe & Sullivan, 1998).

As far as we are aware, prior to this work, there have been no results on enumeration of the numbers of distinct isohedral tilings by tiles of a given number of faces, although some important related enumerations have been reported recently. Of these we mention that it has been established that there are exactly nine vertex transitive (uninodal) simple tilings (Delgado-Friedrichs & Huson, 1999); the Kelvin structure is the only isohedral one. Interestingly, seven of the uninodal structures correspond to the frameworks of known zeolite structures.

2. Method

The generation of isohedral simple tilings was performed as follows: first, all simple polyhedra were generated using the program *plantri* by Brinkmann & McKay (2001). More precisely, *plantri* generated simplicial polyhedra (polyhedra with only triangular faces) with up to a specified number of vertices and dualized each of the results to obtain a simple polyhedron with the corresponding number of faces. The generation strategy used in that program goes back to an idea of Eberhard (1891), who proved that every triangulated polyhedron can be obtained from the tetrahedron by a series of simple modifications. These are of three types:

(*a*) a triangle is subdivided into three triangles around a common new vertex;

(*b*) a pair of adjacent triangles is replaced by a configuration of four triangles around a common new vertex;

(*c*) a triple of triangles that together form a pentagon is replaced by five triangles around a common new vertex.

The generation of triangulated polyhedra is achieved by systematically performing all possible sequences of such transformations until the desired number of vertices is obtained.

The generation is very fast owing to a clever optimization technique known as the canonical predecessor method (McKay, 1998). This technique guarantees that every polyhedron the program reports is new without the need to check this by explicitly looking at the list of previous results. This is very important because the same polyhedron would otherwise be obtained by a large number of different modification sequences.

For each simple polyhedron in the list, we determined all topologically different isohedral simple tilings by that poly-

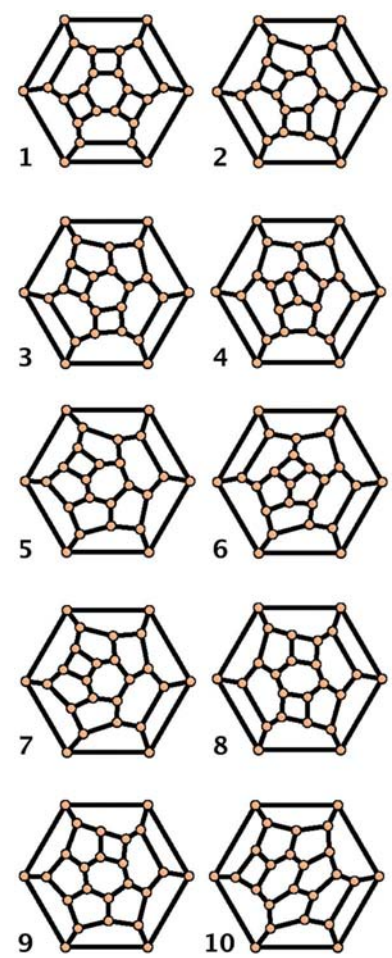

Figure 1
Schlegel diagrams for 14-face polyhedra that form isohedral simple tilings. The numbers are the same as in Table 2.

hedron, if any, in the following way [*c.f.* steps (A1) to (A5) as described by Delgado-Friedrichs & Huson, 1999].

(A1) First, we specified the site symmetry that the polyhedron should have in the completed tiling. This can be any subgroup of its full symmetry group that fulfilled the crystallographic restriction. Thus we started by enumerating all these subgroups.

(A2), (A3) For each of the subgroups, we systematically generated all the ways in which adjacent copies of the polyhedron could be attached to it and which were compatible with the given symmetry. An important restriction here is that the final tiling must be simple, so at each edge we must have exactly three copies coming together. Thus, steps (A2) and (A3) as described before (Delgado-Friedrichs & Huson, 1999) were combined into one step. In essence, this step produced a list of 'blueprints' or building instructions for tilings.

(A3′) As in this study we are only interested in topological types, we kept only those blueprints that did not allow for any additional symmetries. To illustrate this, imagine a tiling of the plane by rectangles in the fashion of bricks in a brick wall. Although this tiling is topologically equivalent to a regular honeycomb, it does not exhibit the full symmetry of the honeycomb and may therefore be rejected. This criterion can be determined from its blueprint even without knowing the actual tiling.

(A4) Not every blueprint produced in the previous steps was actually realizable. We had to solve the existence problem for each blueprint, *i.e.* determine if it corresponded to a tiling of ordinary space (Delgado-Friedrichs, 2001).

(A5) Finally, for each realizable blueprint, we constructed a corresponding tiling. As an efficient way to represent blueprints of tilings in the computer, we used the Delaney symbol approach as described, for example, by Delgado-Friedrichs *et al.* (1999).

3. Results

3.1. The numbers of distinct tilings

In Table 1, we list the number of simple polyhedra with N faces, the number of polyhedra (tilers) that form isohedral tilings and the number of isohedral tilings. Note that, as a given polyhedron may form more than one tiling, the number of tilings is larger than the number of tilers. A chiral polyhedron will have left and right enantiomorphs but these are counted as just one tiler and an isohedral tiling may contain both enantiomorphs.

Notice in particular that there are no isohedral simple tilings with tiles of less than 14 faces, but respectively 23, 136 and 710 isohedral simple tilings for tiles with 14, 15 and 16

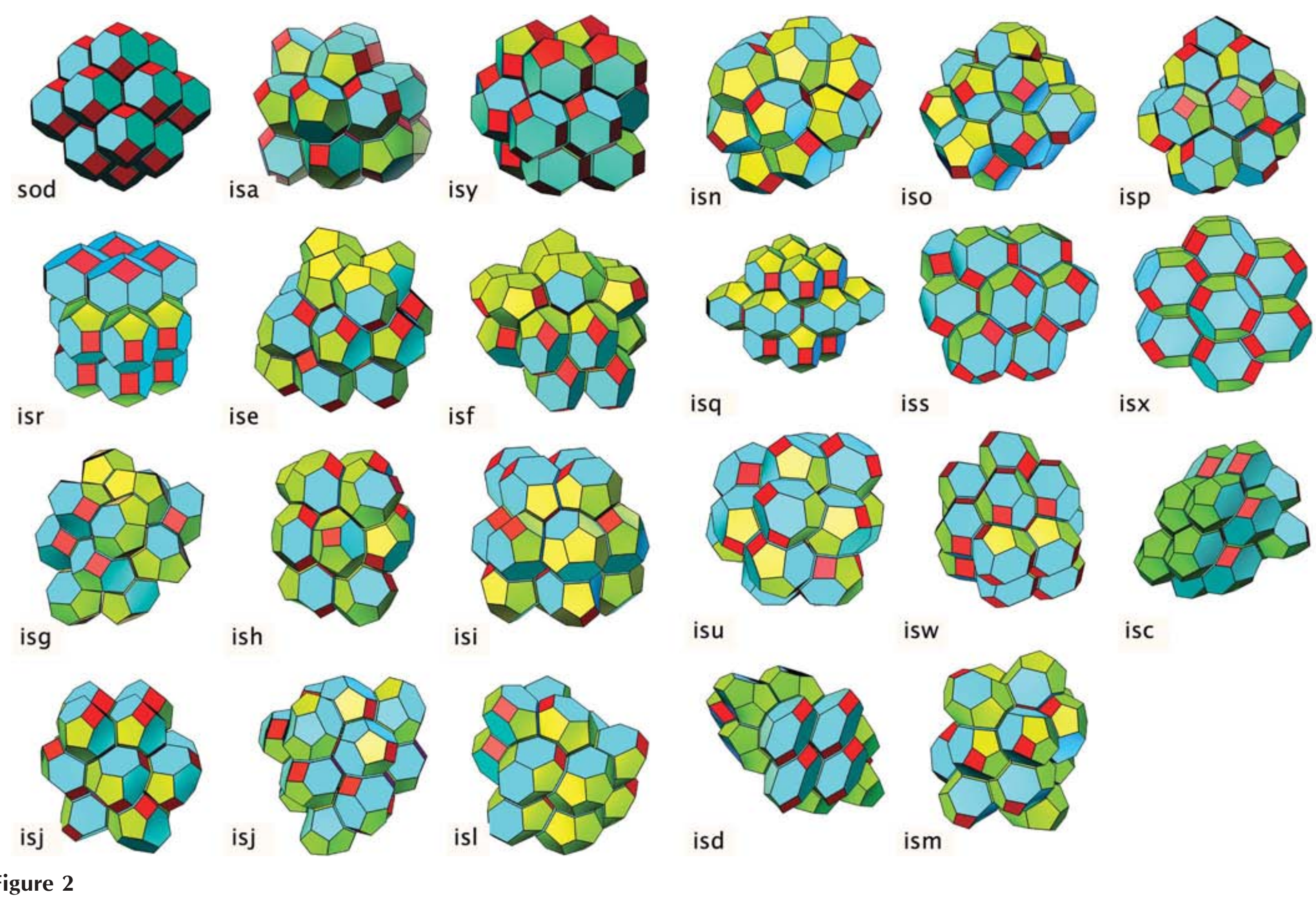

Figure 2
Slightly exploded views of fragments of the 23 isohedral simple tilings by 14-face tilers. The symbols are the same as in Table 2.

Table 1
The numbers of simple polyhedra (total) with N faces, the numbers of those that tile space (tilers) and the number of isohedral tilings (iso tilings).

The last three columns refer to polyhedra with only four-, five- and/or six-sided faces.

N	Total	Tilers	Iso tilings	4–6	4–6 tilers	4–6 tilings
<14	58716	0	0	80	0	0
14	339722	10	23	59	10	23
15	2406841	65	136	93	11	24
16	17490241	434	710	153	5	25

faces. As the number of distinct simple polyhedra increases exponentially with the number of faces [Tutte (1980); $>5 \times 10^{10}$ with 20 faces (Brinkmann & McKay, 2001)], we expect the number of isohedral simple tilings to increase dramatically also, and indeed with present computers and algorithms, even if desired, the generation would not be practical for polyhedra with more faces.

Crystallographic data (unit-cell parameters, coordinates of vertices *etc.*) can be found for all the structures discussed here at http://okeeffe-ws1.la.asu.edu/RCSR/home.htm.

3.2. Tilings with 14-face tiles

The 14-faced polyhedra of the isohedral simple tilings all have faces that are 4-, 5- or 6-gons; in Table 1, they are referred to as '4–6 tilers' and the corresponding tiling as '4–6 tilings'. Schlegel diagrams of the polyhedra are shown in Fig. 1 in which each tile is assigned a number. Table 2 lists the tilings and they are illustrated in Fig. 2. Notice that the number of four-sided and five-sided faces are related by $2n_4 + n_5 = 12$.

Table 2
Data for isohedral simple tilings by 14-faced tiles.

The tile number refers to the tiles identified in Fig. 2. n_5 is the number of five-sided faces per tile. p, q and r are the numbers of kinds of vertices, edges and faces respectively in the tiling. The symbols under OK98 are those of O'Keeffe (1998).

Tile	n_5	Tiling	Symmetry	p	q	r	OK98
1	0	**sod**	$Im\bar{3}m$	1	1	2	K
2	4	**isa**	$P4_2/mbc$	5	7	7	W_2
2	4	**isy**	$Pnma$	3	7	6	O
3	4	**isr**	$P4_2/ncm$	4	5	5	
4	6	**ize**	$Pccn$	7	12	9	
4	6	**isf**	$I4_1/acd$	9	12	10	
4	6	**isg**	$I4_1/a$	8	12	9	
4	6	**ish**	$P4_2/nbc$	10	12	11	
4	6	**isi**	$C2/c$	7	12	10	
4	6	**isj**	$Pbca$	6	12	8	
4	6	**isk**	$P2_1/c$	6	12	9	
5	8	**isl**	$Pbcn$	3	7	5	
6	6	**isn**	$P4_2/n$	8	12	9	
6	6	**iso**	$Pbca$	6	12	8	
6	6	**isp**	$P2_1/c$	6	12	9	
7	8	**isq**	$P4_2/mnm$	2	3	3	W_1
8	4	**iss**	$P6_422$	3	4	4	K'_Q
8	4	**isx**	$Fddd$	2	4	4	K'_D
8	4	**isu**	$I4_1/acd$	5	6	6	
8	4	**isw**	$Fddd$	5	7	7	K'_{DQ}
9	8	**isc**	$Pbcn$	4	7	6	
9	8	**isd**	$I4_1/a$	5	7	6	
10	8	**ism**	$I\bar{4}2d$	5	7	5	

If the number of kinds of vertex, edge, face and tile in the tiling is p, q, r, s, the *transitivity* (Delgado-Friedrichs & Huson, 2000) is $pqrs$ – for isohedral tilings it is $pqr1$. Generally speaking, the structures of most interest in crystal chemistry have small values of transitivity (considering the array $pqrs$ as a single number, Delgado Friedrichs *et al.*, 2003*a*,*b*); it may be seen that the structures of Table 2 mainly have large values. In this connection, we remark that, although the number of isohedral simple tilings is (presumably) infinite, the number of uninodal (vertex transitive) simple tilings is only nine and only one of these (**sod**) is isohedral. In fact of the 869 tilings found in this work, only one, two and nine are respectively uninodal, binodal and trinodal. All the tiles have three- and/or four-sided faces.[2]

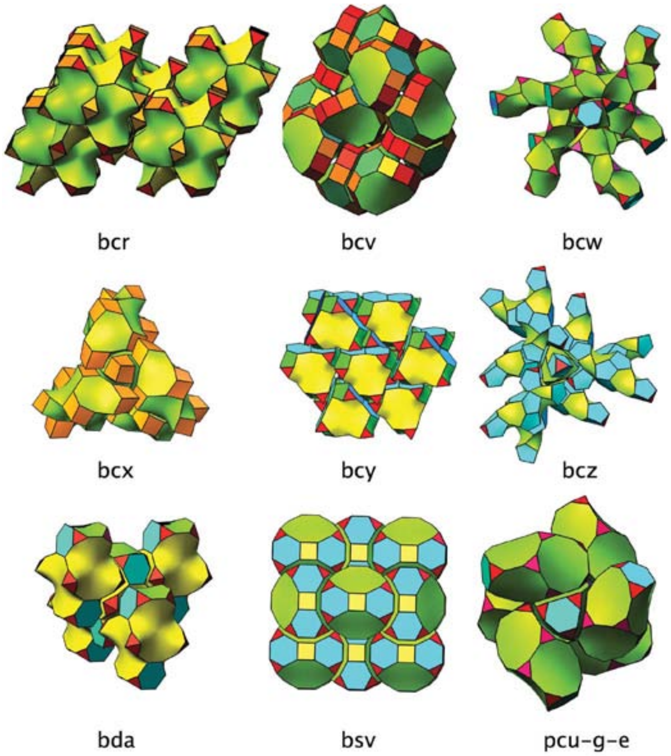

Figure 3
Nine binodal isohedral tilings. For details see Table 3.

3.3. Binodal isohedral simple tilings

The duals of simple tilings are tilings by tetrahedra, and an alternative approach to enumerating simple tilings is to enumerate tilings by tetrahedra. Delgado-Friedrichs *et al.* (1999) found 117 2-isohedral tilings of tetrahedra of which 11 were vertex transitive. Dualization of these gives 11 binodal (vertex 2-transitive) isohedral tilings. We have met two already (**isq** and **isx**, *cf.* Table 2), a third (**bsv**) is the β-Sn dual

[2] Binodal isohedral simple tilings are discussed next. The trinodal tilings with ≤ 16 faces mentioned in this paper are **isl**, **iss** and **isy** of Table 2; **abr** described by O'Keeffe (1997); **ksx** and **wsx** (K16 and W216 of O'Keeffe, 1999*a*). The others are **jsc**, **jsd**, **jse**. Crystallographic data for these are to be found at http://okeeffe-ws1.la.asu.edu/RCSR/home.htm.

Table 3
Binodal isohedral tilings.

The point group refers to the symmetry of the tile. **bcr** and **bda** are not simple tilings *sensu stricto* (see text).

Symbol	Space group	Point group	Faces	Face symbol	Transitivity
bcr	$R\bar{3}m$	$\bar{3}m$	32	$[3^1 8.4^6.14^6.18^2]$	2441
bcv	$Ia\bar{3}d$	32	17	$[4^{12}.6^2.10^3]$	2331
bcw	$Pa\bar{3}$	$\bar{3}$	26	$[3^1 2.6^2.10^1 2]$	2431
bcx	$P4_3 32$	32	18	$[4^1 2.8^6]$	2421
bcy	$R\bar{3}c$	32	20	$[3^6.5^6.6^6.12^2]$	2441
bcz	$P4_3 32$	32	20	$[3^2.5^1 2.7^6]$	2431
bda	$I4_1/amd$	$\bar{4}m2$	26	$[3^{16}.6^4.8^2.14^4]$	2441
bsv	$I4_1/amd$	$\bar{4}m2$	18	$[3^8.4^2.6^4.10^4]$	2341
isq	$P4_2/m$nm	mmm	14	$[4^2.5^8.6^4]$	2331
isx	$Fddd$	222	14	$[4^4.5^4.6^6]$	2441
pcu-g-e	$Ia\bar{3}$	$\bar{3}$	20	$[3^1 2.6^2.10^6]$	2331

tile (O'Keeffe & Sullivan, 1998) and a fourth, here symbolized **bcv**, was illustrated as 2-067 by Delgado-Friedrichs *et al.* (1999). As far as we know, the others have not been described before, so we give data and illustrations in Table 3 and Fig. 3, respectively. Notice that the number of faces can be quite large and in most cases the tiles are very far from spherical.

In two of the above 11 structures, those symbolized **bcr** and **bda**, the tiles have pairs of faces with two common non-adjacent edges. The graphs of these tiles are accordingly not 3-connected.[3] Such tiles would not appear in our generation of simple polyhedra if carried out to sufficiently large numbers of faces, and the corresponding tilings perhaps should not be considered as *simple* tilings.

bcr is a nice example of a complex solid (32 faces!) that fills space using only translations.

A simple tiling may not be a natural tiling in the sense of Delgado Friedrichs *et al.* (2003*a*,*b*). In those works, a natural tiling associated with a net is defined as the tiling by the smallest possible tiles that (*a*) preserves the symmetry and (*b*) in which all the faces are strong rings (rings that are not the sum of smaller rings). For structure **bcw**, the simple tile has a six-membered strong ring around the waist and including this as a tile face gives the natural tiling (also isohedral, but not simple) which has tiles with 14 faces, and the transitivity is now 2441.

[3] A connected graph is one in which there is a continuous path of edges between every pair of vertices. A 3-connected graph is a connected graph for which there is no pair of vertices whose deletion would leave the graph no longer connected.

This work was supported by the US National Science Foundation (grants nos. DMR 0103036 and 0451443) and by the donors of the American Chemical Society Petroleum Research Fund.

References

Aste, T., Boosé, D, & Rivier, N. (1996). *Phys. Rev. E*, **53**, 6181–6191.
Brinkmann, G & McKay, B. D. (2001). http://cs.anu.edu.au/~bdm/plantri.
Delgado-Friedrichs, O. (2001). *Discrete. Comput. Geom.* **26**, 549–571.
Delgado-Friedrichs, O., Dress, A. W. M., Huson, D. H., Klinowski, J. & Mackay, A. L. (1999). *Nature (London)*, **400**, 644–647.
Delgado-Friedrichs, O. & Huson, D. H. (1999). *Discrete Comput. Geom.* **21**, 299–315.
Delgado-Friedrichs, O. & Huson, D. H. (2000). *Discrete Comput. Geom.* **24**, 279–292.
Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003*a*). *Acta Cryst.* A**59**, 22–27.
Delgado Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2003*b*). *Acta Cryst.* A**59**, 515–525.
Delgado Friedrichs, O., Plévert, J. & O'Keeffe, M. (2002). *Acta Cryst.* A**58**, 77–78.
Eberhard, V. (1891). *Zur Morphologie der Polyeder.* Berlin: Teubner.
Ferro, A. C. & Fortes, M. A. (1985). *Z. Kristallogr.* **173**, 41–57.
Kusner, R. (1992). *Proc. R. Soc. (London) Ser. A*, **439**, 683–686.
Luo, F. & Stong, R. (1993). *Trans Am. Math. Soc.* **337**, 891–906.
McKay, B. D. (1998). *J. Algorithms*, **26**, 306–324.
O'Keeffe, M. (1997). *Philos. Mag. Lett.* **76**, 423–426.
O'Keeffe, M. (1998). *Acta Cryst.* A**54**, 320–329.
O'Keeffe, M. (1999*a*). *Z. Kristallogr.* **214**, 438–442.
O'Keeffe, M. (1999*b*). In *Foams and Emulsions*, edited by J. F. Sadoc & N. Rivier. Dordrecht: Kluwer Academic Publishers.
O'Keeffe, M. & Hyde, B. G. (1996). *Crystal Structures I: Patterns and Symmetry*. Washington, DC: Mineralogical Society of America.
O'Keeffe, M. & Sullivan, J. M. (1998). *Z. Kristallogr.* **213**, 374–376.
Rosa, M. E. & Fortes, M. A. (1986). *Acta Cryst.* A**42**, 282–286.
Taylor, J. E. (1976). *Ann. Math.* **103**, 489–539.
Thomson, W. (1887). *Philos. Mag.* **24**, 503–516.
Tutte, W. T. (1980). *J. Combinatorial Theory B*, **28**, 105–126.
Weaire, D. & Hutzler, S. (1999). *The Physics of Foams.* Oxford: Clarendon Press.
Weaire, D. & Phelan, R. (1994*a*). *Philos. Mag. Lett.* **69**, 107.
Weaire, D. & Phelan, R. (1994*b*). *Philos. Mag. Lett.* **70**, 345.
Williams, R. W. (1968). *Science*, **161**, 276–277.