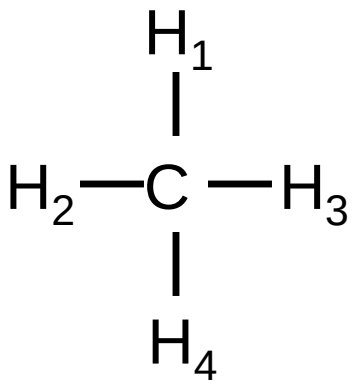
Crystal Nets as Graphs

Michael O'Keeffe

Introduction to graph theory
and its application to crystal nets

Molecular topology is a graph



edges:

C H_1

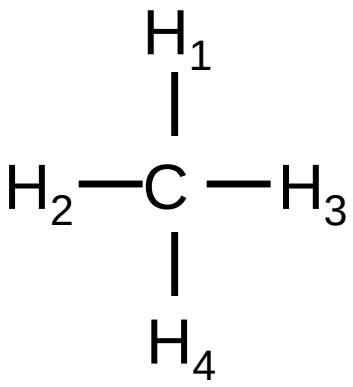
C H_2

C H_3

C H_4

atoms (vertices) joined by bonds (edges)
mathematical graph theory is highly developed

Crystals e.g. diamond have topology
specified by an **infinite periodic** graph
The mathematics of periodic structures is
highly **un**developed.



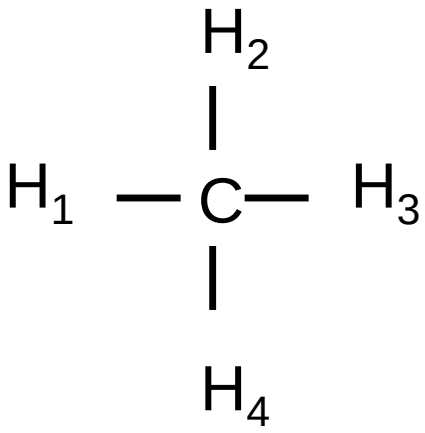
edges:

C H_1

C H_2

C H_3

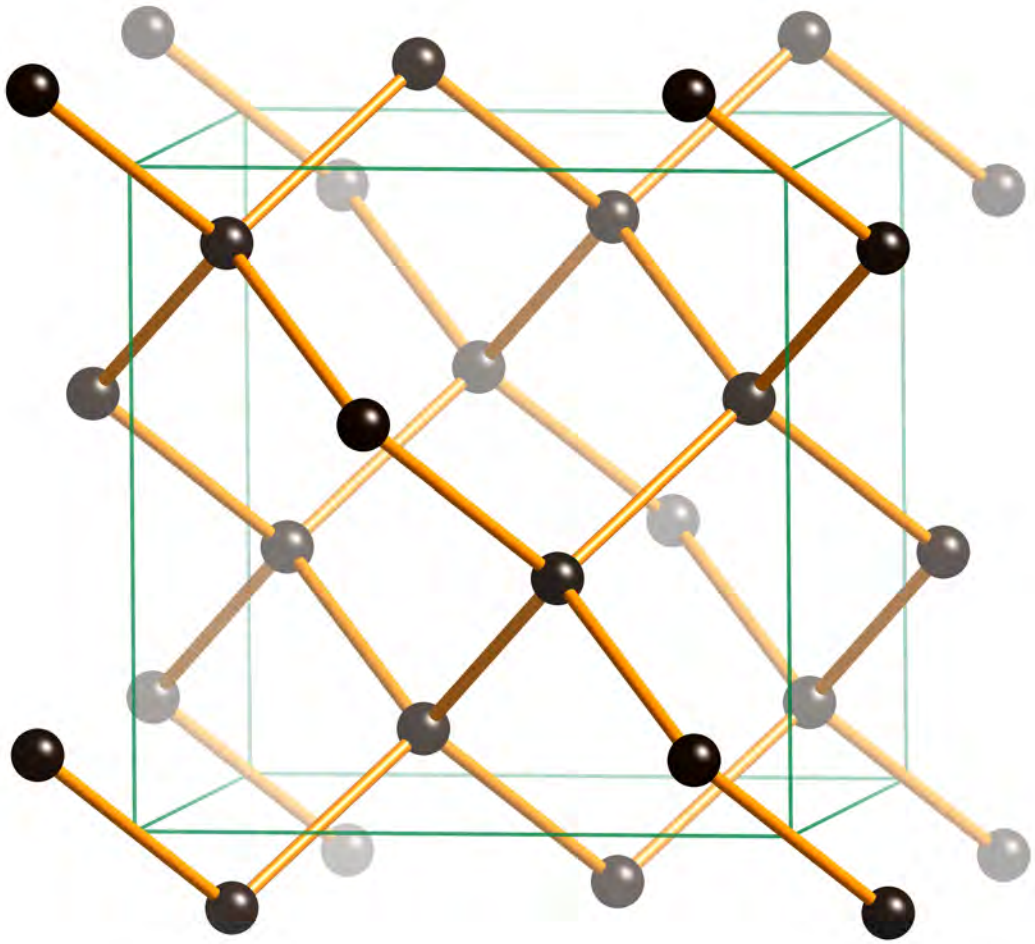
C H_4



same edges

interchanging H_1 and H_2 is an *automorhism* of the graph

→ automorphism group (“symmetry” group)



part of the diamond met - a periodic infinite graph

graph (**net** is a special kind of graph)
is an abstract mathematical object.

network is a real thing:

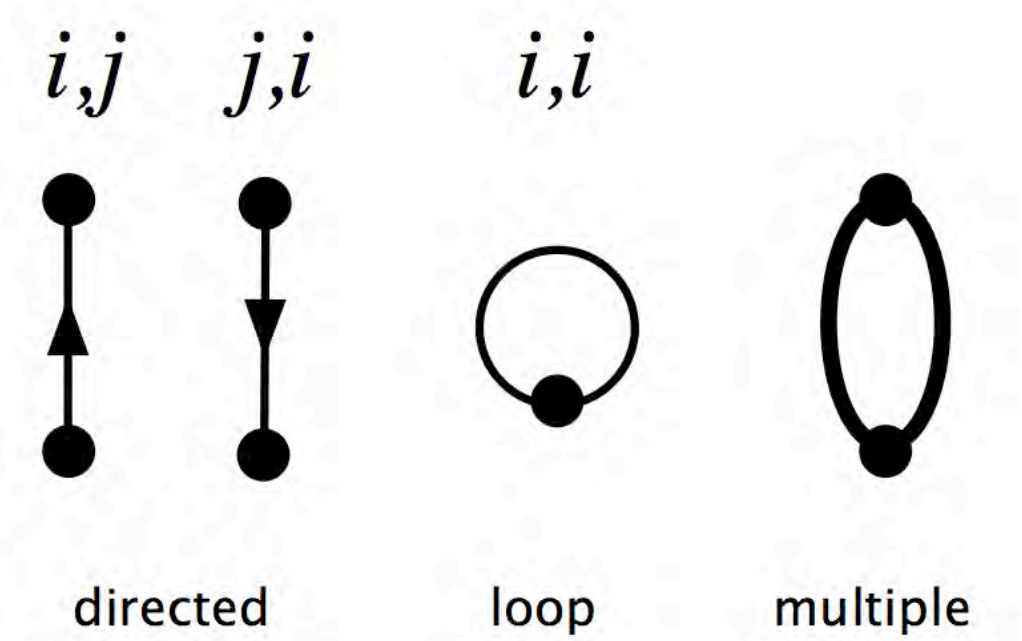
rail network
neural network
coordination network
diamond consists of a network of C atoms joined by chemical bonds.

The diamond structure has the "**dia** topology"
means the graph (net) is **dia**

It is not correct to say diamond has a 6^6 topology!

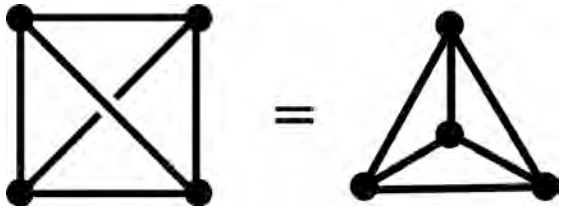
Graph consists of **vertices** ... v_i, v_j ,...
edges (i, j) connect two vertices

special kinds of edge



A **faithful embedding** is a realization (e.g. coordinates for vertices) in which edges are finite and do not intersect. Graphs which admit a 2-dimensional faithful embedding are **planar**

The graphs of all convex polyhedra are planar.



planar

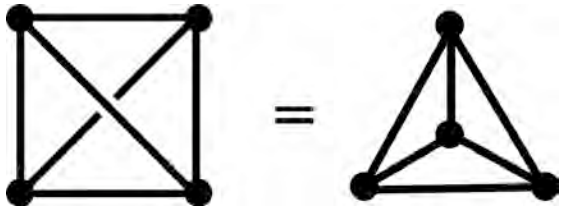
nonplanar

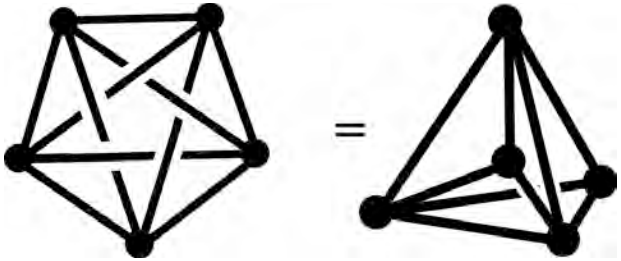
Sometimes we want to distinguish
the abstract graph with **vertices** and **edges**
from an embedding with **nodes** and **links**

For example it is meaningless to talk about
the length of an edge, but we can talk about
the length of a link

We can even have embeddings with links of
zero length.

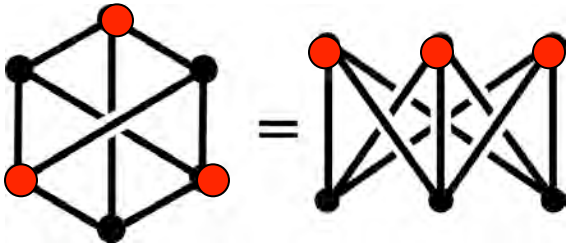
complete graphs –
every vertex linked to every other vertex:

K_4  planar

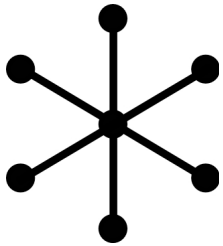
K_5  non-planar

Complete bipartite graph $K_{m\,n}$
Two sets of vertices *m* in one set and *n* in the other
all *m* linked only to all *n*

The graph K_{1n} is the same as the star graph S_{n+1}
(an example of a tree)



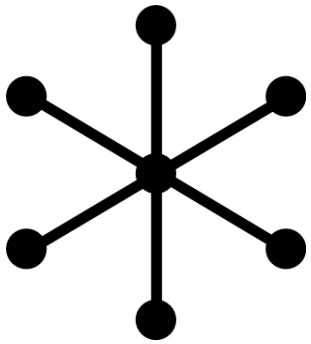
$K_{3\,3}$ (nonplanar)

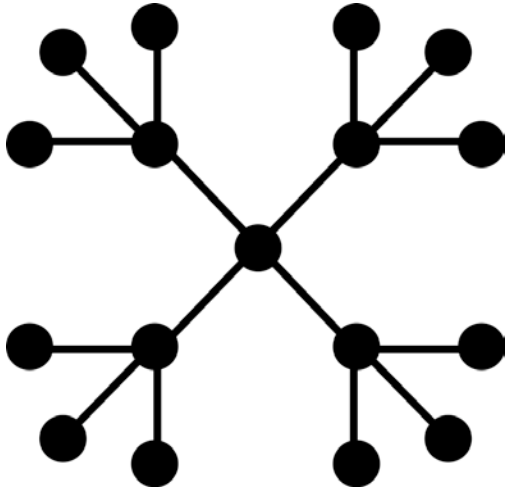


$K_{1\,6} = S_7$

Bipartite two classes of vertex. Vertices in each class linked only to the vertices of the other class
(graphs of ionic crystals)

Tree has no cycles (closed paths)





regular graph

has the same number, n, of edges meeting at each vertex

if $n = 3$ then often called a *cubic* graph.

For odd n the number of vertices is even

(The number o edges is $n/2$ time the number of vertices)

symmetric graph

vertex-and edge-transitive

i.e. one kind of vertex and ne kind of edge

(necessarily regular)

semisymmetric graph

edge- but not vertex-transitive

girth

length of shortest cycle

Transitivity

vertex transitive (“uninodal”)
= one kind of vertex
(all vertices related by symmetry)

vertex 2-transitive (binodal”)
= two kinds of vertex

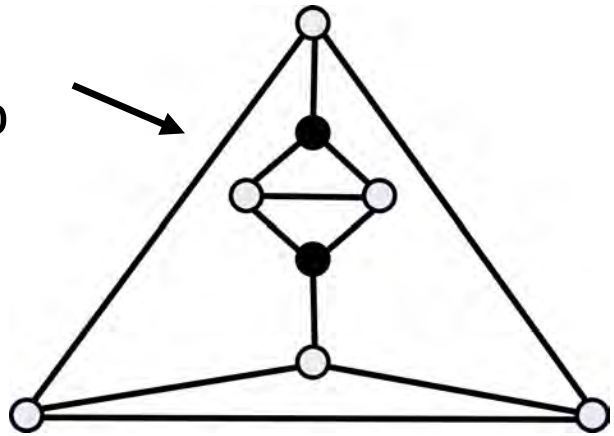
edge transitive
= one kind of edge

A connected graph
has a continuous path between every pair of vertices

A *k*-connected graph is one in which at least *k* vertices (and their incident edges) have to be deleted to separate the graph into two disjoint pieces.

WARNING! Chemists use *k*-connected to mean *k*-coordinated

A 3-valent (3-coordinated) graph that is not 3-connected. Removal of the two vertices shown as filled circles will separate the graph into two pieces.



Note: a k+1-connected graph is necessarily *k*-connected

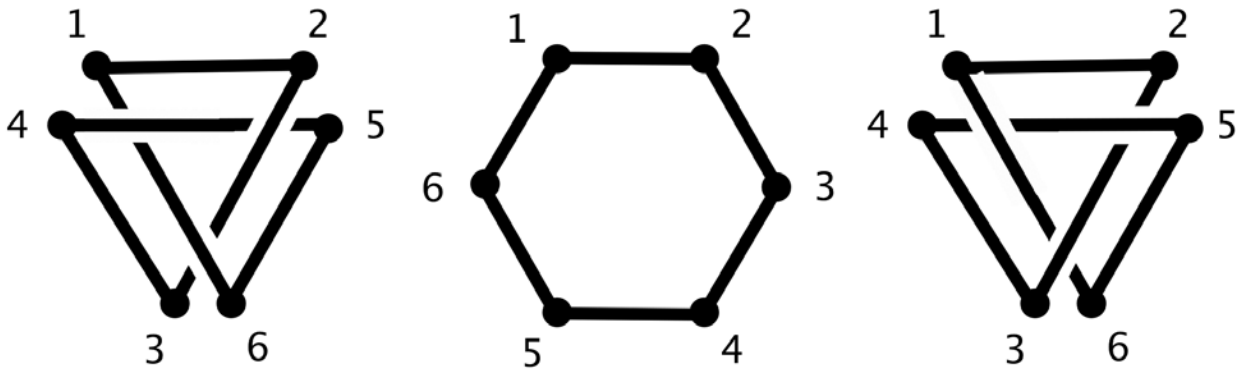
Note:

because of the possible confusion I write k-c to mean a vertex has k incident edges ("k-coordinated").

In a k-c graph (net) all vertices are k-c

In a $(k_1,k_2,...)$-c net. some vertices are k_1-c some are k_2-c, and so on

The graphs below are **isomorphic** – there is a one-to-one correspondence between vertices that induces a one-to-one correspondence between edges (vertex 1 is bonded to 2 and 6 in every case, etc.).
The embeddings are not **ambient isotopic** – they cannot be deformed one into another without bonds intersecting. (or going into higher dimensions)

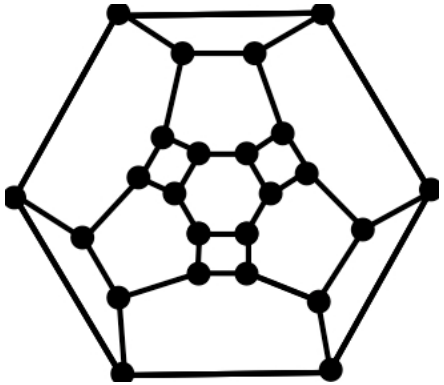


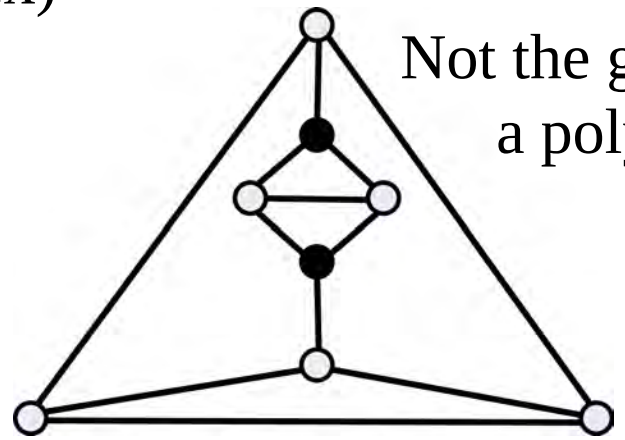
Every 3-connected planar graph can be realized as a convex polyhedron. Steinitz theorem.

A convex polyhedron has planar faces and the line joining any two points on different faces is entirely inside the polyhedron (other than the end points).

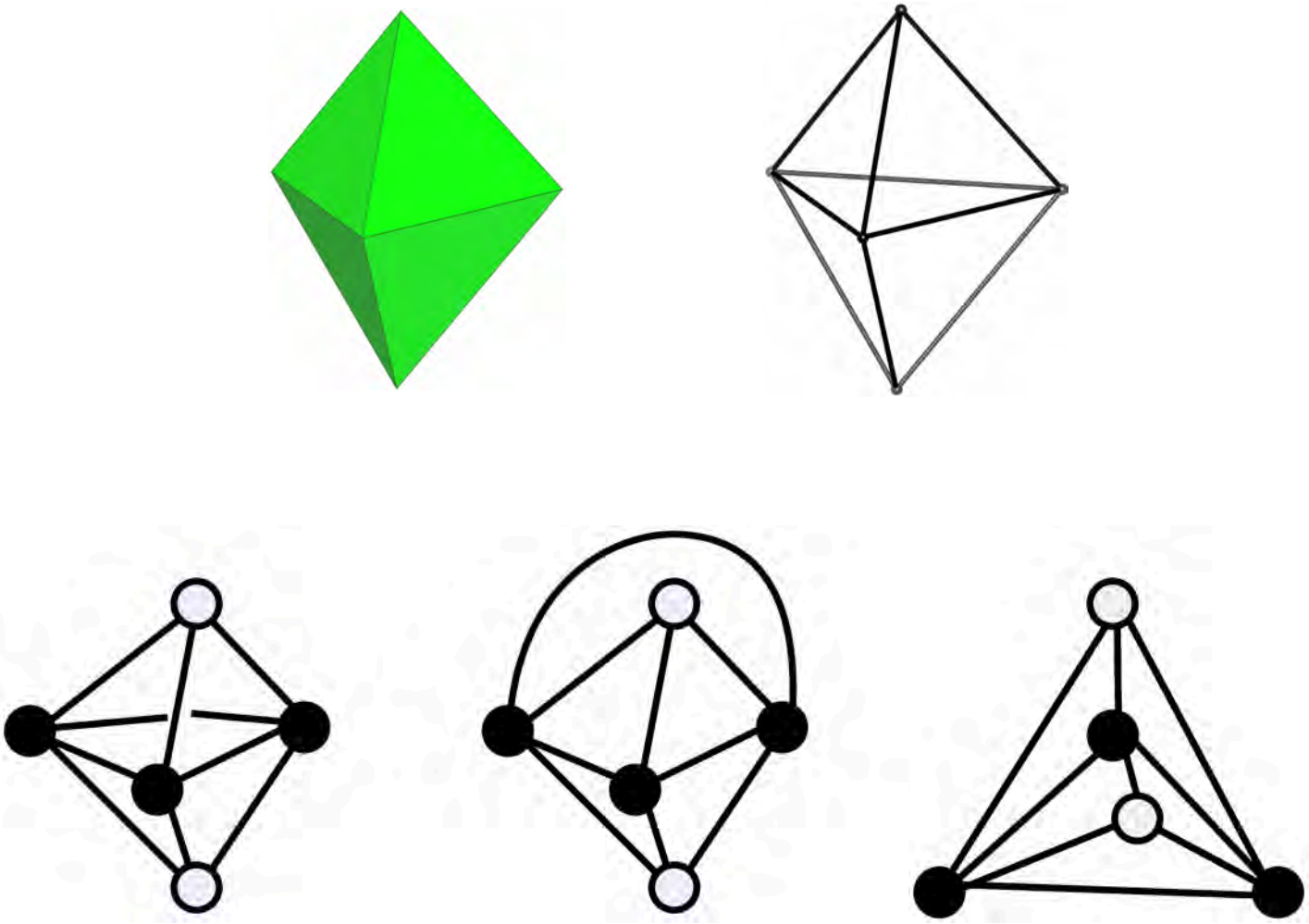
A simple polyhedron has a 3-connected 3-valent graph (three edges meet at each vertex)

Graph of truncated octahedon (simple)





Not the graph of a polyhedron



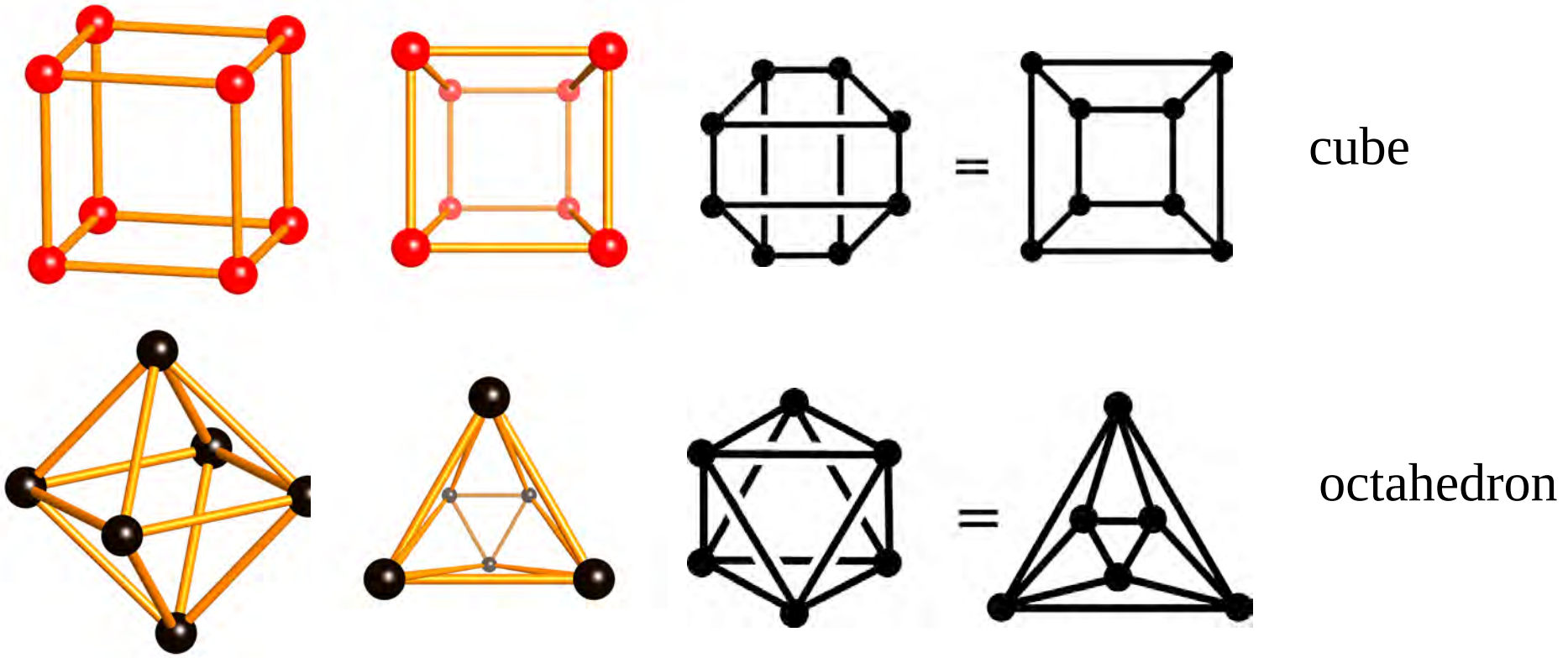
three ways of drawing the graph of a trigonal bipyramid

Steinitz theorem holds for 2-periodic graphs also

(Olaf Delgado-Friedrichs)

Tilings of the plane
which have planar 3-connected graphs
can be drawn with convex polygons as tiles.

More examples of graphs of polyhedra

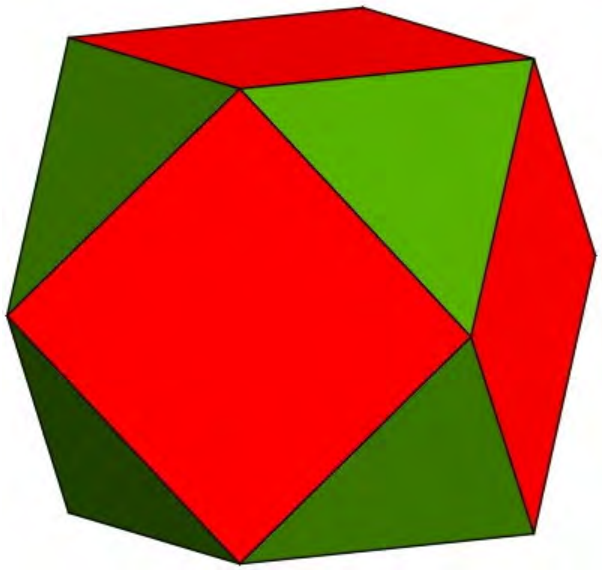


cube

octahedron

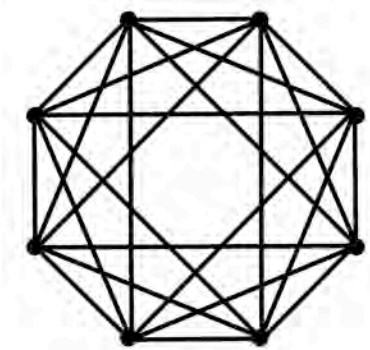
Drawings on the right with linear non-intersecting edges are *Schlegel diagrams.*

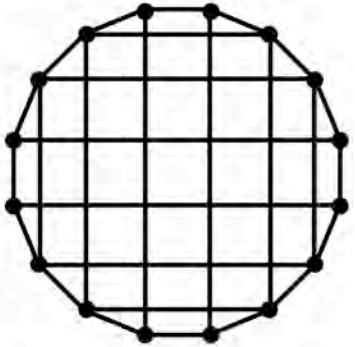
The graphs of the regular polyhedra are vertex- and edge- transitive
Also the graph of the cuboctahedron



Some more symmetric (vertex and edge transitive) graphs

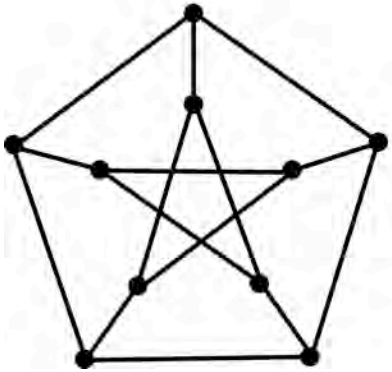
4-D cross polytope
(4-D "octahedron")



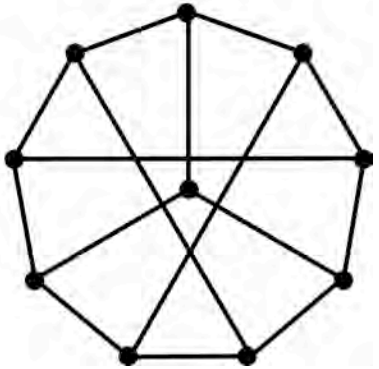


tesseract
(4-D "cube")

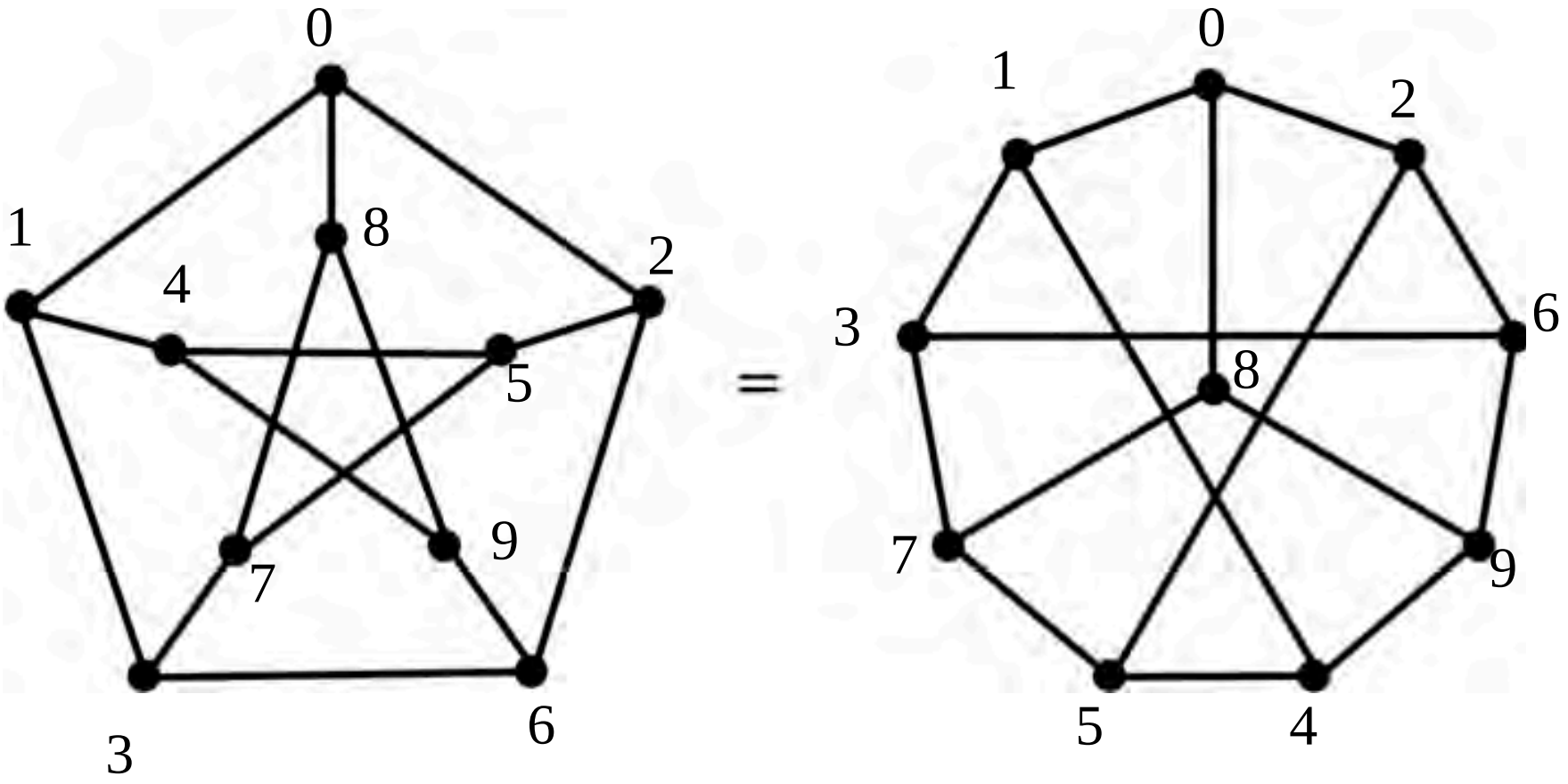
Petersen graph



=



A cage C(*m*,*n*) in graph theory is an *m*-valent graph of girth *n* and the minimum number of vertices. The Petersen graph is C(3,5)
[K_4 = C(3,3) ; K_{33}= C(3,4)]



Proof of isomorphism: each has edges

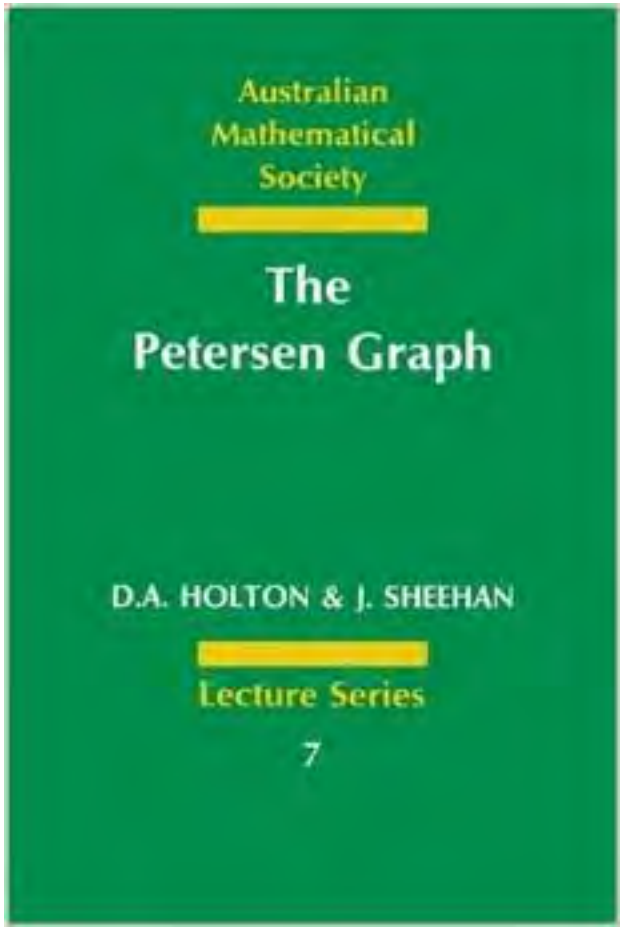
01 02 13 14 2526 36 37 45 49 57 6978 89

Nice book:

The Petersen Graph
by D. A. Holton, J. Sheehan

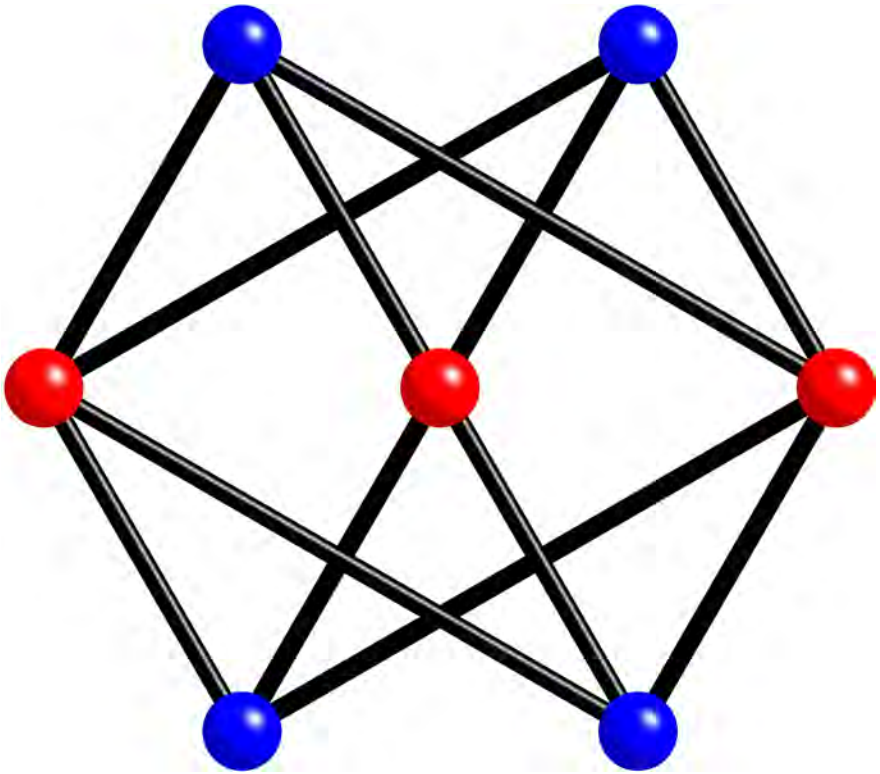
Cambridge University Press

Smallest graph of girth 5
automorphism group same as icosahedral I_h

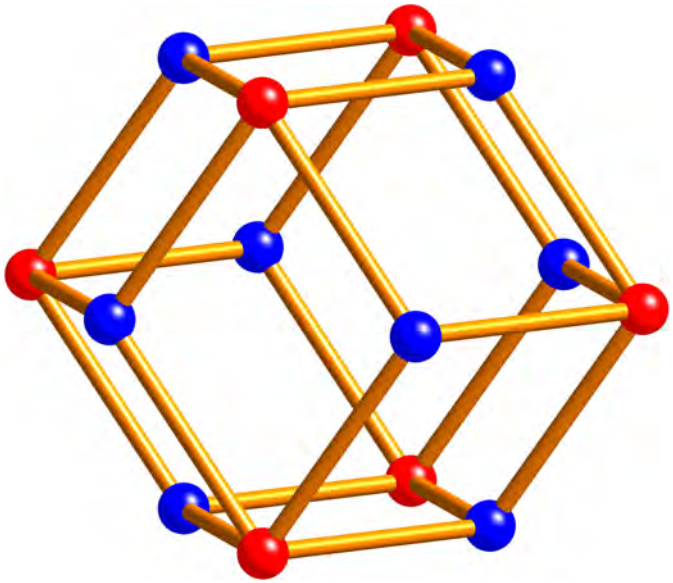


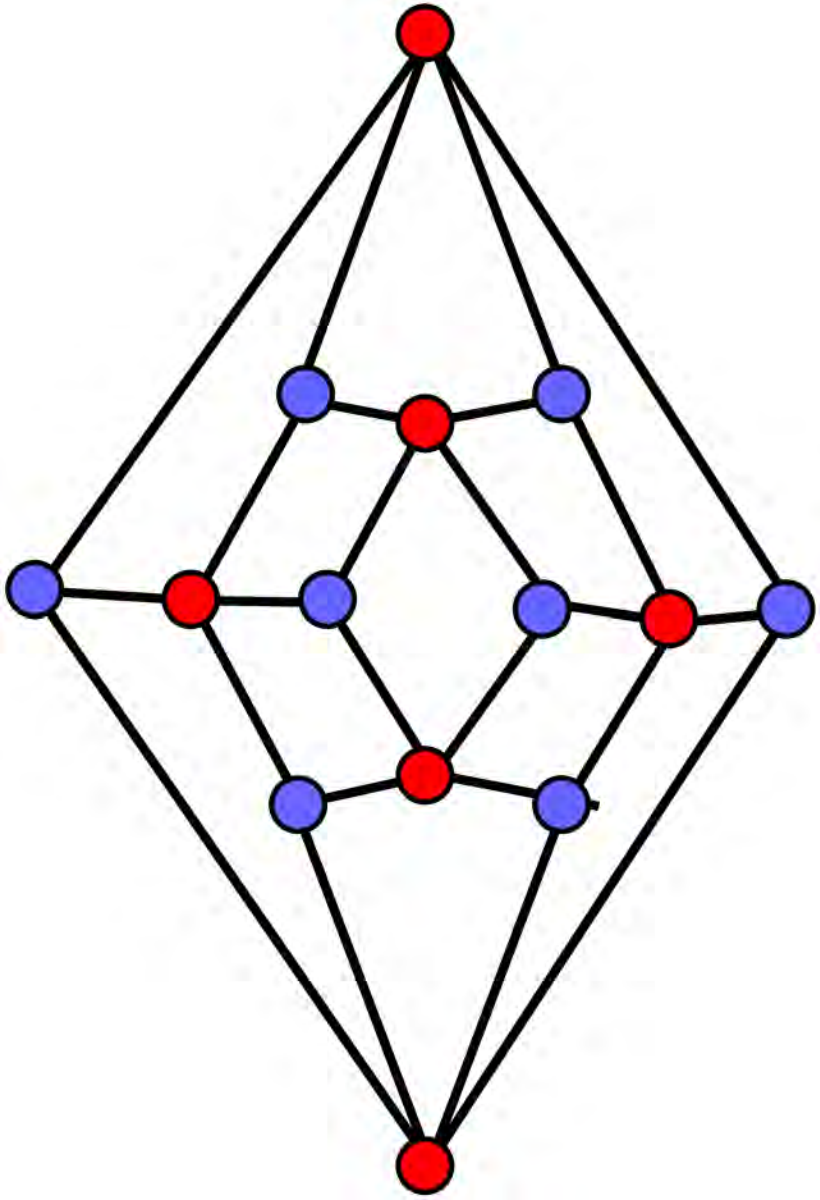
What about graphs that are edge- but not vertex-transitive? Sometimes called “semi-symmetric”.

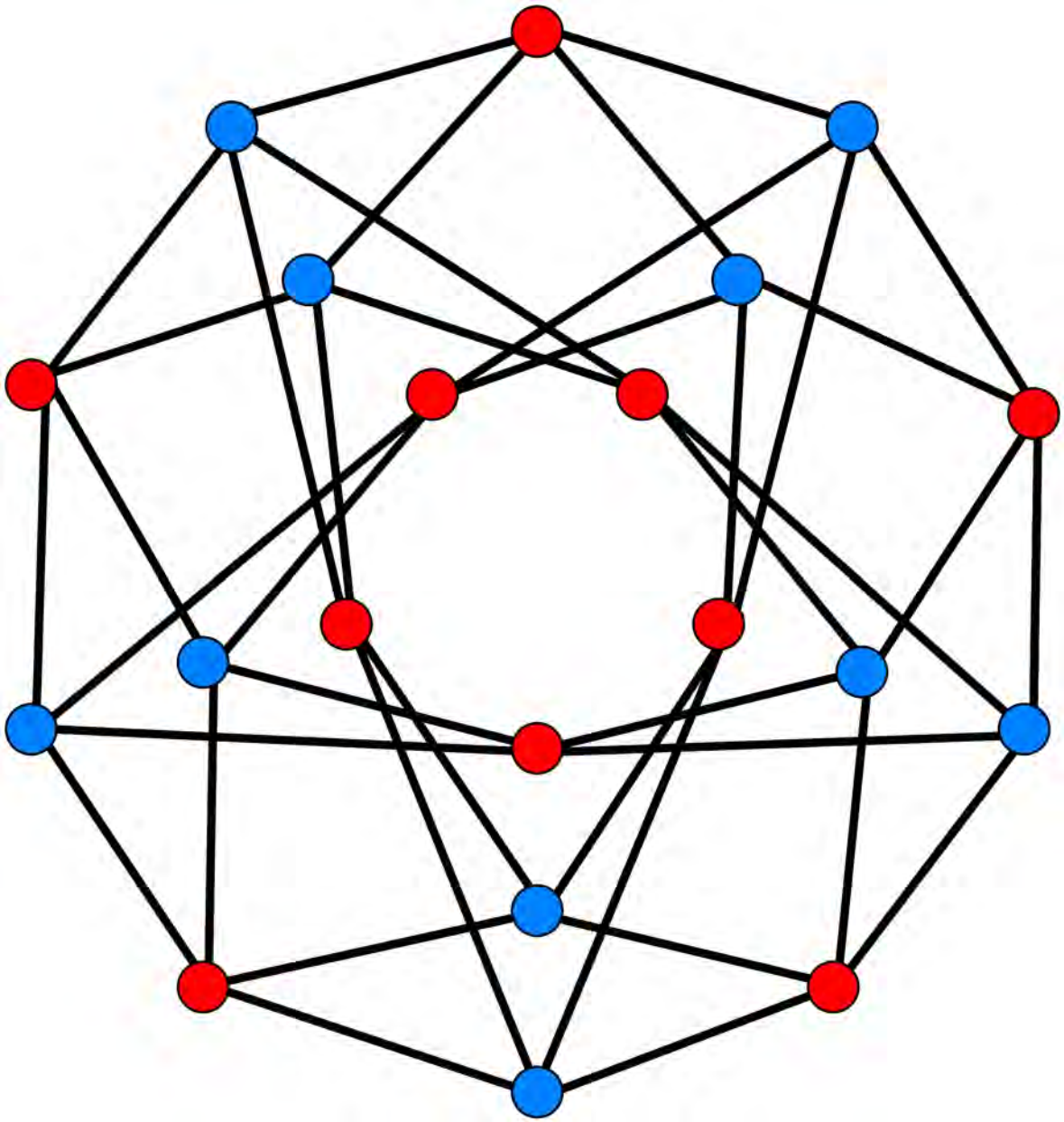
$K_{3,4}$ is an obvious example



Rhombic dodecahedron is one of two edge-transitive polyhedra with two kinds of vertex.





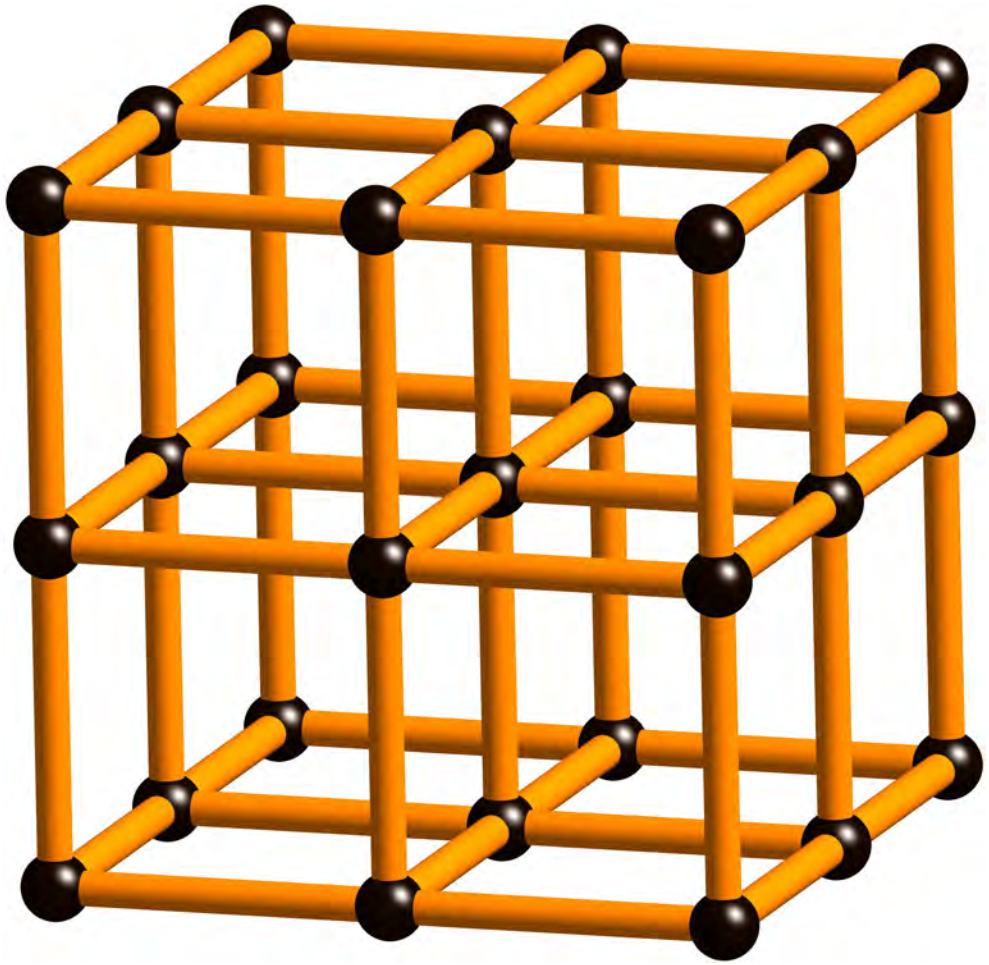


Folkman graph. Smallest semi-symmetric graph with all vertices same coordination (regular graph).

Note blue vertices connected to all other blue vertices by a path of length two.

Not true for red

Another finite graph, just for fun



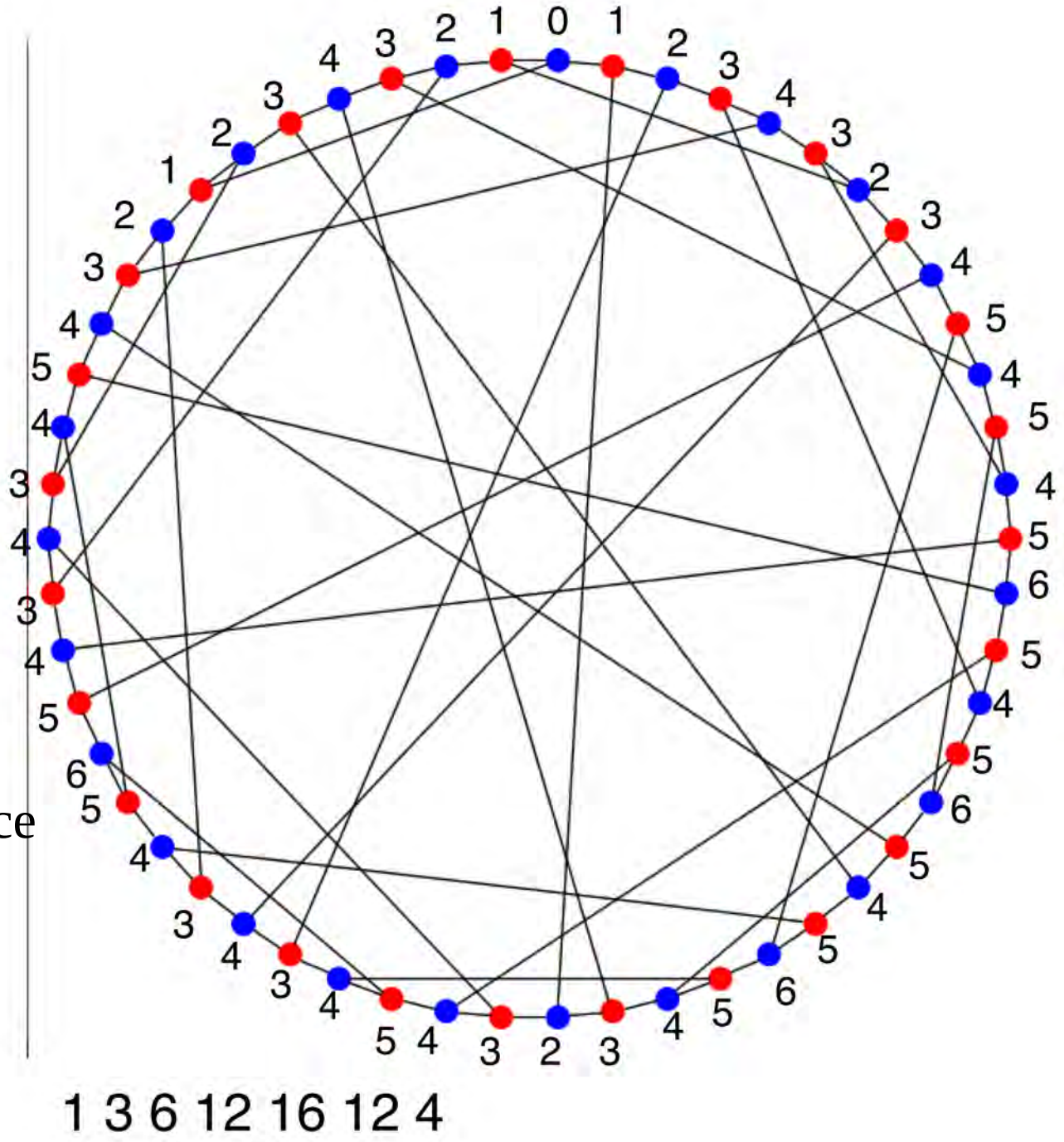
This figure has 27 rods and 27 balls. Each ball is on (connected to) 3 rods and each rod has (is connected to) 3 balls. So we can make a cubic (3-regular) graph:

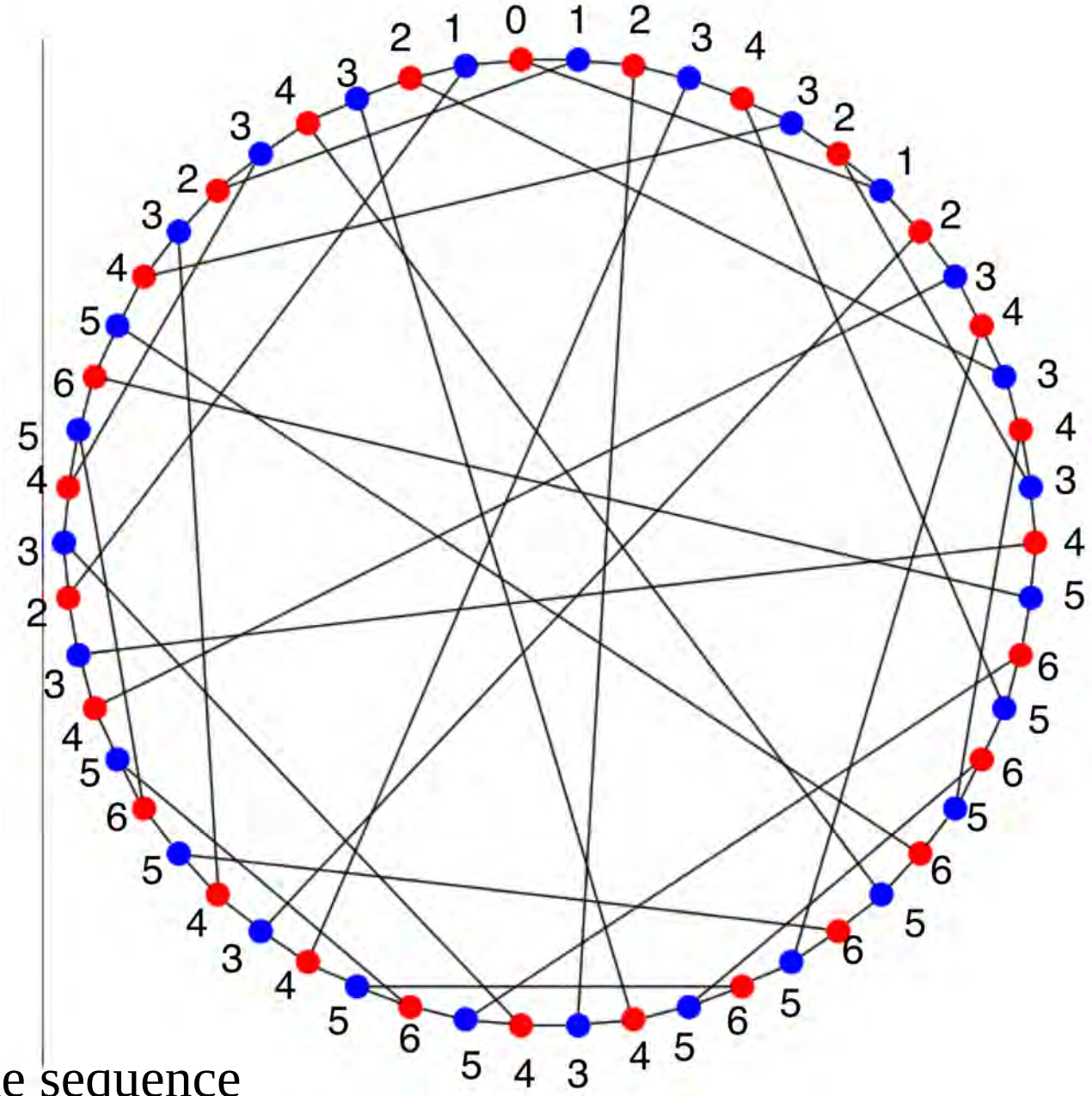
The Gray graph.

This is the smallest seni-regular cubic graph (trivalent).

We can tell that the red and blue vertices are different by looking at the distance sequence.

This is sequence
or blue (rods)

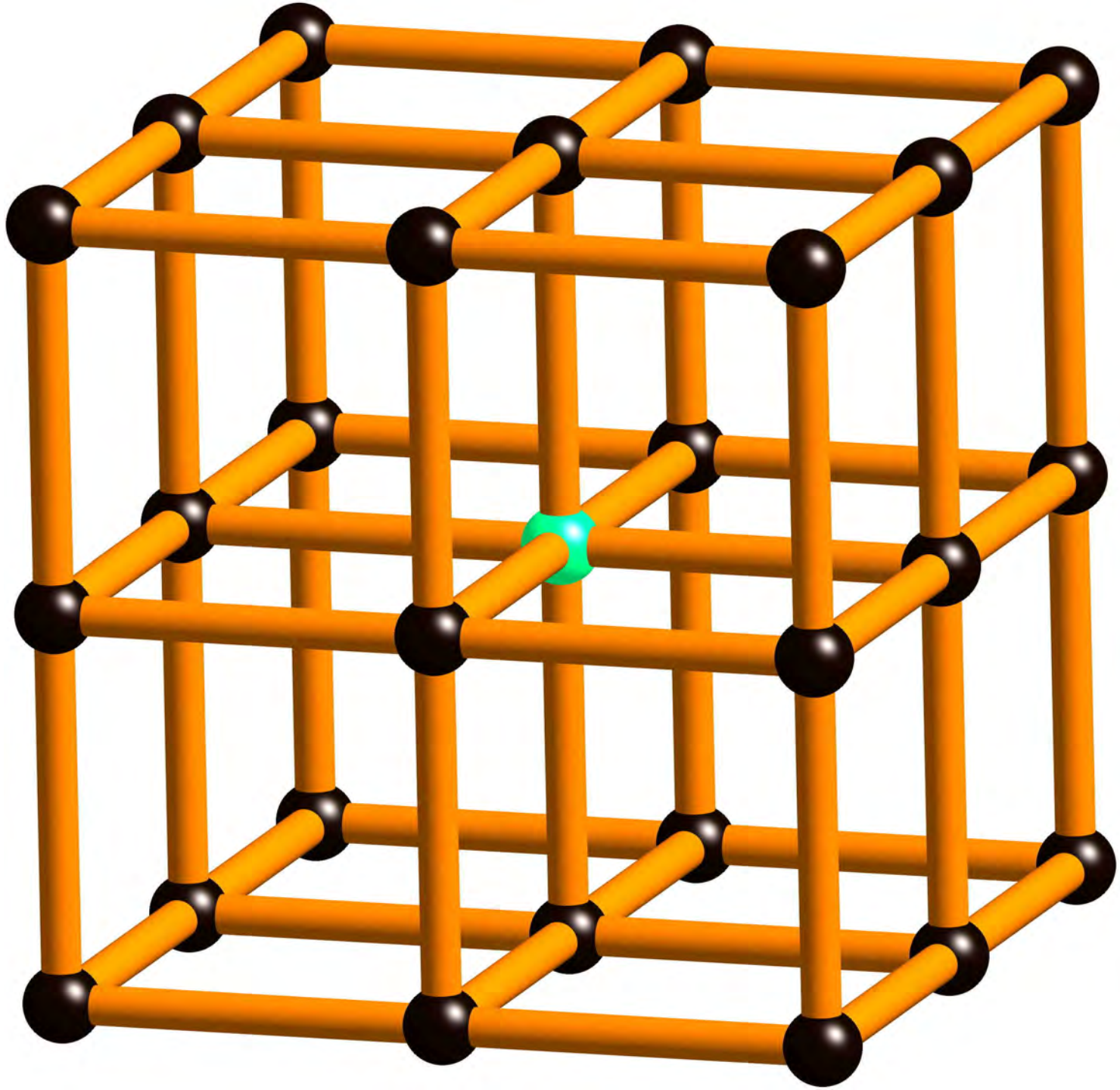


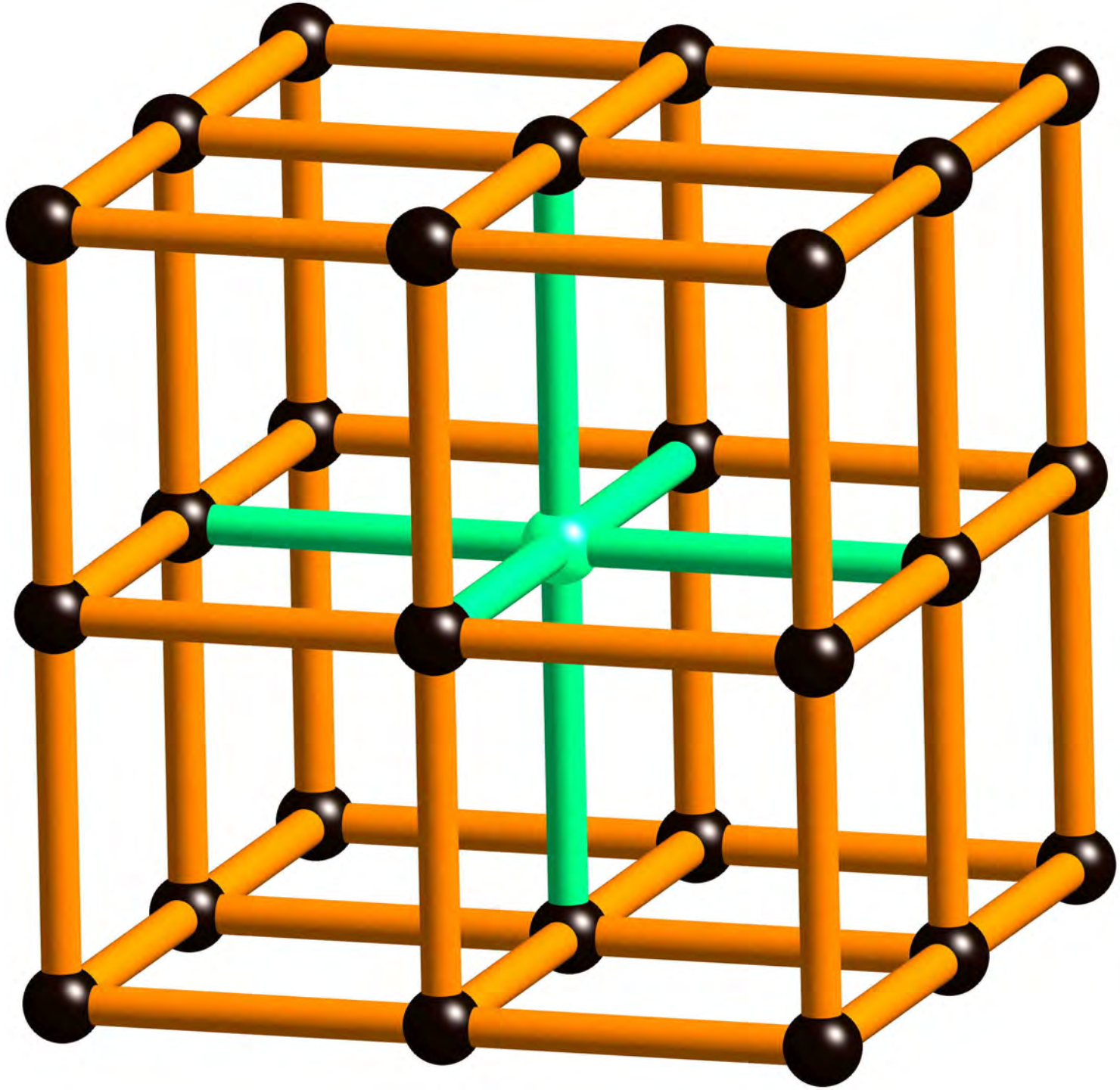


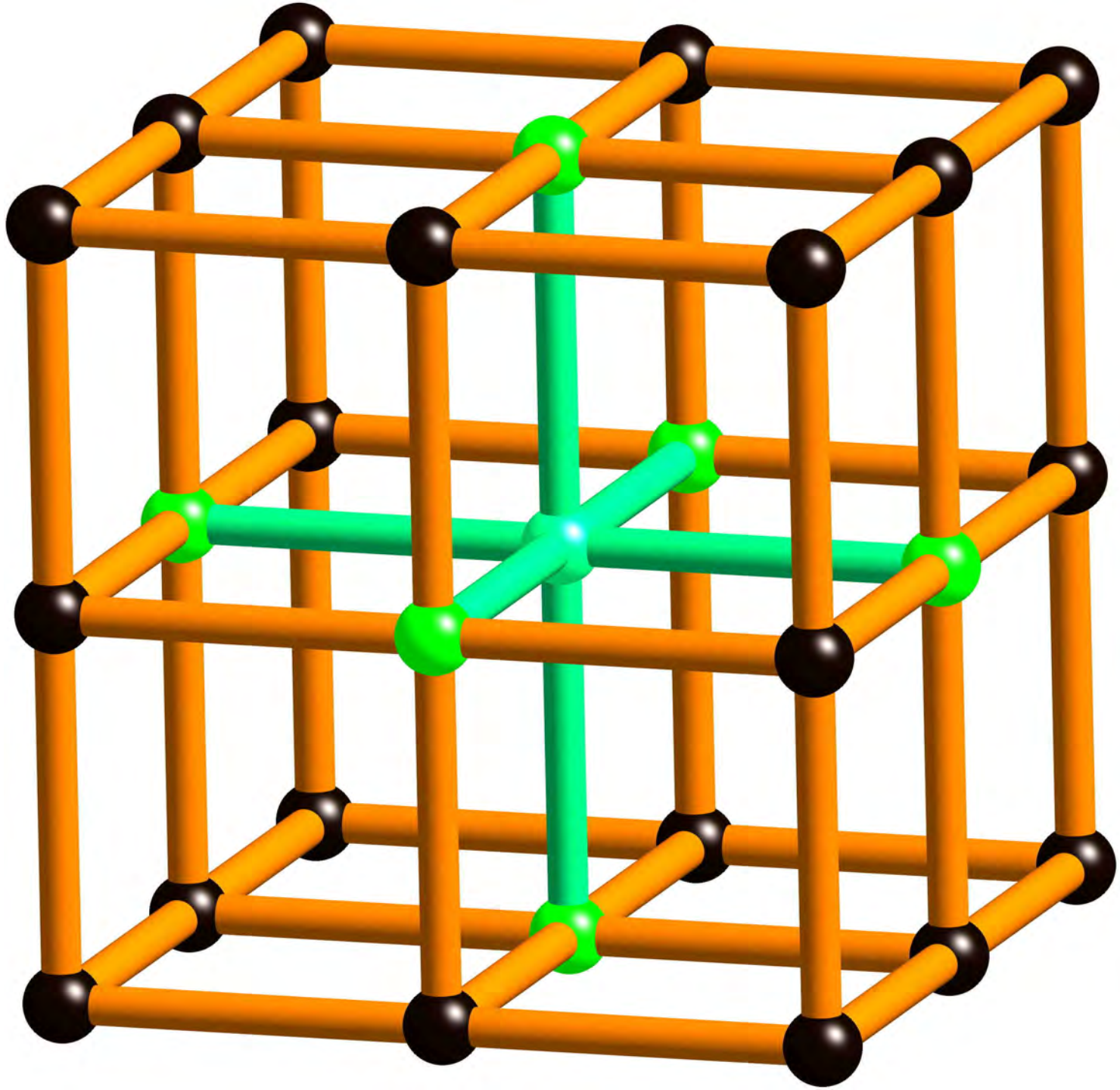
This is the sequence for red (balls)

1 3 6 12 12 12 8

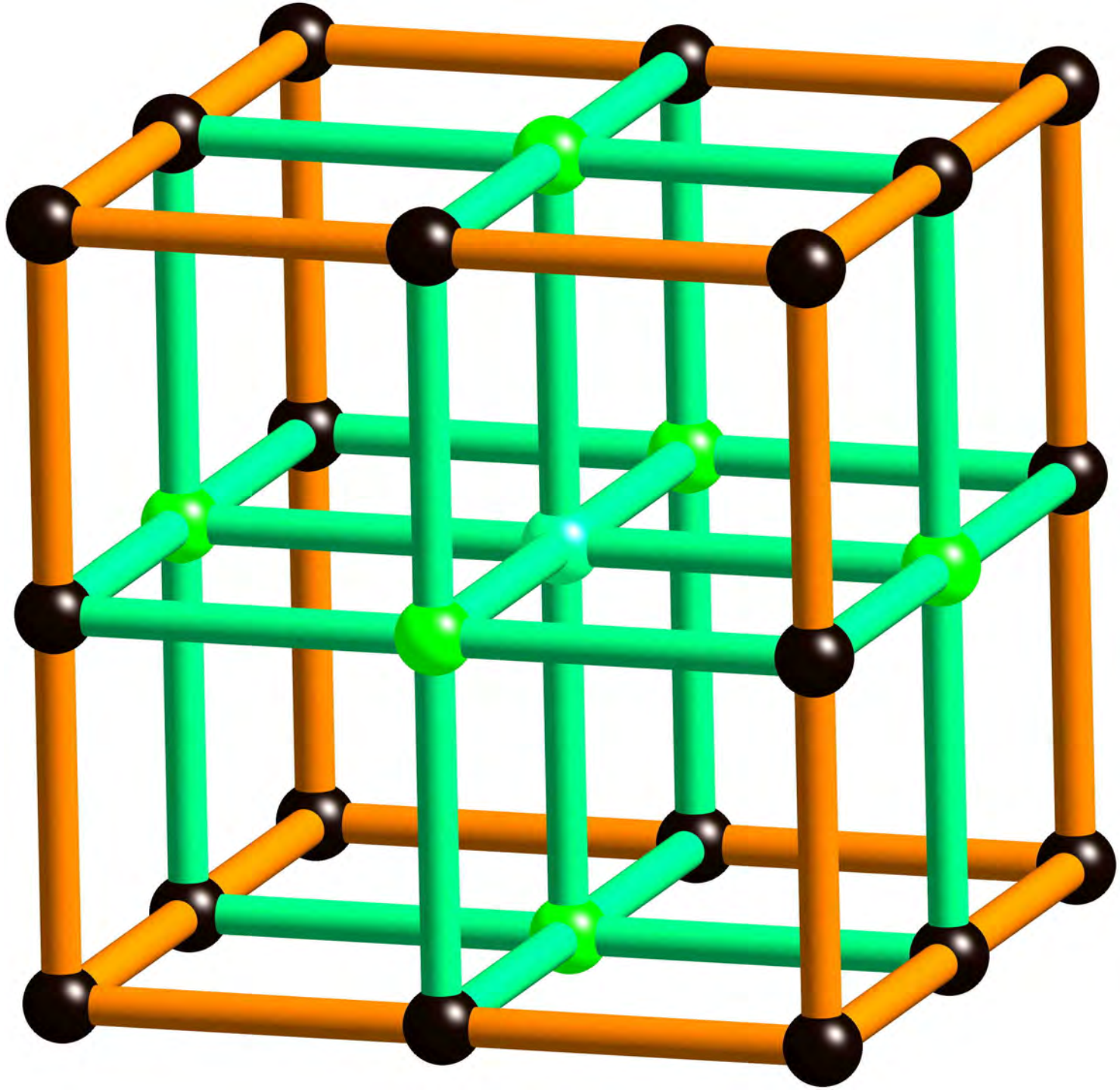
let’s do it on the model...



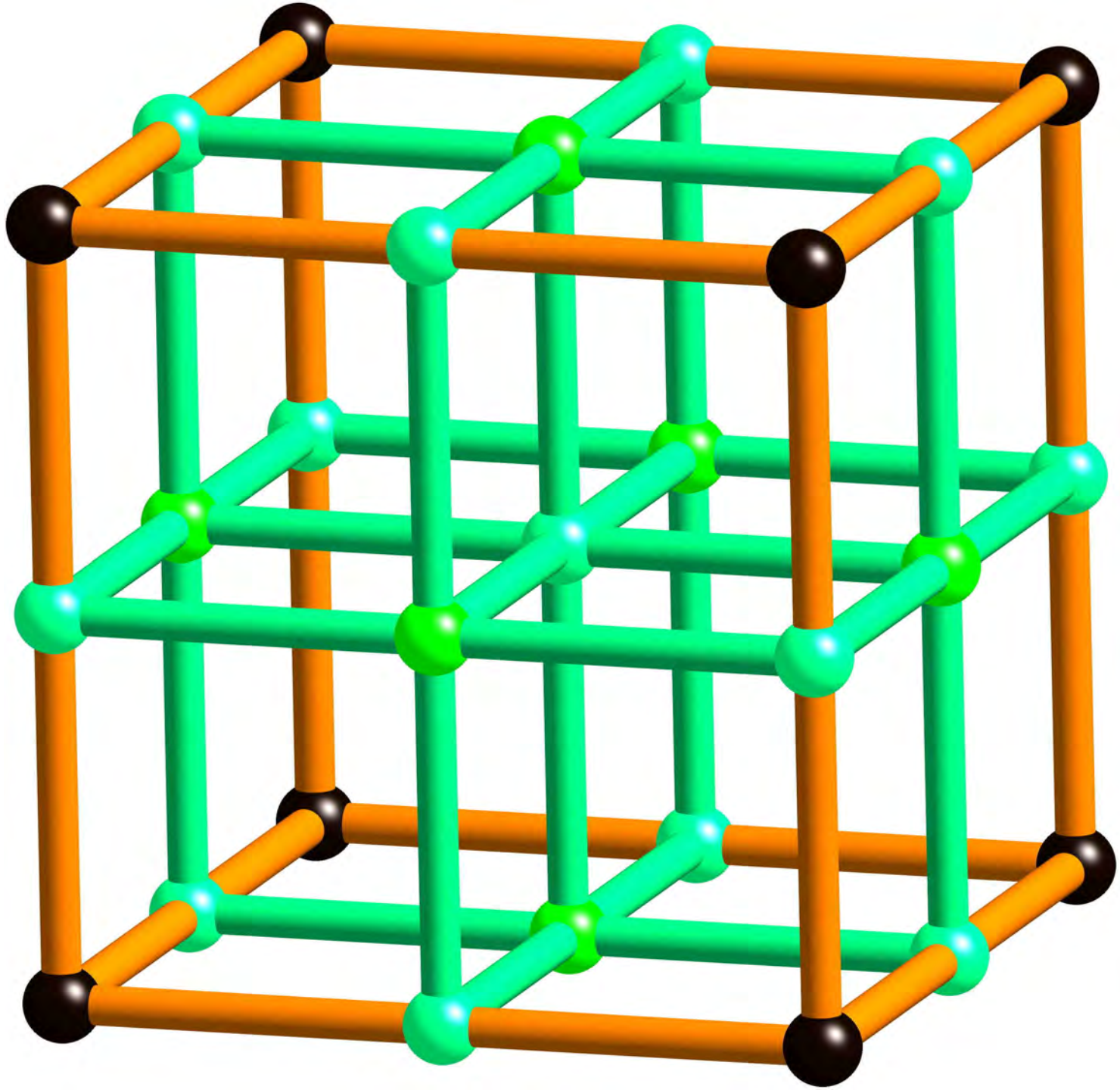




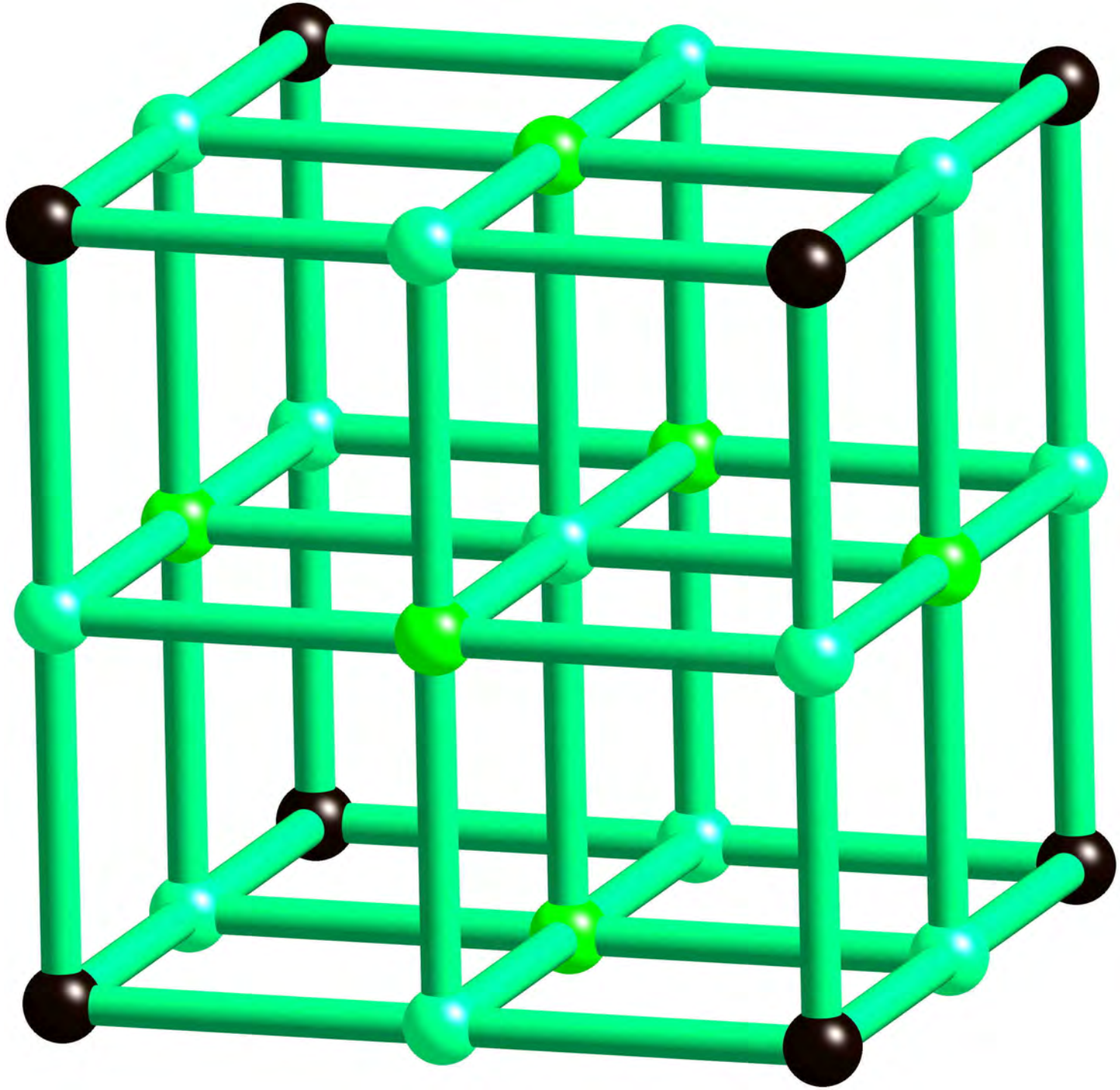
136



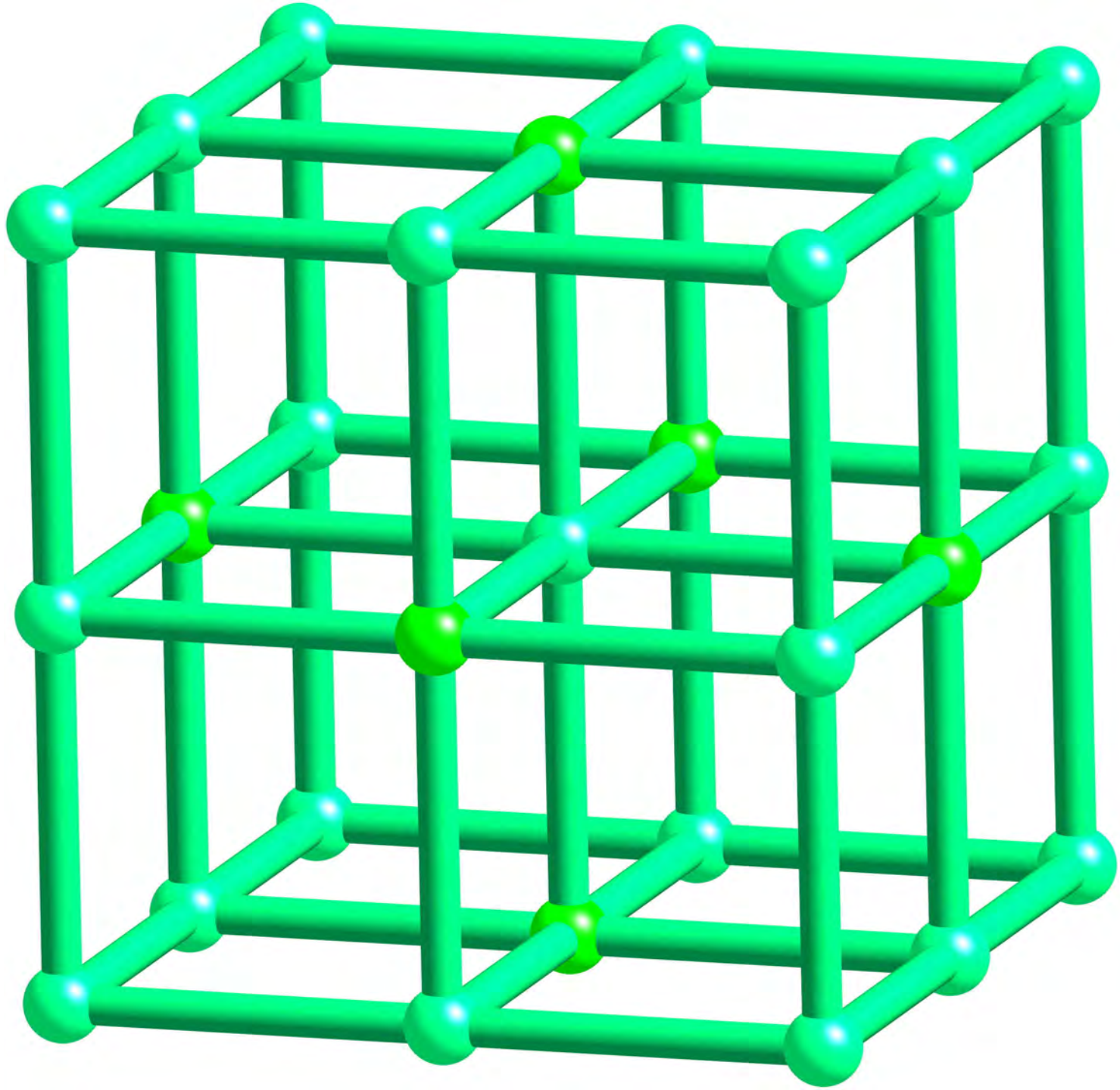
1
3
6
12



1
3
6
12
12



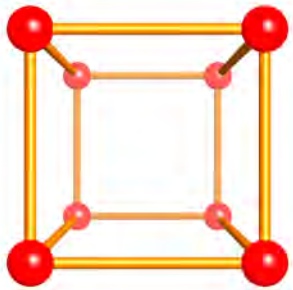
1
3
6
12
12
12

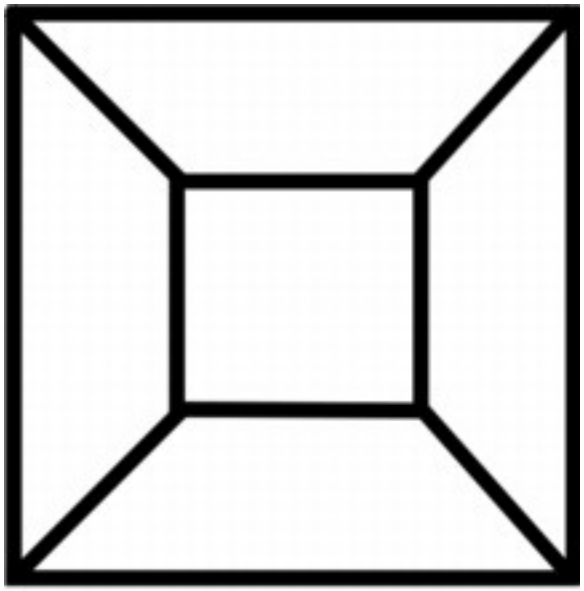


1
3
6
12
12
12
8

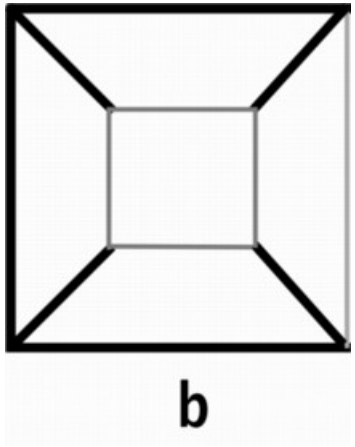
In crystal graphs (nets) the distance sequence is called the coordination sequence

Now something about cycles (closed paths) rings and strong rings...





This is the graph of a cube (Schlegel diagram)
Note that it is planar



The heavy lines are a connected subgraph without circuits that connects all vertices.

It is a **spanning tree**.

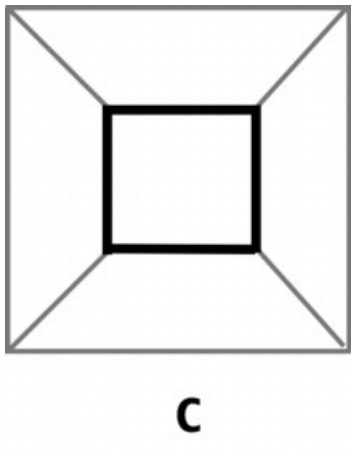
The number of edges necessary to complete the graph is the **cyclomatic number**, *g*, of the graph (= 5 in this case)

In molecular chemistry this is the number of rings

If there are *v* vertices and *e* edges

$$g = 1 + e - v = 1 + 12 - 8 = 5$$

(cubane is pentacyclo-octane)



The heavy lines outline a **cycle**
In this case it is also a **strong ring**
as it is not the sum of smaller cycles

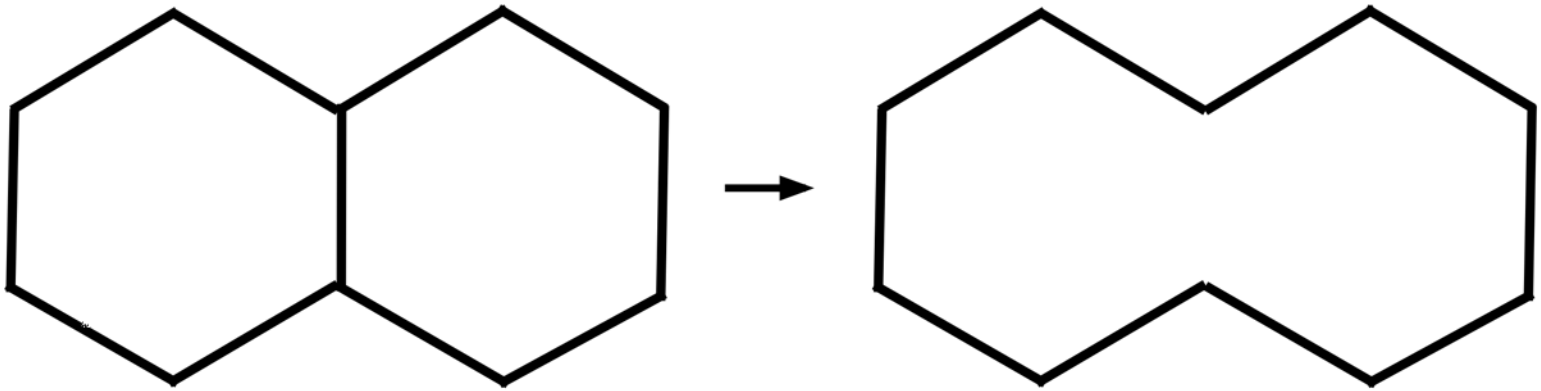
Ring (cycle) sum

The sum of two rings (cycles) is the set of edges that occur exactly once.

The sum of *n* rings (cycles) is the set of edges that occur an odd number of times.

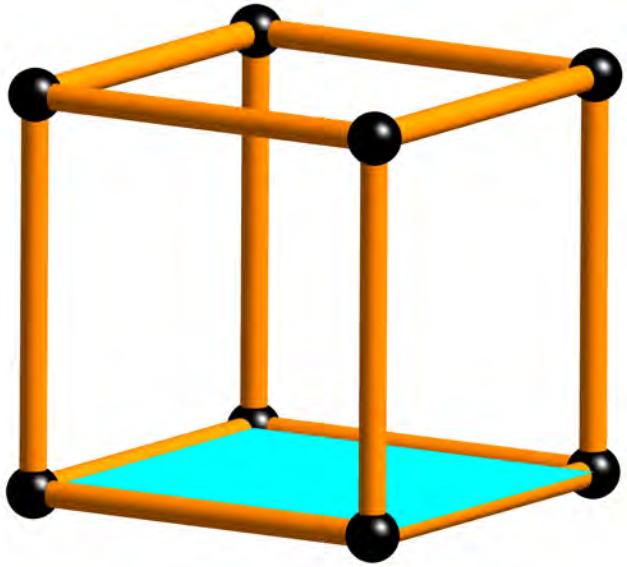
In solid state chemistry (not molecular chemistry!)
A **ring** is a cycle that is not the sum of two smaller cycles

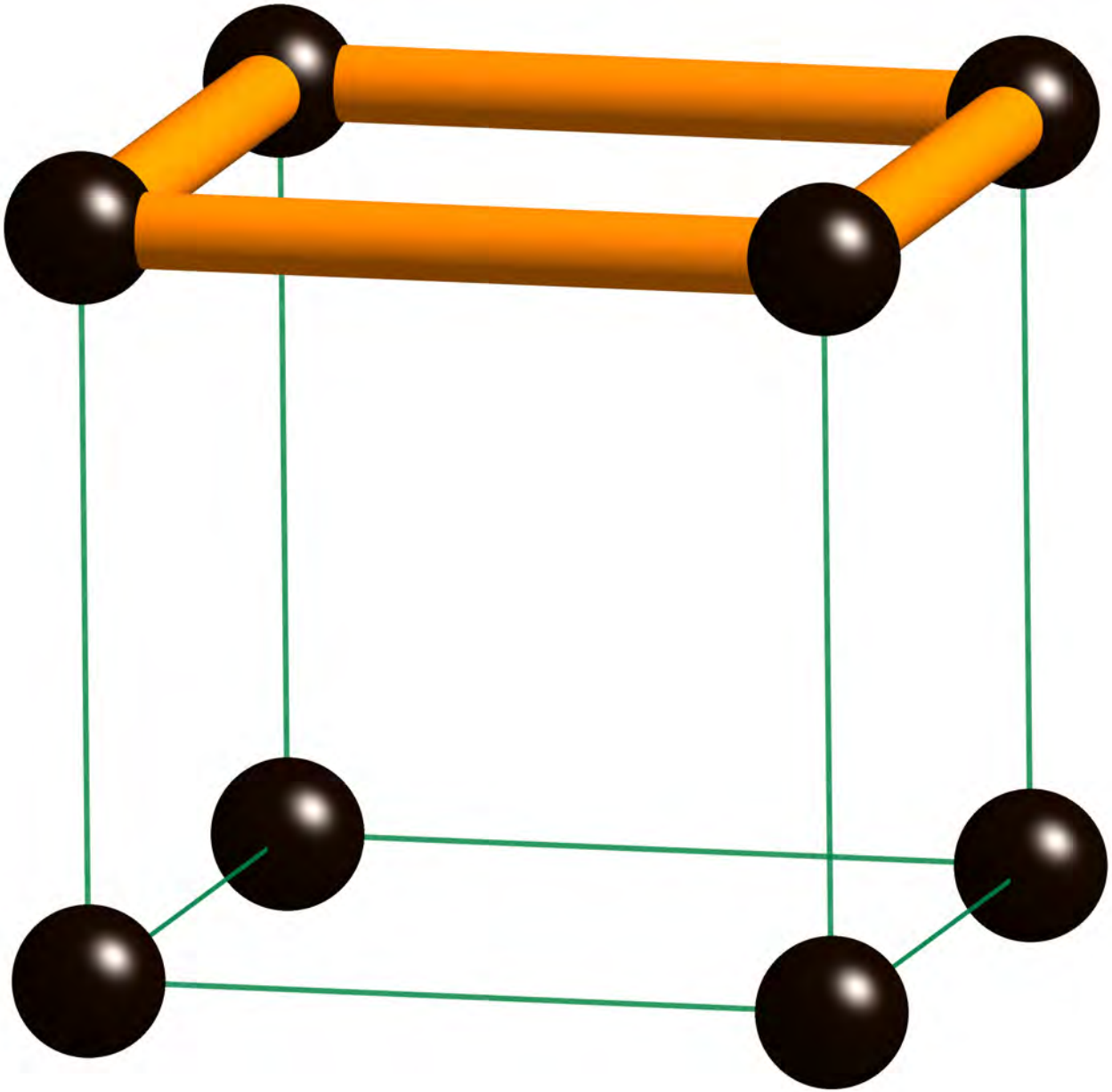
examples of ring sums



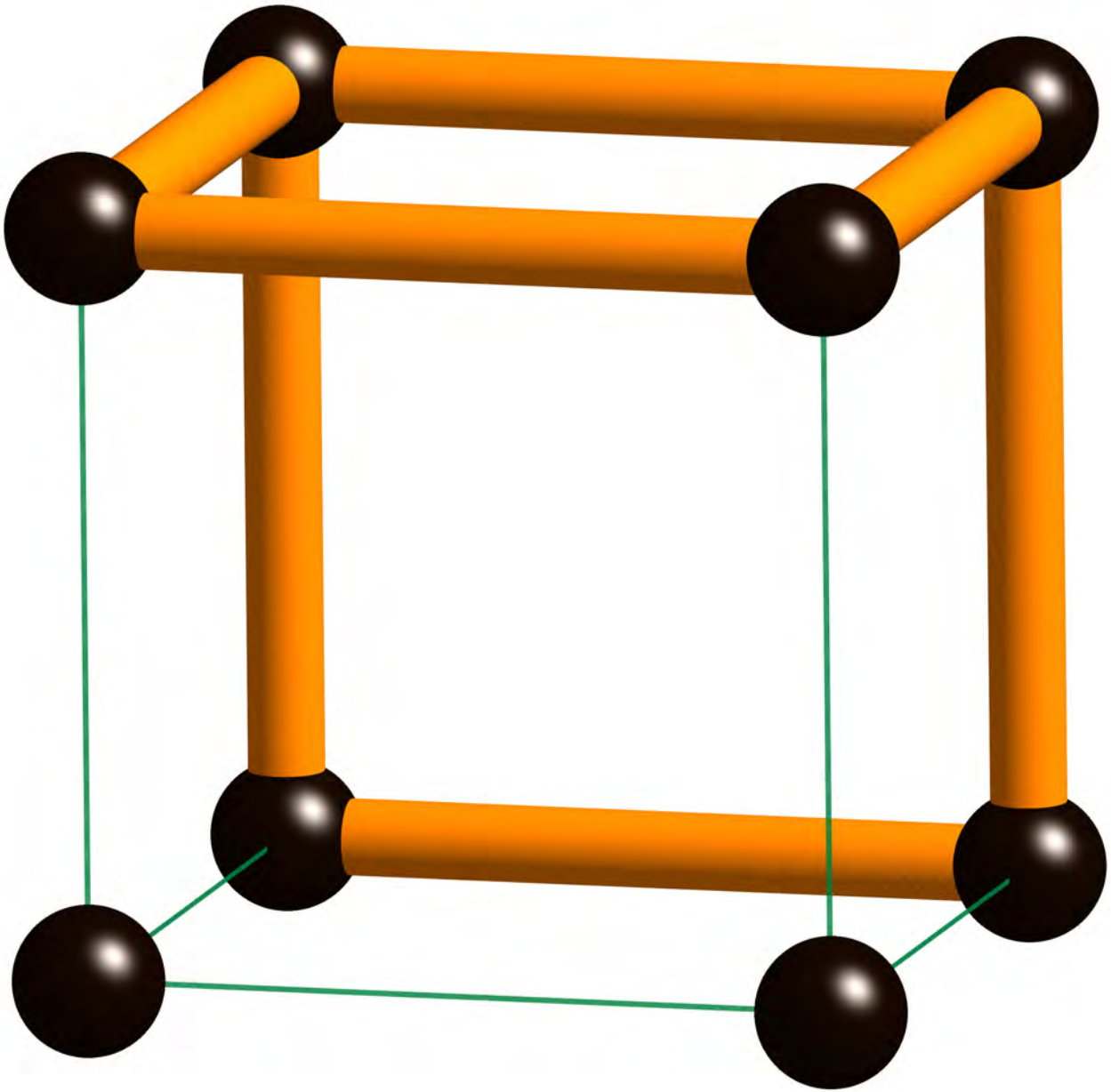
Two rings -> sum

one face of a polyhedron is the sum of all the rest

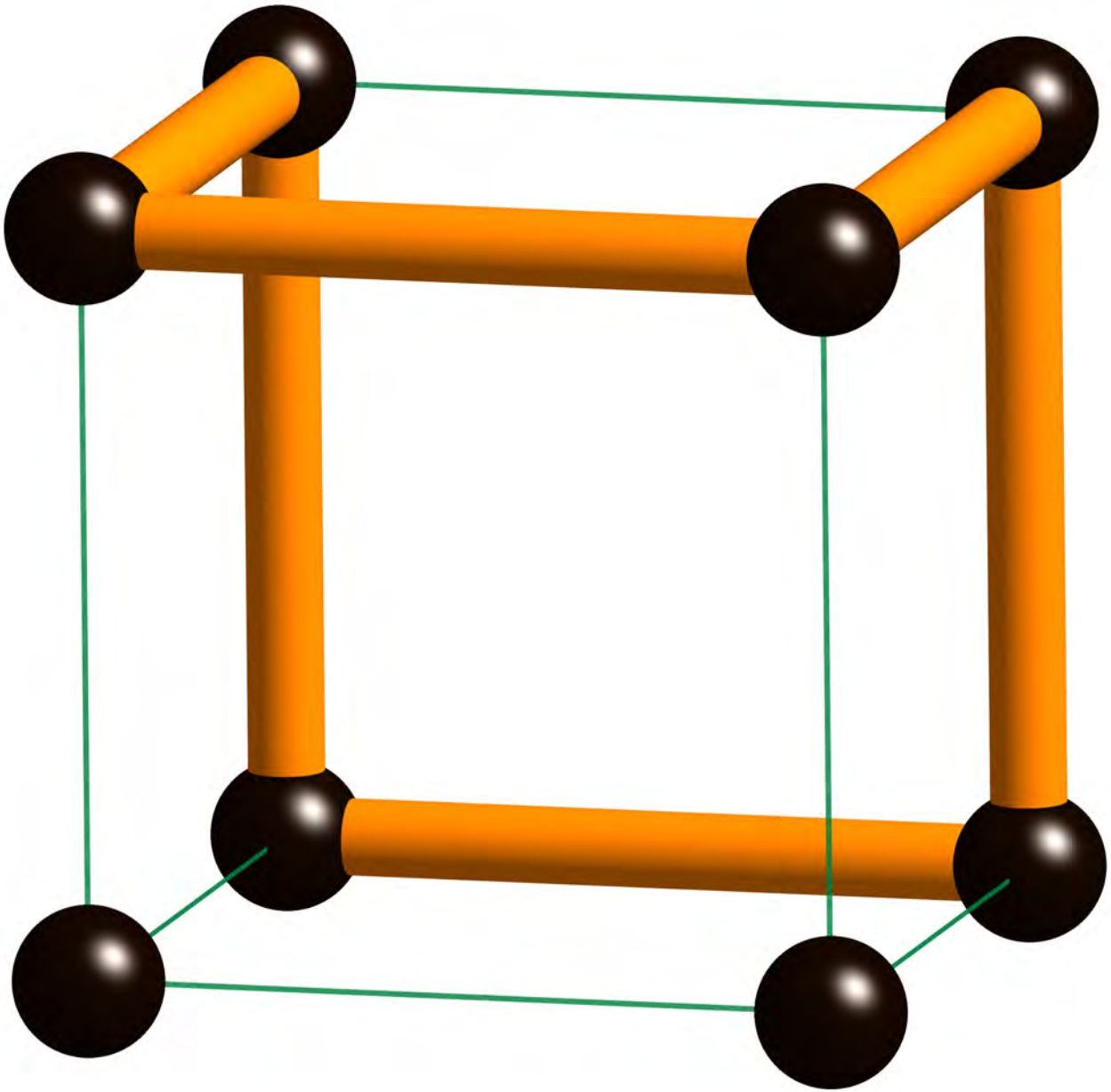




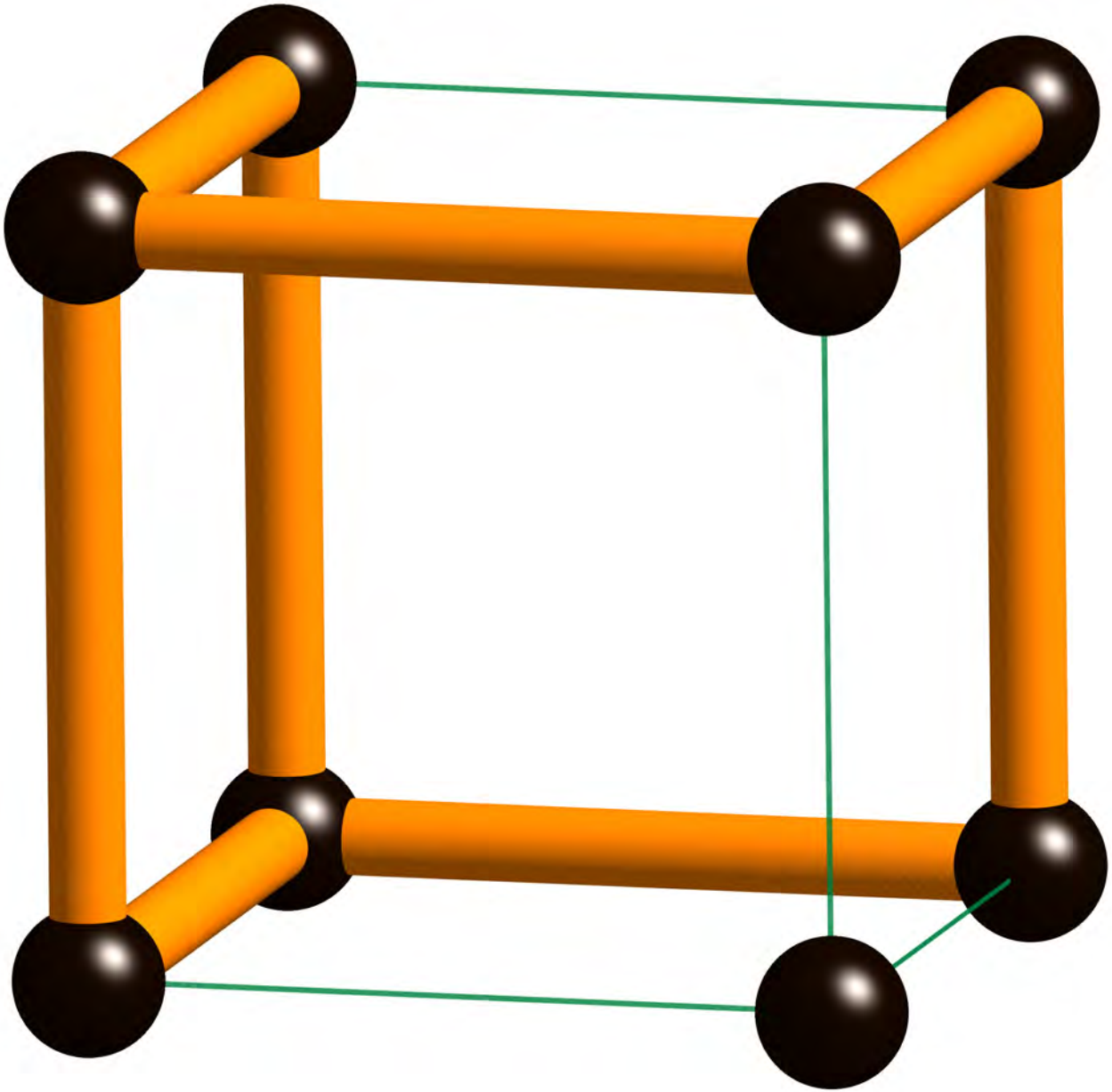
Face 1
now add
face 2



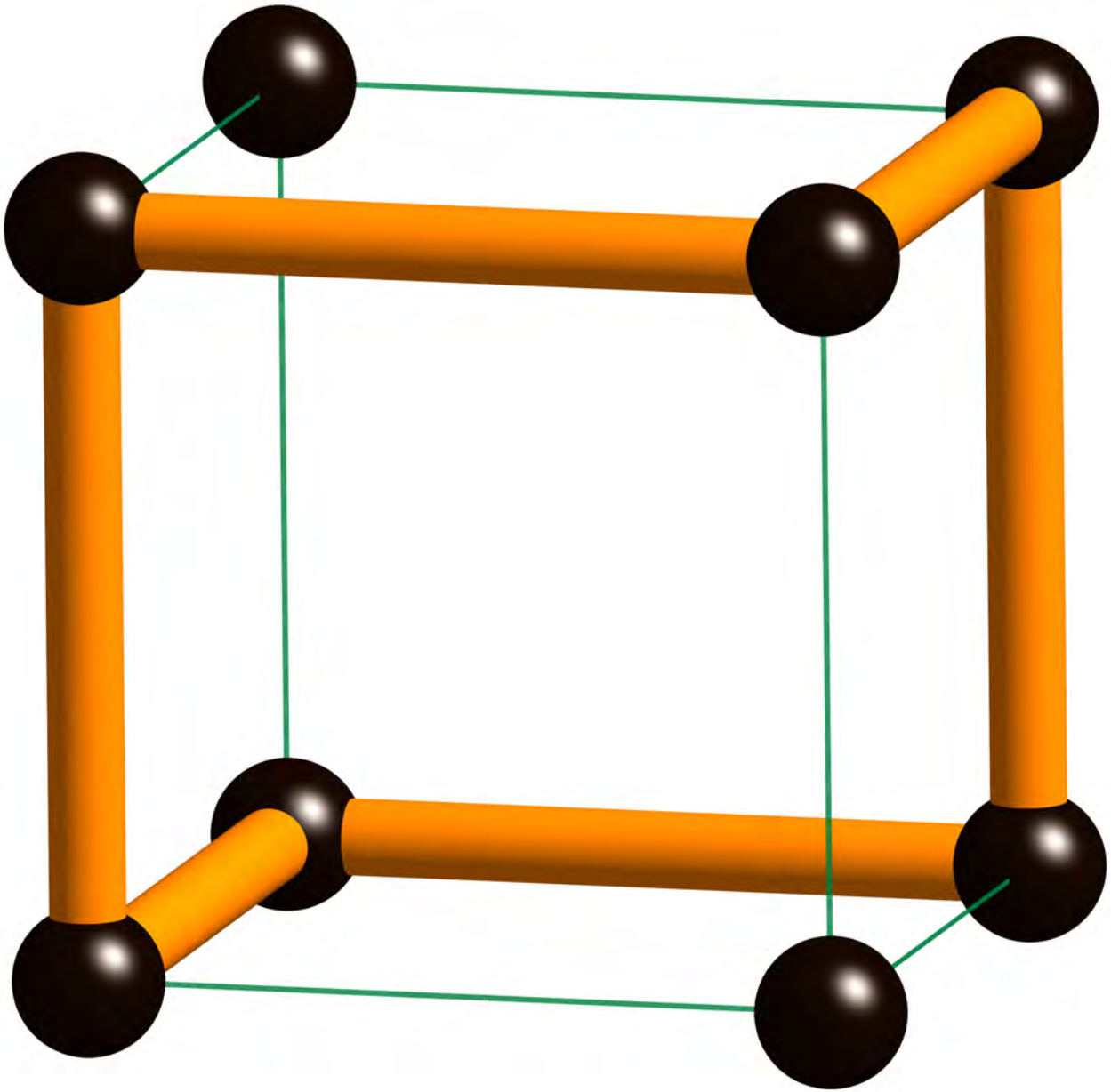
done
now delete
common
edge



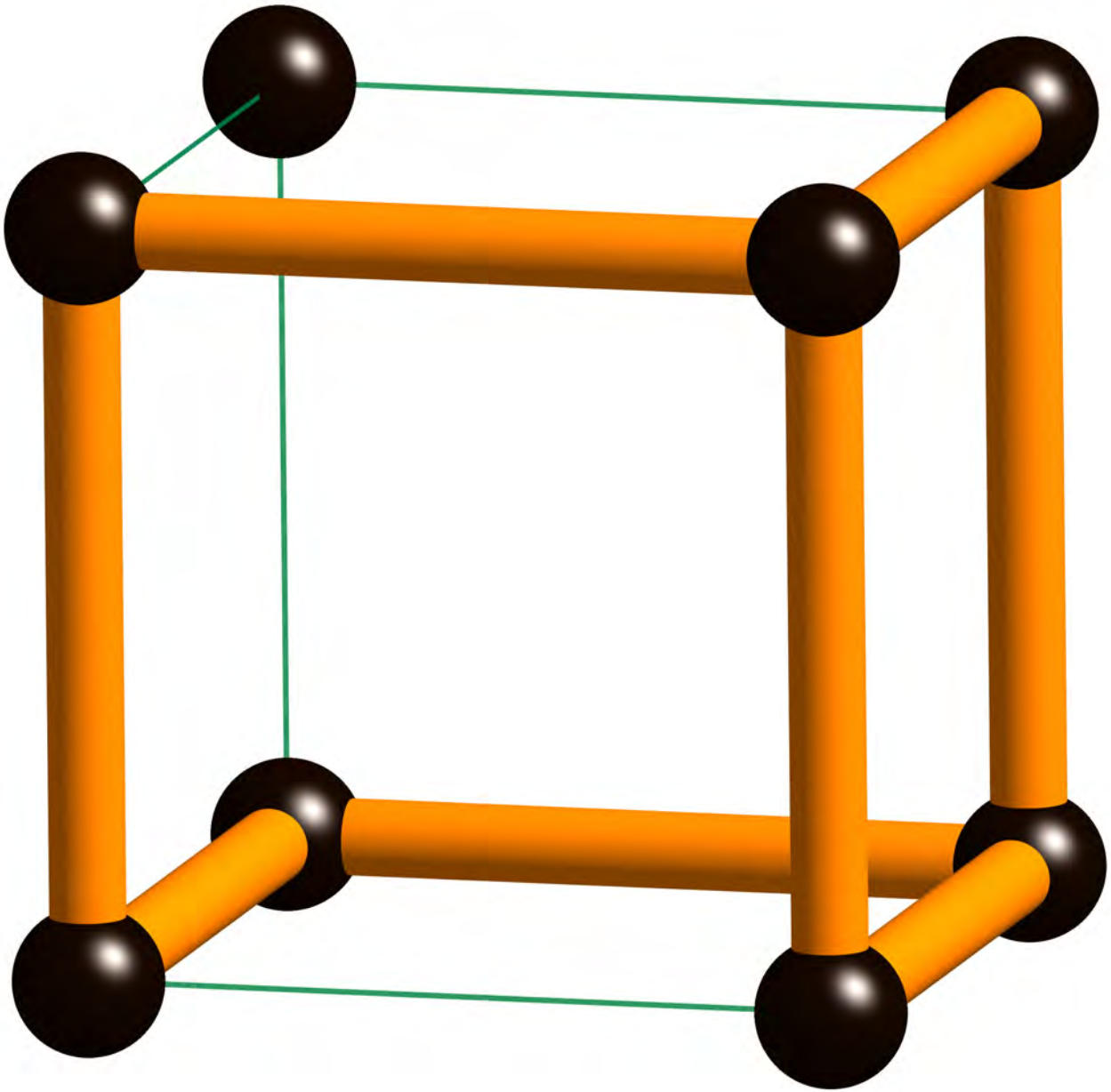
common edge deleted now add face 3



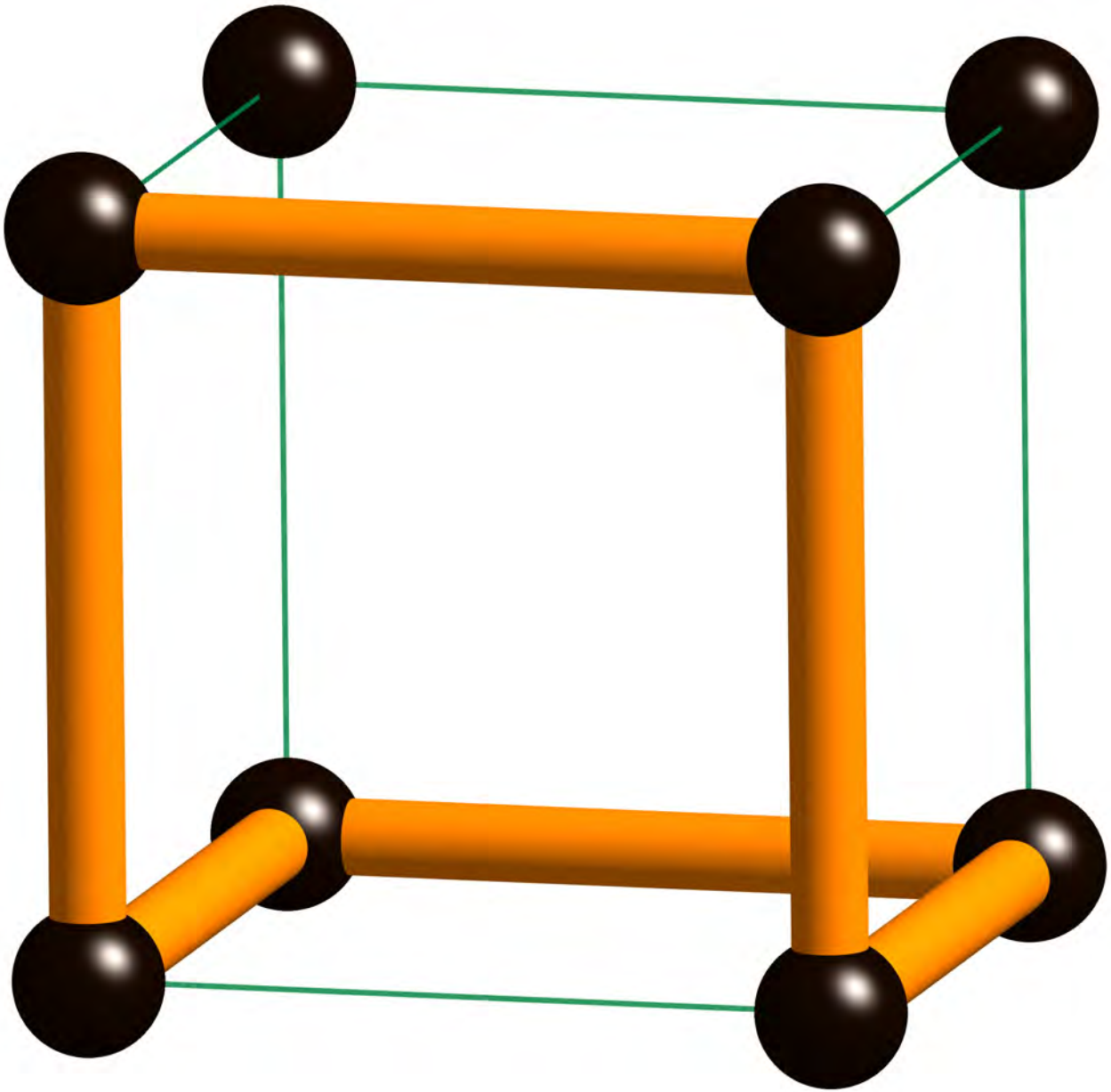
add face 3
now
delete
common
edges



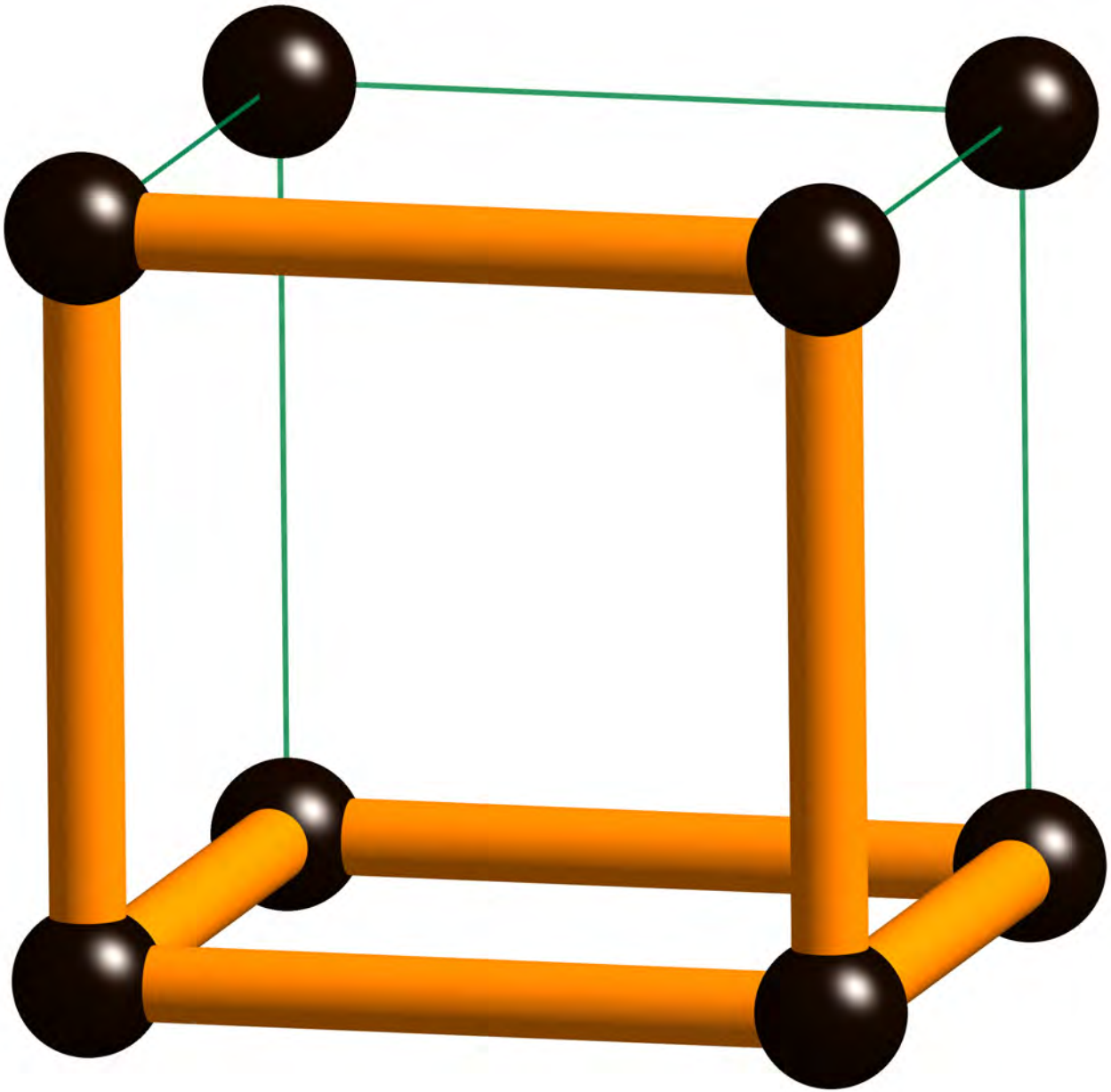
done
now
add
face 4



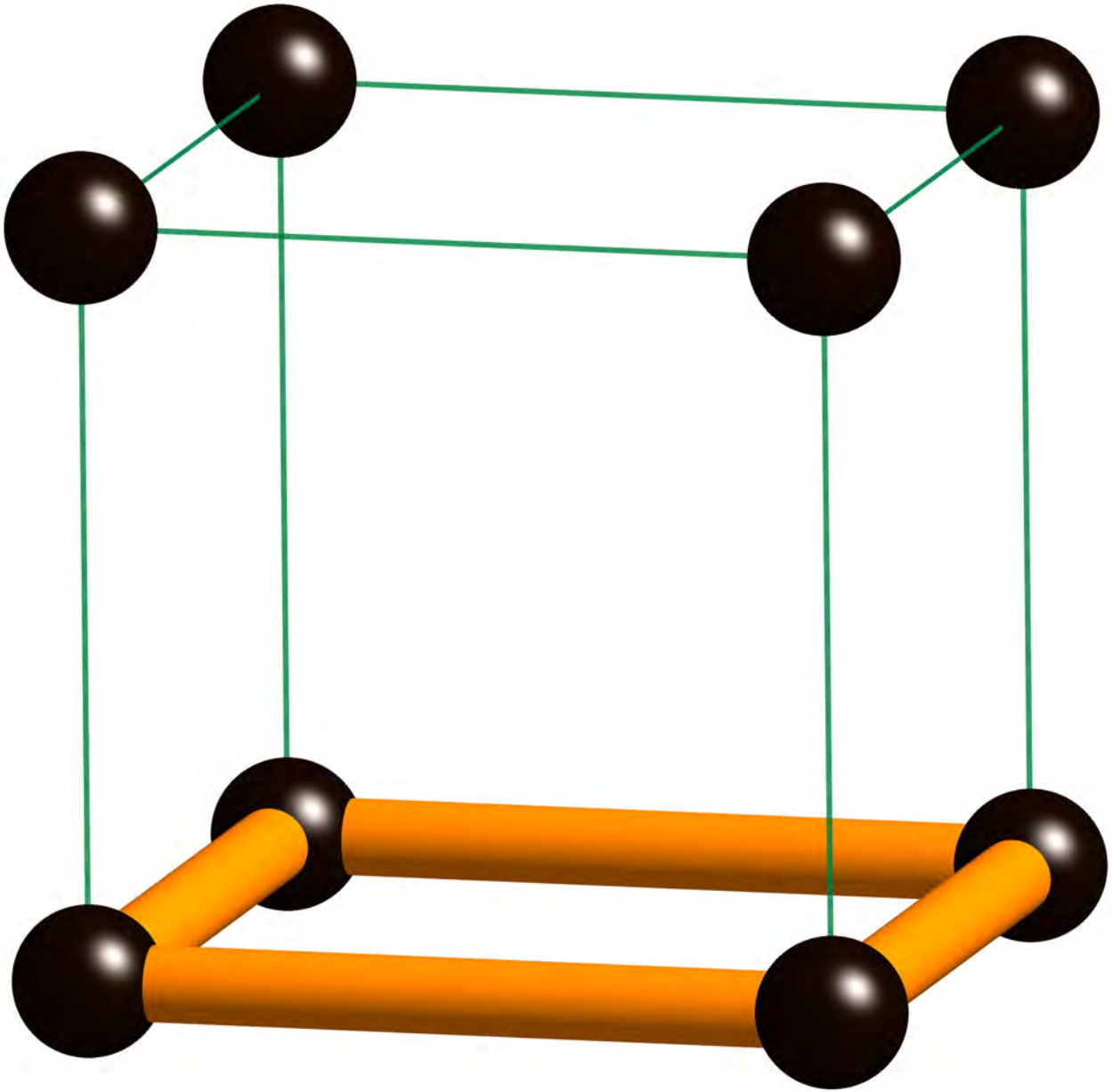
done
now
delete
common
edges



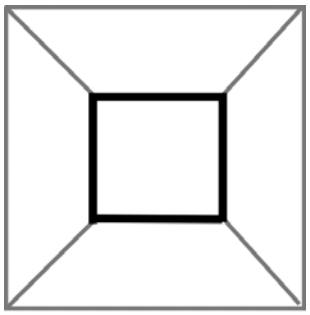
done
now add
face 5



done
now
delet
common
edgs

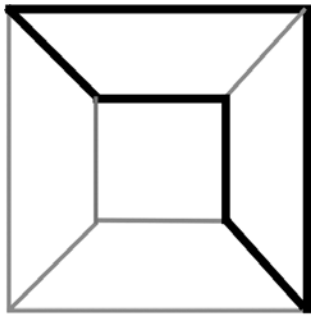


done
this is
the sum
of the
five faces



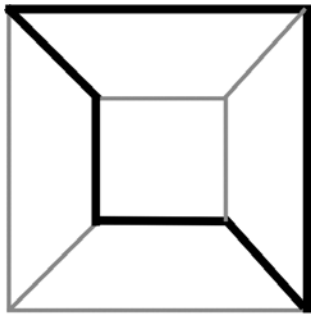
c

A cycle that is a **strong ring** (not the sum of smaller cycles).



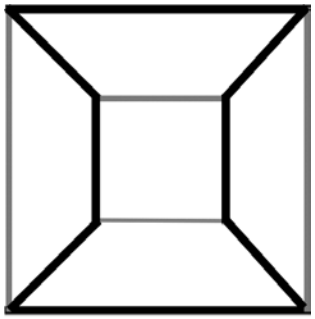
d

A cycle that is not a ring. (It is the sum of two smaller cycles.)



e

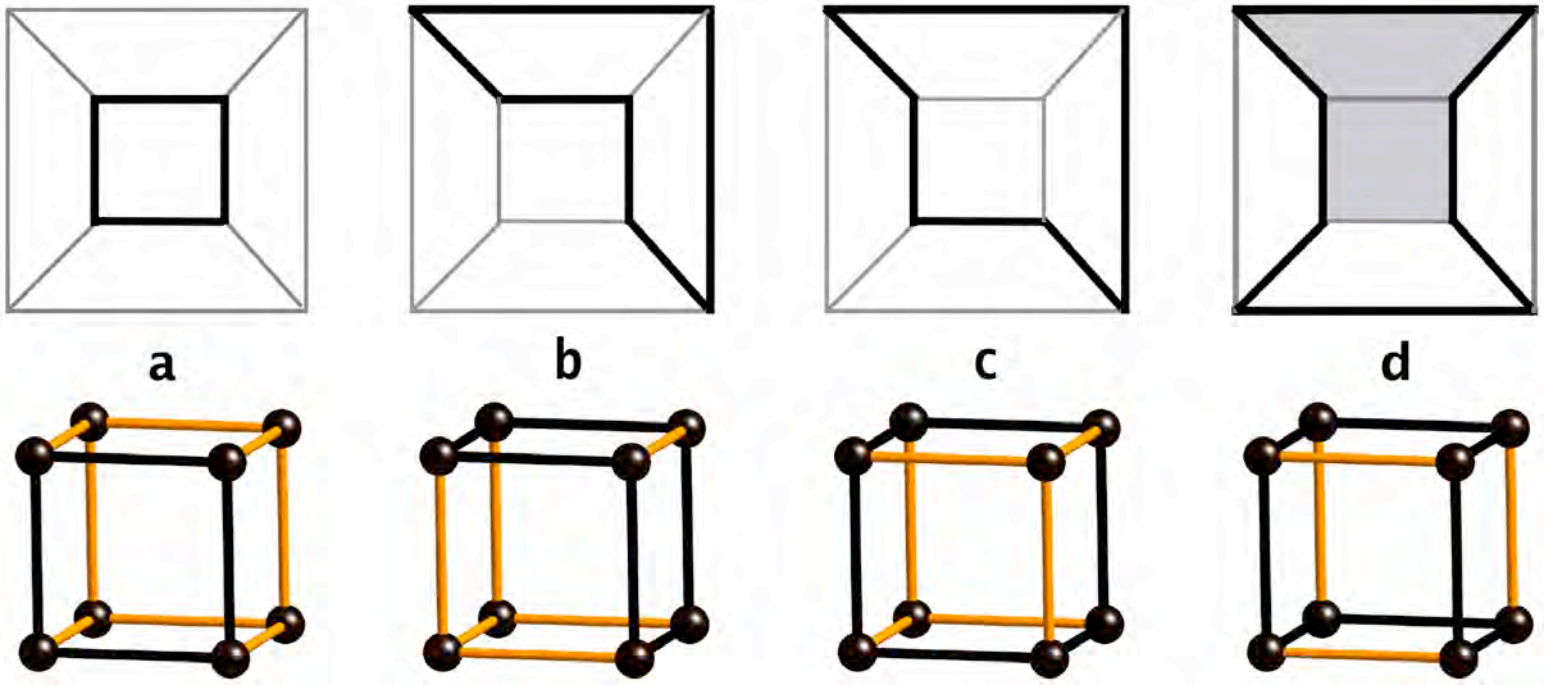
A cycle that is a **ring** (not the sum of two smaller cycles) But **no**t a strong ring (it is the sum of three smaller cycles).



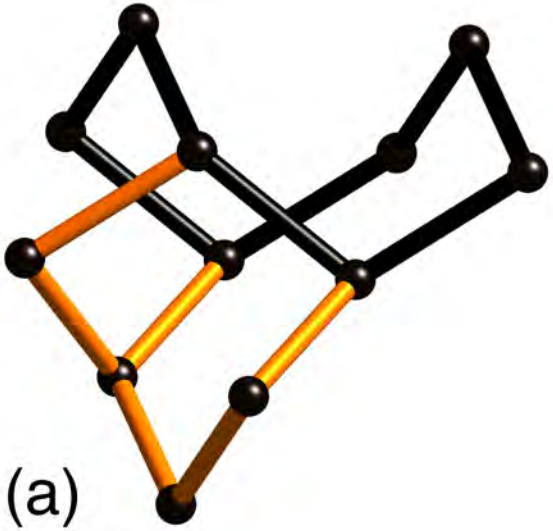
f

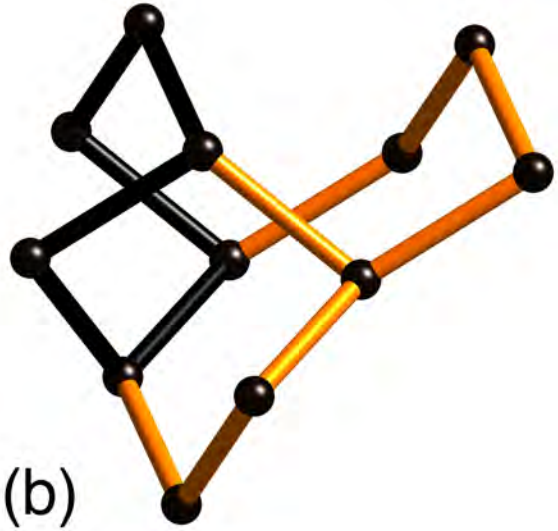
A cycle that is **not** a ring. It is the sum of two *smaller* cycles: a 6-cycle and a 4-cycle. (Contrast **e** on left.)

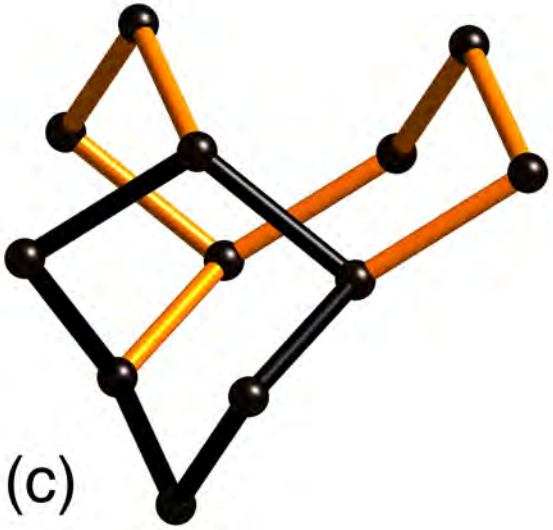
Repeated…

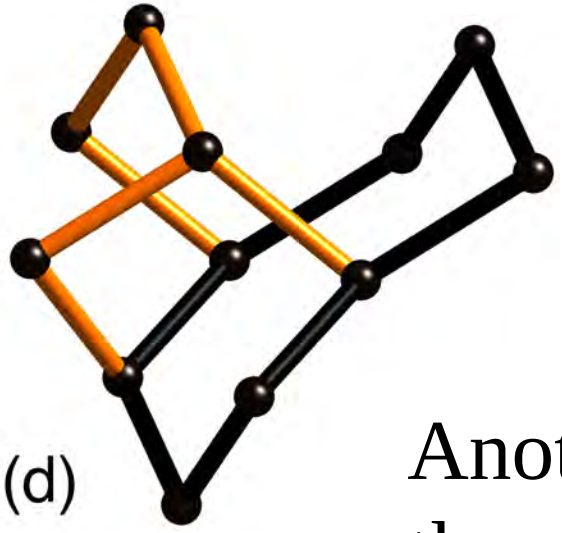


a	b	c	d
strong ring	6-cycle not a ring (sum of two 4-rings)	6-ring not a strong ring (sum of three 4-rings	8-cycle not a ring (sum of a 4-ring and a 6-ring)





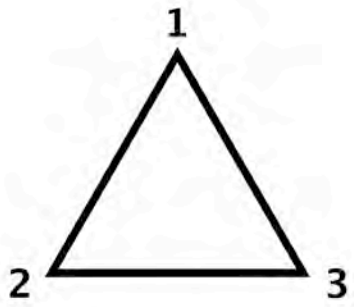




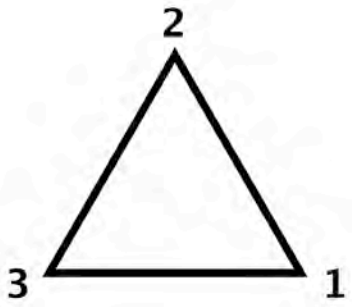
black in (d) is black once in (a), (b), (c)
yellow in (d) is black twice in (a), (b), (c)

Another example the ring in (d) is the sum of (a), (b) and (c)

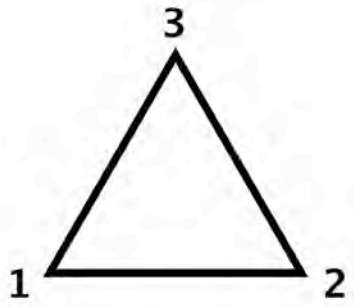
Symmetries of graphs: the automorphism group
An automorphism is a permutation of vertices that preserves the edges.



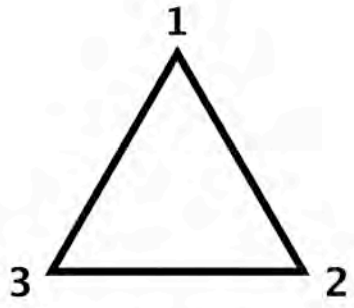
1 2 3



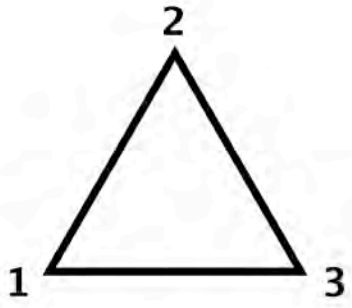
2 3 1



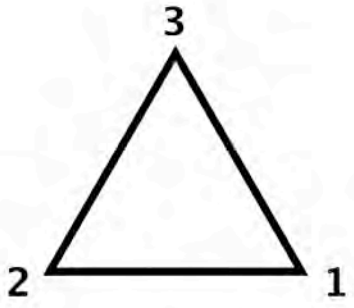
3 1 2



1 3 2



2 1 3



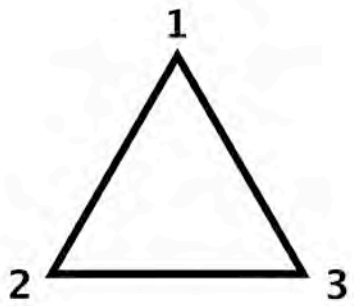
3 2 1

Note 1 2 3 -> 2 3 1

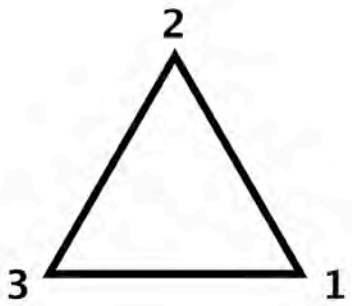
means

put vertex 2 where vertex 1 was
put vertex 3 where vertex 2 was
put vertex 1 where vertex 3 was

Symmetries of graphs: the automorphism group of a planar 3-connected graph is isomorphic to a rigid body symmetry

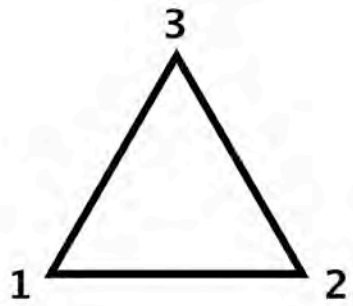


1 2 3



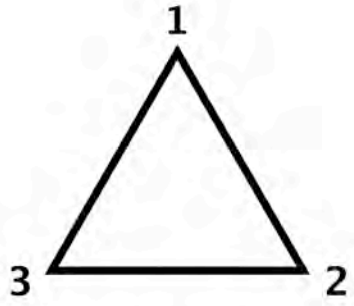
2 3 1

rotate clockwise



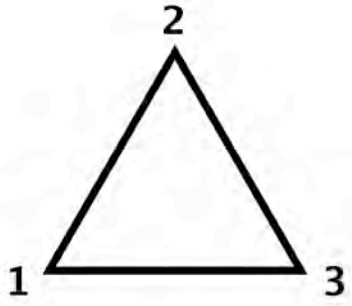
3 1 2

rotate anticlockwise



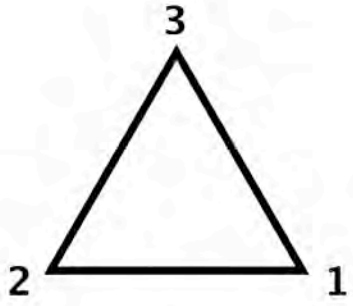
1 3 2

reflect



2 1 3

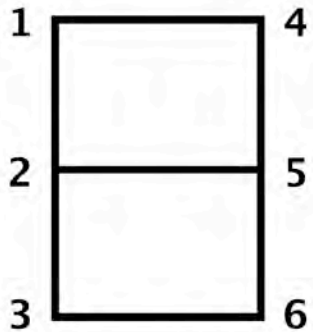
reflect



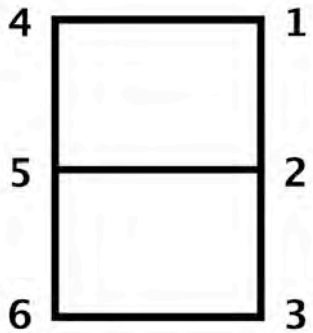
3 2 1

reflect

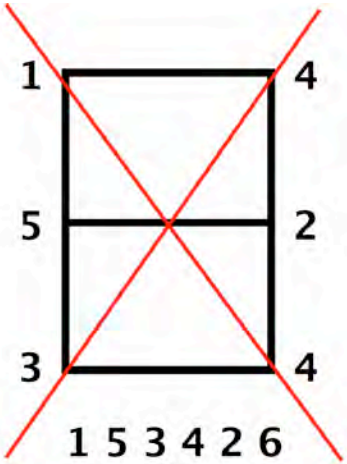
isomorphic to 3*m*



1 2 3 4 5 6

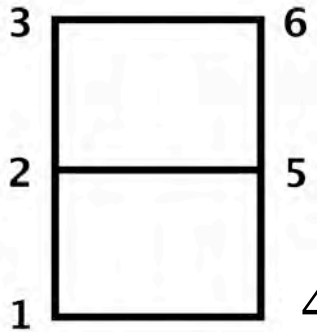


4 5 6 1 2 3



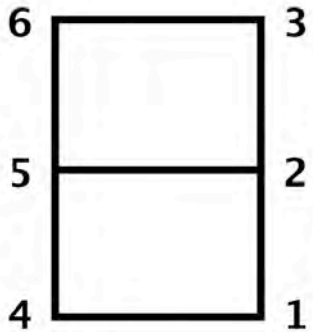
1 5 3 4 2 6

there is no edge 15 in the graph



4

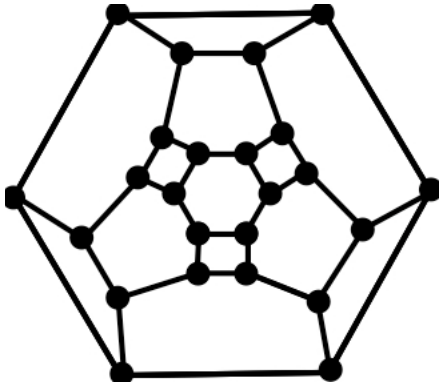
3 2 1 6 5 4



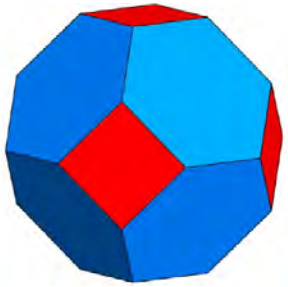
6 5 4 3 2 1

isomorphic to 2*mm*

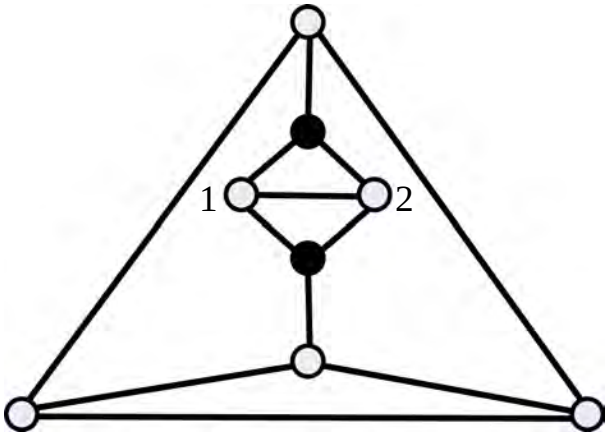
A planar 3-connected graph has combinatorial symmetry isomorphic to the symmetry group of the most-symmetric embedding.



graph of truncated octahedron



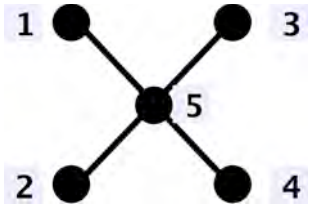
symmetry *m*-3*m*. Order 48



A graph that is not 3-connected can have symmetries that do not correspond to rigid-body symmetries. Interchange of vertices 1 and 2 leaving the rest fixed is a graph automorphism

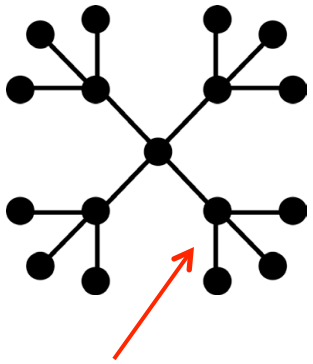
symmetries of molecular graphs

methane CH_4



any permutation of vertices 1,2,3,4 is an automorphism of the graph. The automorphism group has order 4! = 24 and is isomorphic to -43*m* (T_d).

neopentane $C(CH_3)_4$
The symmetry of the flexible molecule has order
3x3x3x3x24 = 1944



it's not 3-connected! if I delete this vertex, three vertices are isolated

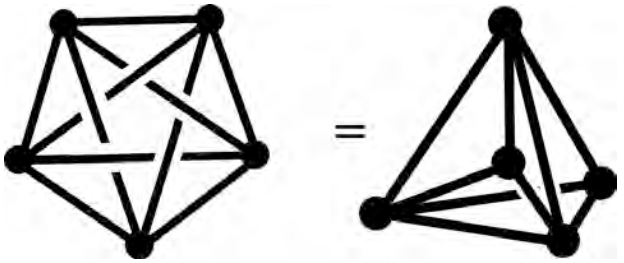
The symmetry groups of non-rigid moledules

C Longuet-Higgins, *Mol. Phys.* ***6***, 445-463 (1963)

Before passing on to consider other types of non-rigid molecule it is amusing to consider briefly one with a very much larger symmetry group, namely boro trimethyl, B(CH3)3. I mention it merely to show how very rapidly the effective symmetry of a molecule increases with its number of internal rotations.
The heavy-atom skeleton of boron trimethyl has symmetry D_{3h} , of order 12. But for each orientation of the skeleton there are 3 x 3 x 3 = 27 possible orientations of the three methyl groups. The order of the molecular symmetry group is thus 12 x 27 = 324.

Neopentane, C(CH3)4, has an even larger symmetry group, of order 1944. But the torsional barrier in this molecule is undoubtedly much higher than in boron trimethyl, so that for most practical purposes one may regard neopentane as a rigid molecule belonging to the point group T_d.

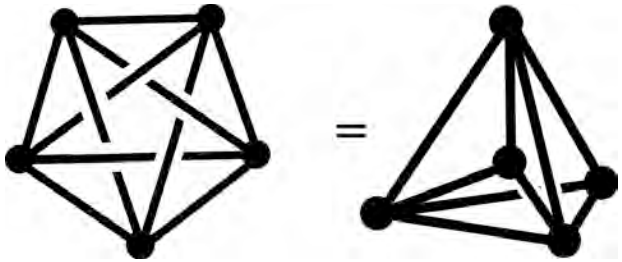
Remember K_5?
In four dimensions it has a symmetrical embedding a simplex (generalization of tetrahedron). Order of symmetry = 5! = 120

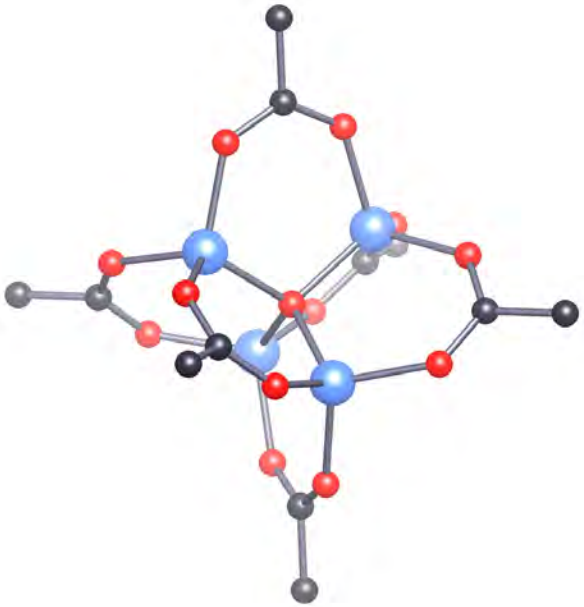


The graph automorphism ("symmetry") group is isomorphic to the symmetric group S_5 corresponding to the group of permutations of 5 things.

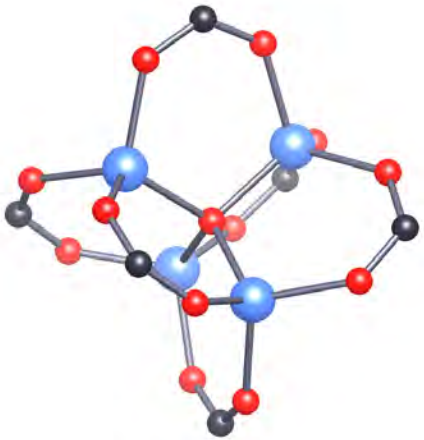
It is also isomorphic to I_h, the group of symmetries of a regular Icosahedron.

K_5





basic Zn acetate
(no H)



methyl carbon
deleted

underlying graph
is K_5

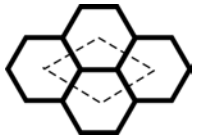
An ***n*-periodic** graph has a realization (not necessarily an embedding) with translational symmetry in exactly *n* independent directions.

Distinguish *n*-periodic from *n*-dimensional

K_4 (graph of tetrahedron) is 2-dimensional but 0-periodic

K_5 is 3-dimensional but 0-periodic

net of graphite layer (honeycomb) is 2-dimensional and 2-periodic.



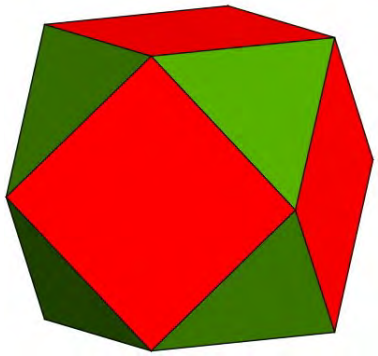
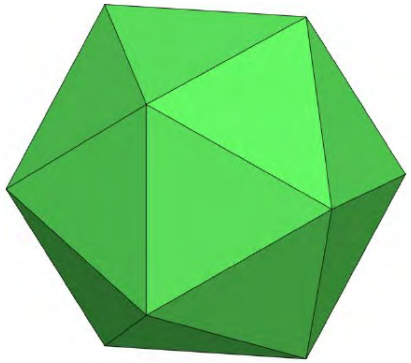
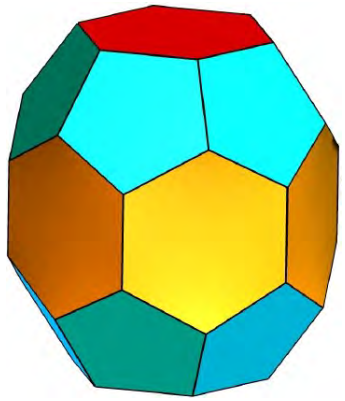
A **net**, as used in solid state chemistry, is a (periodic) connected simple graph.
(*connected* = there is a continuous path between every pair of vertices)
(*simple* = at most one undirected edge for a pair of vertices)

Vertex and face symbols for polyhedra and plane nets

(both of these are tilings of two-dimensional surfaces - the surface of a sphere and the Euclidean plane respectively).

Vertex Symbol. Give the size of faces in cyclic order around each kind of vertex.

Face symbol. Only for polyhedra (and 3-D cages) Give the size and total number of faces

vertex symbol (used mainly when one kind of vertex)

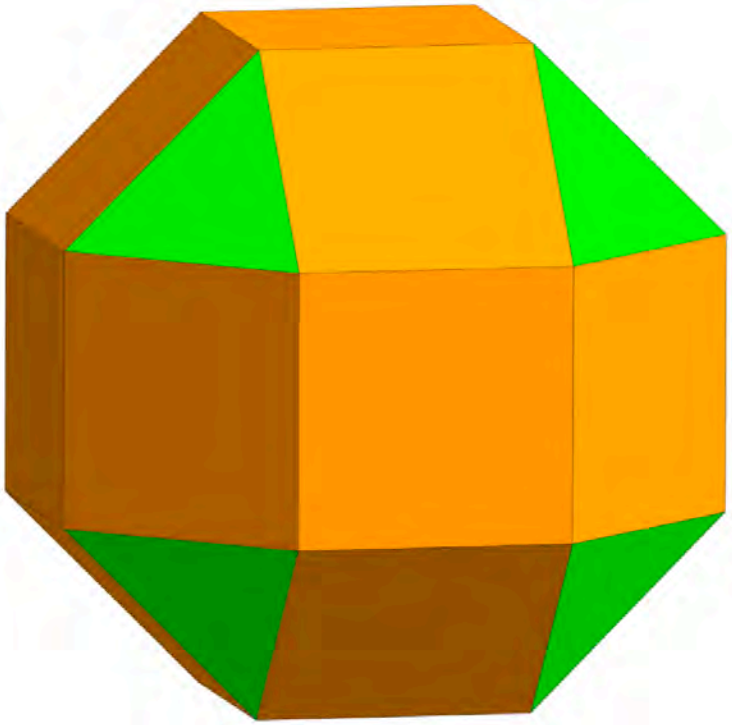
3.4.3.4 3^5 $(5^2.6)_2(5.6^2)$

(not 4.3.4.3) (short for 3.3.3.3.3)

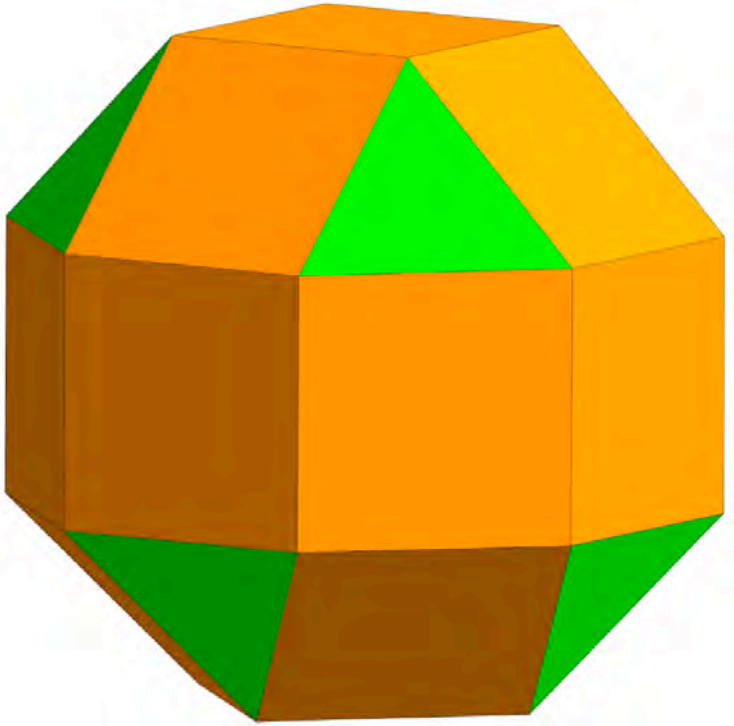
face symbol

$[3^8.4^6]$ $[3^{20}]$ $[5^{12}.6^8]$

Two distinct polyhedra with the same
vertex symbol 3.4^3
face symbol $[3^8.4^{18}]$

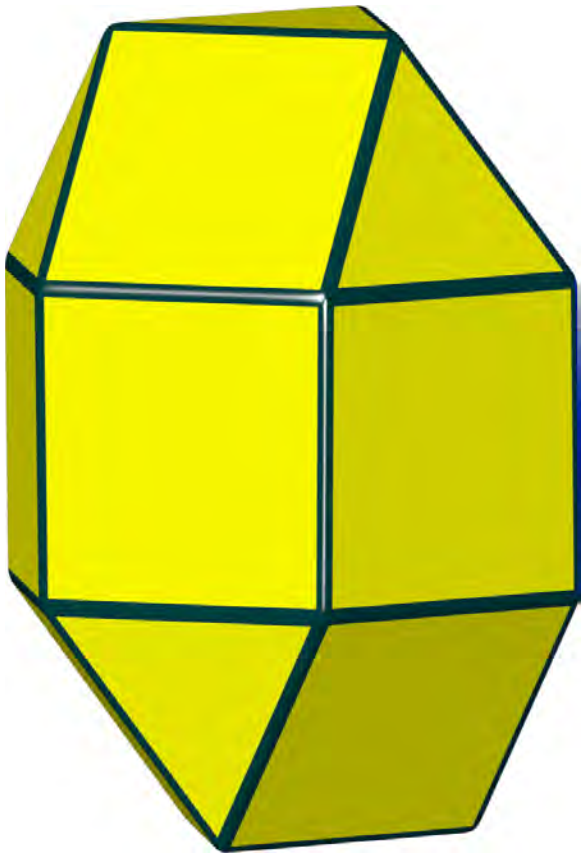


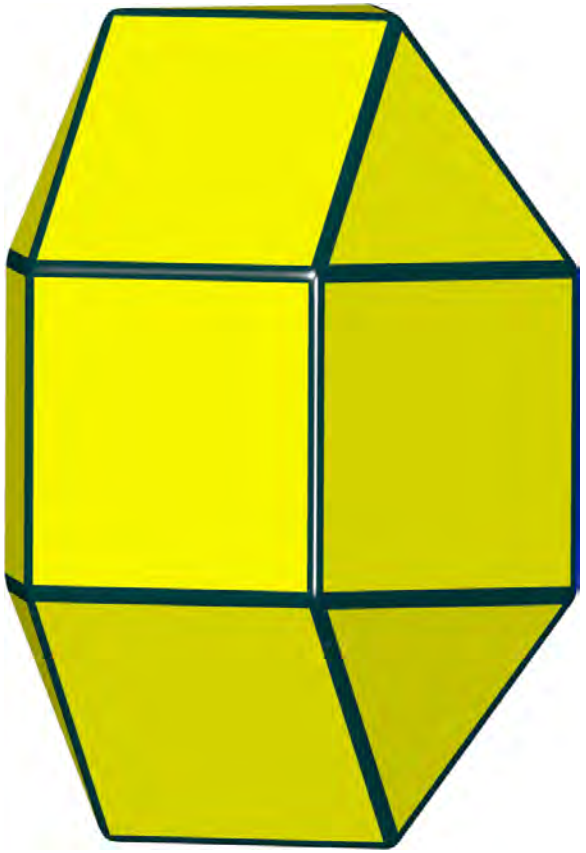
symmetry O_h



symmetry D_{4d}

Another expamle of a pair with the same vertex and face symbols
vertex symbol; $(3.4.3.4)(3.4^3)_2$. face symbol $[3^8.4^{12}]$

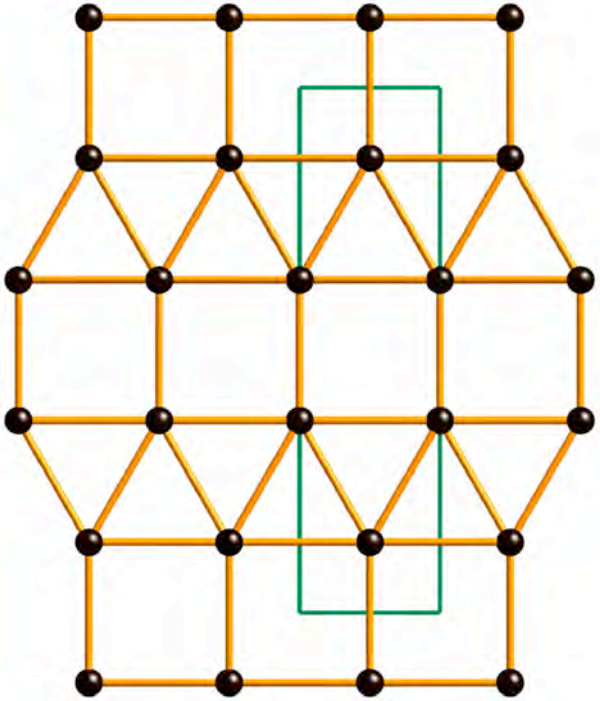


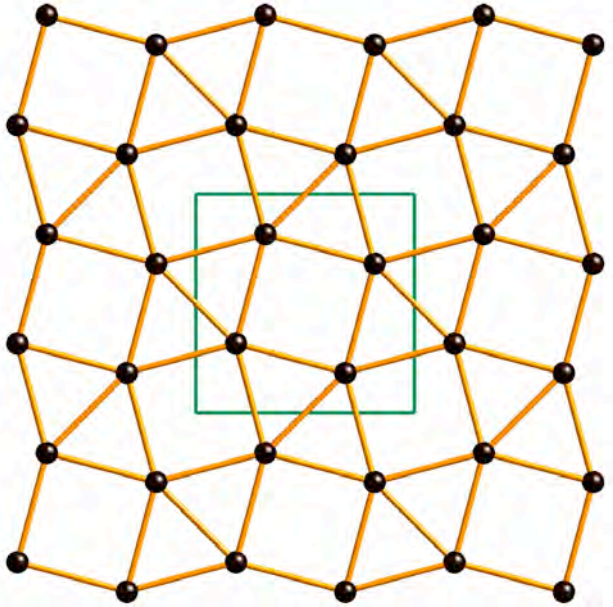


-3*m* -6*m*2

these are examples of Johnson polyhedra – convex polyhedra with regular faces

plane nets





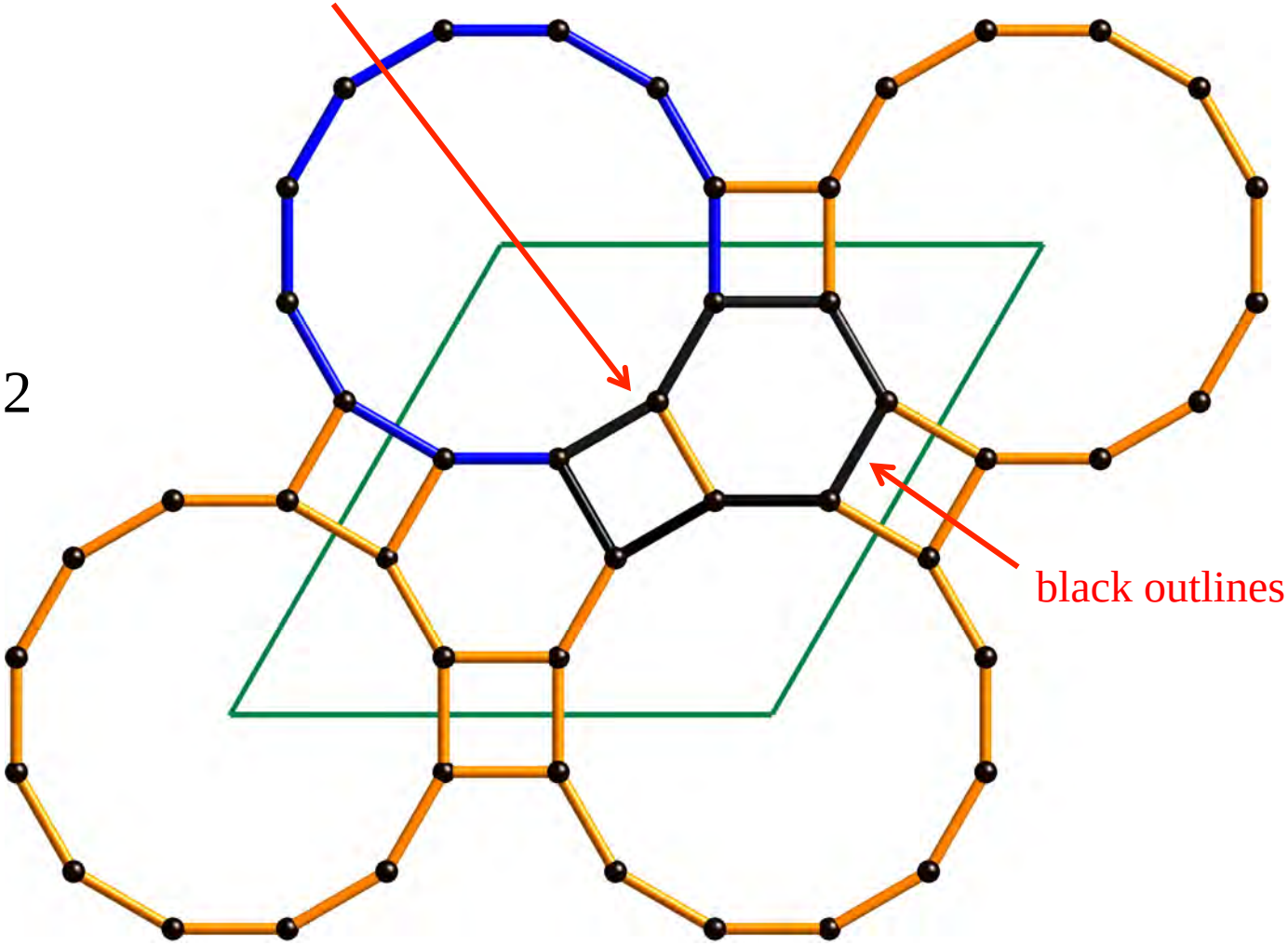
$3^3.4^2$

$3^2.4.3.4$

note that giving rings in cyclic order distinguishes these two

notice the 12-ring is not a shortest cycle

4.6.12

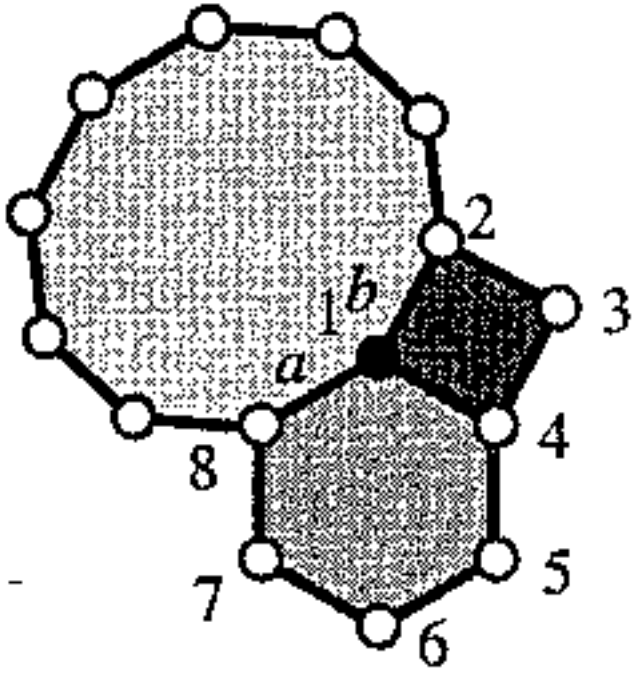


black outlines an 8-cycle

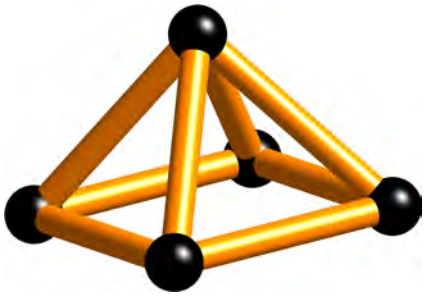
Fragment of the polyhedron vertex symbol 4.6.10

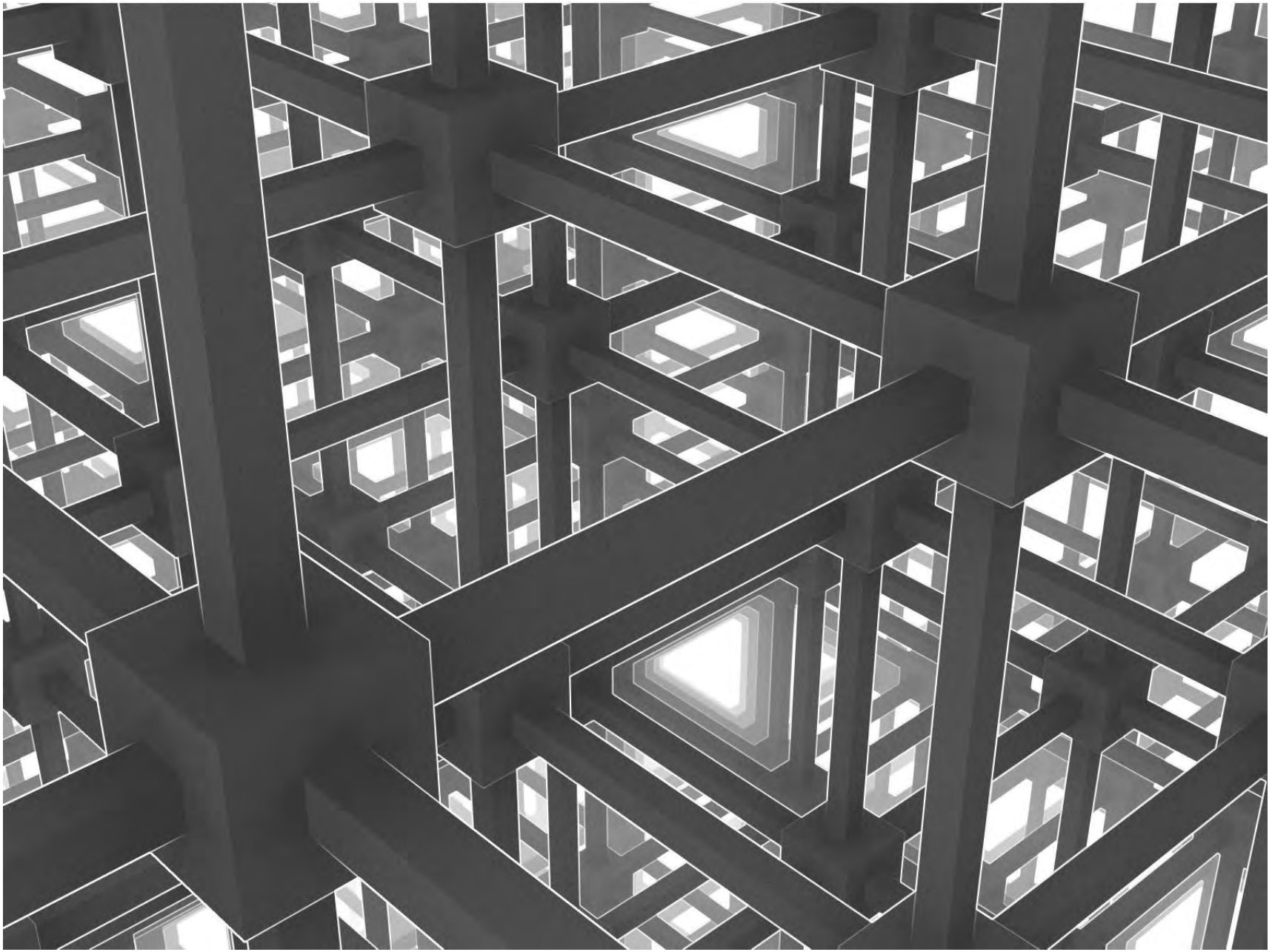
Note we use rings not cycles. In the angle with edges *ab* there is an 8-cycle.

So in the vertex symbols for nets we use rings



(notice that the faces of polyhedra are rings but may not be strong rings. Think of a pyramid – vertices are 3^4 and $3^2.4$)



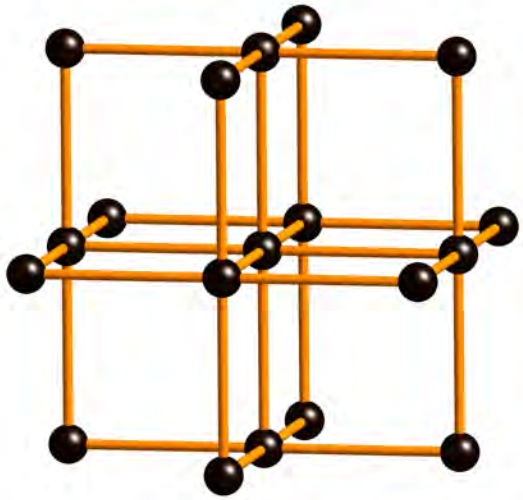


3-periodic nets (graphs) – figure by Maurits Escher

Point symbols for 3-periodic nets

At each *n*-coordinated vertex there are $N = n(n\text{-}1)/2$ angles
"Point symbol" $A^aB^bC^c$... gives the size (*A*, *B*, *C*...) of the shortest cycle at each angle and the numbers of shortest cycles of each size so that $a + b + c + \ldots = N$.

Diamond (**dia**) 4-coordinated; shortest cycle at each angle is 6-cycle. The point symbol is 6^6.
Primitive cubic lattice (**pcu**) $4^{12}6^3$.



Point symbol is often called "Schläfli symbol"*

This is unfortunate because in mathematics "Schläfli symbol" refers to a symbol for a tiling

*including in some of my older papers! Mea culpa

Please

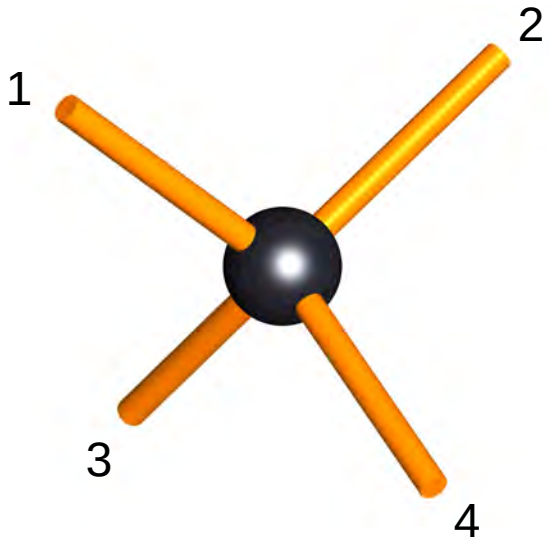
DO NOT USE “SCHLÄFLI SYMBOL” FOR POINT SYMBOL OR VERTEX SYMBOL

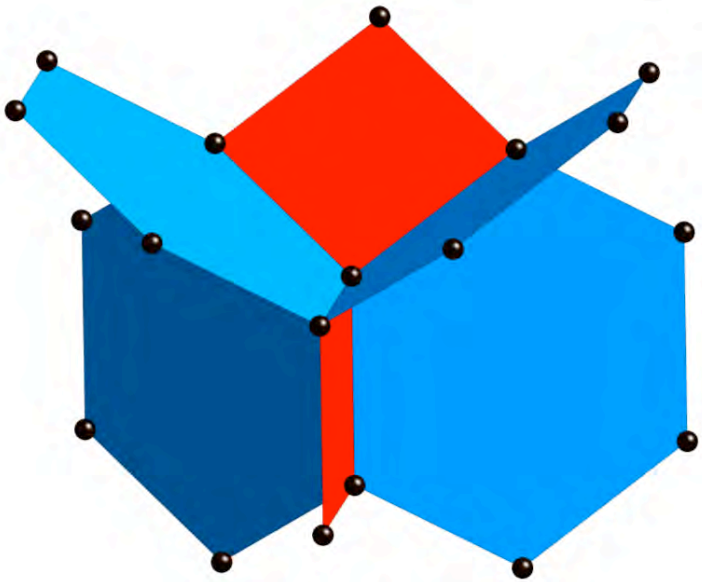
A POINT SYMBOL IS NOT A "TOPOLOGY"

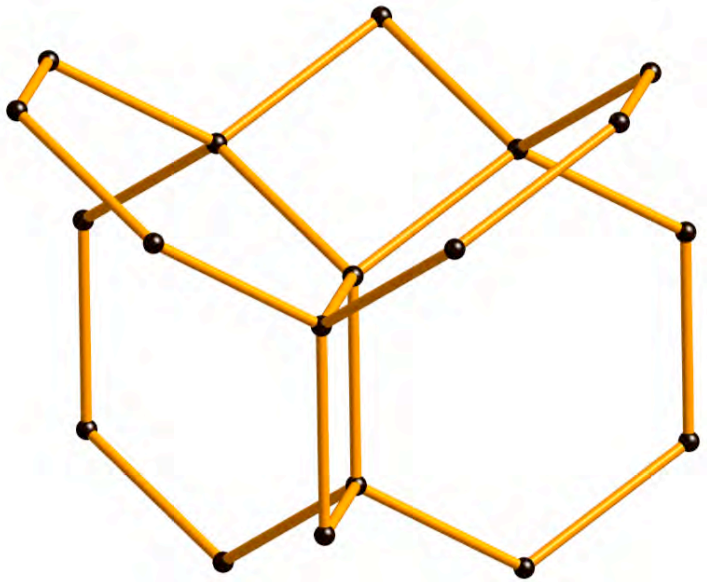
V. A. Blatov. M. O'Keeffe, D. M. Proserpio
CrystEngComm **2010**, *12*, 44

Vertex symbols for 3-periodic nets

(used mainly for 3- or 4-coordinated vertices)
$A_a \cdot B_b \cdot C_c$.... with $n(n\text{-}1)/2$ entries for n-coordination
A, *B*, *C* ... are the sizes of the smallest *ring* at an angle and *a*, *b*, *c* ... are the numbers of those rings.
For 4-coordinated only angles are grouped in opposite pairs; 12,34 and 13,24 and 14,23





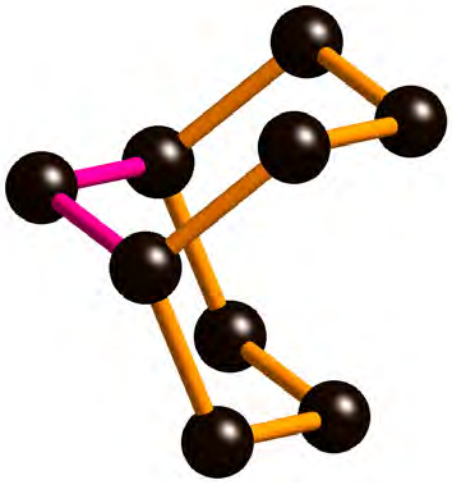


Environment of a vertex of the sodalite net (**sod**)

point symbol $4^2.6^4$

vertex symbol 4.4.6.6.6.6 this tells us the 4-rings don't share n edge

In diamond (**dia**) there are two 6- rings at each angle



vertex symbol $6_2.6_2.6_2.6_2.6_26_2$

If rings are planar (flat) only one per angle

For feldspar (**fel**) with two kinds of vertex, both with point symbol $4^2.6^3.8$, the vertex symbols are $4\cdot6\cdot4\cdot6\cdot8_2\cdot10_{10}$ and $4\cdot6_2\cdot4\cdot8\cdot6\cdot6_2$. Notice that, subsequent to the constraint that opposite angles are paired, the numbers are written in lexicographic order (smallest numbers first).

Can be many shortest rings:

uml $4.6_{2.}4.6_3.6.18_{1422}$

For coordination > 4 the symbol is sorted so smallest rings come first. For a 6-coordinated net known as **pcu-m** it is

$$3.3.3.3.4.4.4.8_2.8_2.8_3.9_2.9_3.9_4.9_5.9_6$$

Sometimes an angle does not contain a ring
Vertex symbol for 4-coordinated **cds** net is

$$6.6.6.6.6_2.*$$

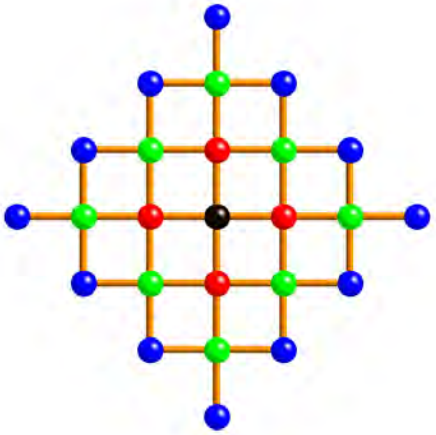
For the 6-coordinated **pcu** net it is:

$$4.4.4.4.4.4.4.4.4.4.4.4.*.*.*$$

Coordination sequence for a vertex

$n_1, n_2, n_3, n_k, \ldots$

n_k is the number of vertices linked to the reference vertex by a path of exactly k steps



square lattice coordination sequence is 4, 8, 12,…

cumulative sequence

$c_k = \Sigma_{1 \text{ to } k}\, n_k$

$TD_{10} = 1 + c_{10}$

If there is more than one kind of vertex, then for TD_{10} use weighted average of c_{10}

used as a search tool for zeolite-like nets

topological density:
2-periodic limit $k \rightarrow \infty$, $c_k/2k^2$
3-periodic limit $k \rightarrow \infty$, $c_k/3k^3$

for some simple 3-periodic nets

$n_k = ak^2 + bk + c$

topological density = $a/3$

sod $n_k = 2k^2 + 2$

pcu $n_k = 4k^2 + 2$

bcu $n_k = 6k^2 + 2$

hex $n_k = 6k^2 + 2$ same

dia $n_k = [5k^2/2] + 2$ […] means round down

lon $n_k = [21k^2/8] + 2$

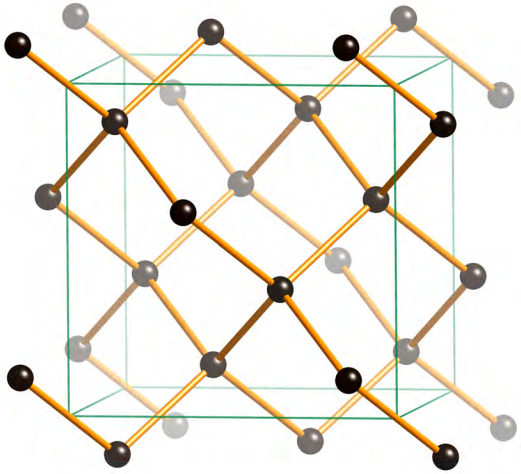
M. O'Keeffe, *Z. Kristallogr.* **196**, 21 (1991); **210**, 905 (1995), **211**, 73 (1996)

next nets as periodic graphs

Crystal nets as periodic simple connected graphs

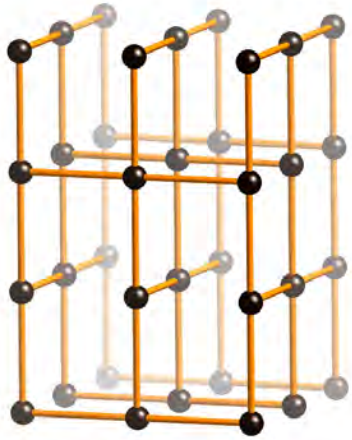
periodic
simple - no loops or mutiple edges
connected - a path from every vertex to every other

diamond net (**dia**)

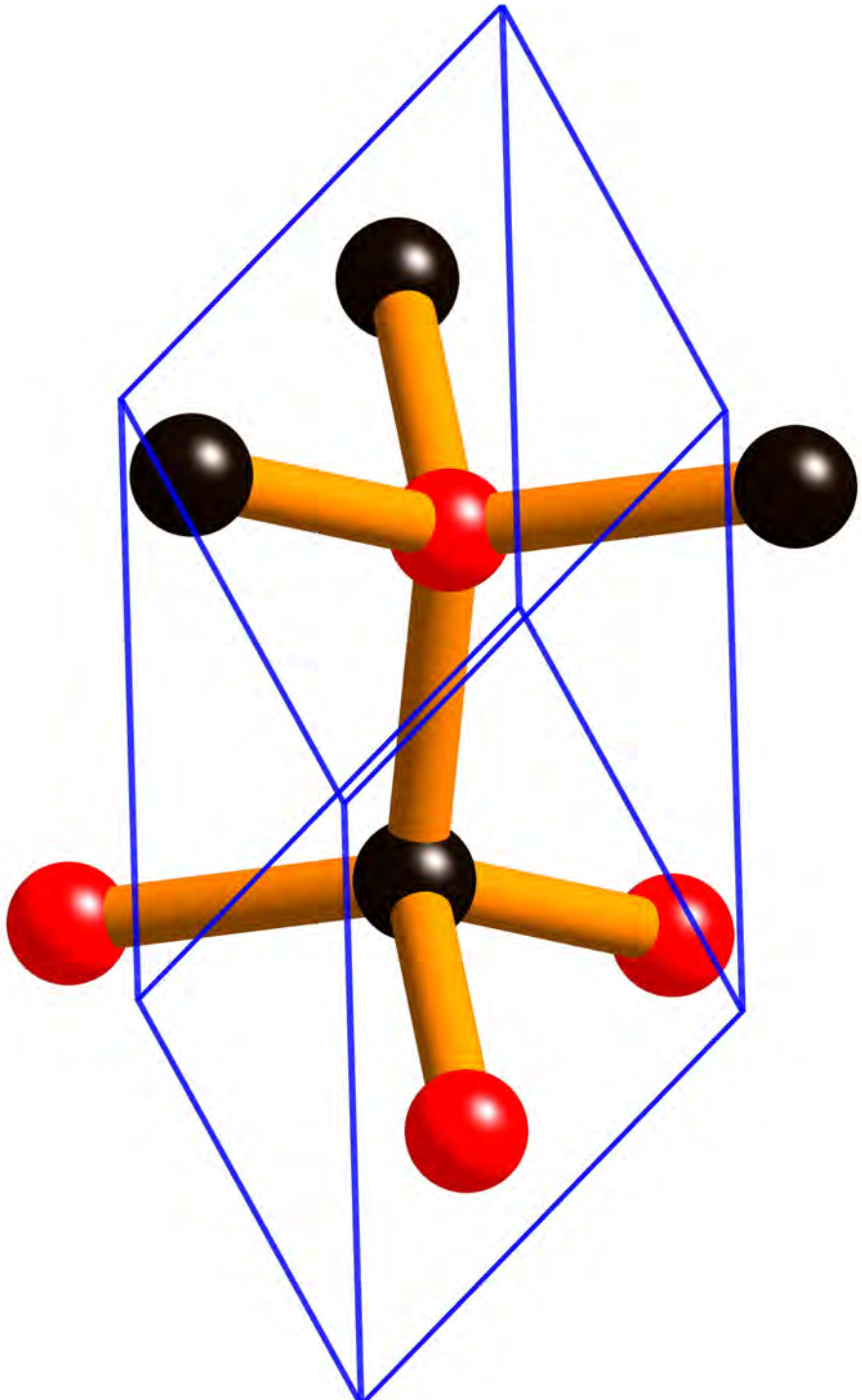


minimum repeat unit
2 vertices, 4 bonds

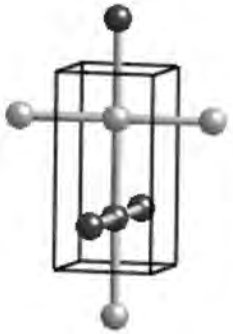
$CdSO_4$ net (**cds**)



Primitive cell
of diamond
structure.
Rhombohedron with
$\alpha = 60^{\circ}$



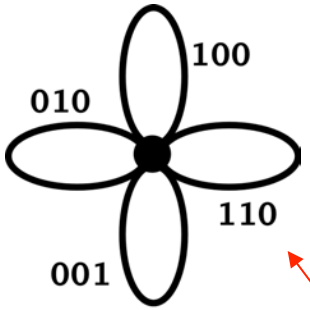
Quotient graph* and **vector representation**

net	unit cell	quotient graph	vector representation		
			from	to	in unit cell
dia			1	2	0 0 0
			1	2	1 0 0
			1	2	0 1 0
			1	2	0 0 1
cds			1	2	0 0 0
			1	1	1 0 0
			2	2	0 1 0
			1	2	0 0 1

*Chung, Hahn & Klee, 1984

The same unlabeled quotient graph may be the graph of different nets. E.g.:

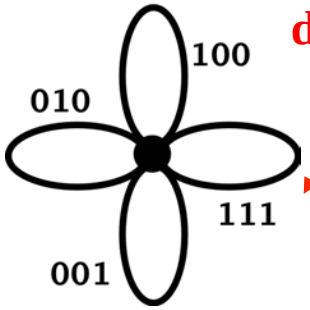
hex
(hexagonal lattice)



1 1 100
1 1 010
1 1 001
1 1 110

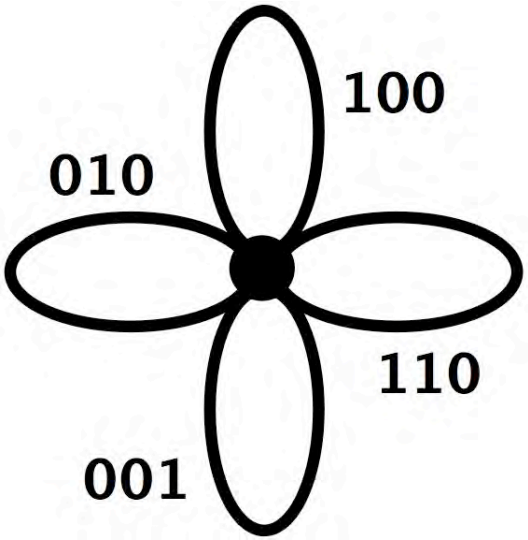
different!

bcu
(body-centered cubic lattice)

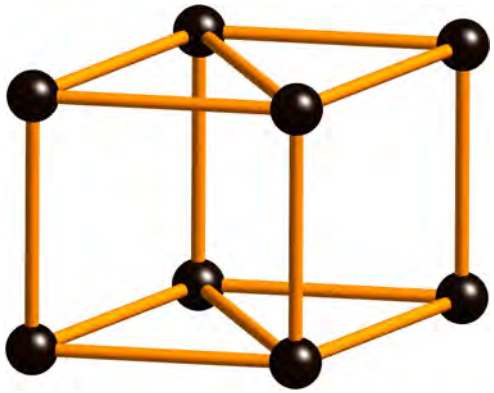


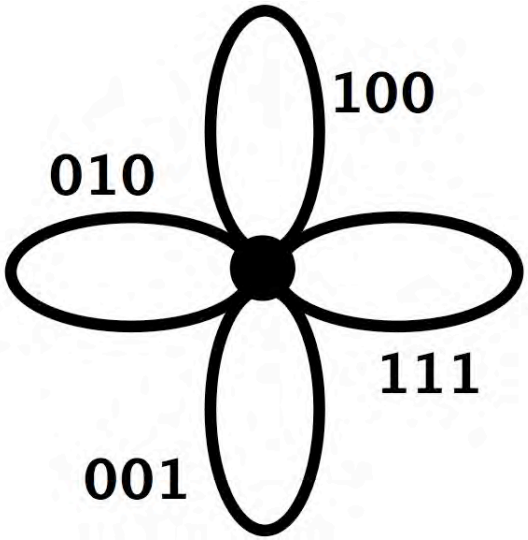
1 1 100
1 1 010
1 1 001
1 1 111

Examples of nets with the same unlabelled quotient graph
(these examples are *lattice nets* - one vertex in the repeat unit)

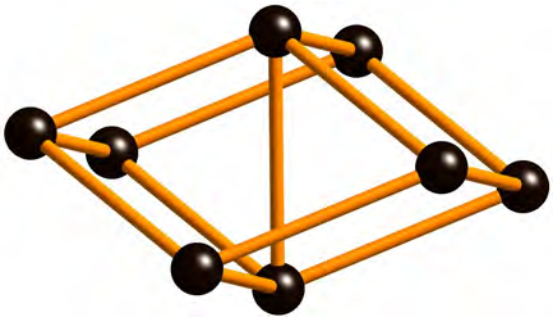


hex

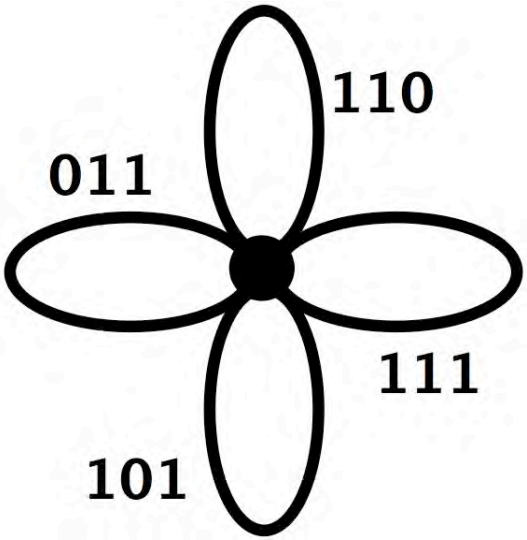




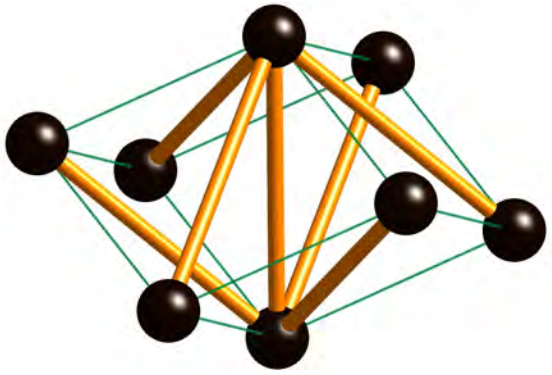
bcu



primitive sell of body-centered cubic

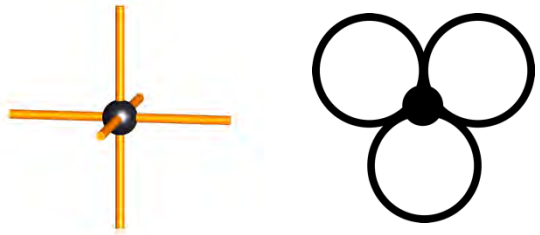


ilc



Notice that the quotient graph has the same number of vertices, *v* and edges, *e*, as the repeat unit (primitive cell) of the net.
The cyclomatic number of the quotient graph is $g = 1 + e - v$
We call this the **genus** of the net.

(The reason is this. Imagine the repeat unit of the net there will be pairs of bonds going to the *uvw* cell and the -*u*-*v*-*w* cell. Join these. Now inflate the bonds to get a *handlebody* of *g* holes.)

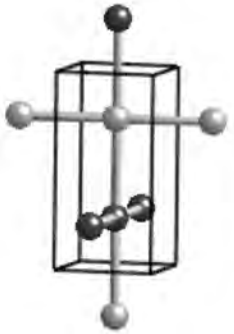


pcu has $v = 1$, $e = 3$ (six half edges)
$g = 1 + e - v = 3$ = cyclomatic number of quotient graph.

An *N*-periodic net must have $g \geq N$. Nets with $g = N$ are **minimal nets** (Beukemann & Klee)

Minimal net. For 3 dimensions there are 15 minimal nets (there are 15 connected graphs with cyclomatic number 3 Beukemann & Klee, *Z. Krist* 1992.

the **dia** and **cds** nets are the only 4-c minimal nets. (2 vertices in the primitive cell)



Each quotient graph of a minimal net refers to a unique net

This means that the labelling is unceccessary as long as there are distinct different non-coplanar vectors.

Examples of **dia**

1 2 1 0 0	1 2 1 1 0	1 2 1 0 0
1 2 0 1 0	1 2 1 0 1	1 2 0 1 0
1 2 0 0 1	1 2 0 1 1	1 2 0 0 1
1 2 0 0 0	1 2 1 1 1	1 2 1 1 1

Try with Systre. You will find the third is **dia-c**

Examples of graphs with simple quotient graphs

sit

1 2 0 0 0
1 3 0 0 0
1 2 0 0 1
1 3 0 0 1
1 2 1 0 0
1 2 0 1 0

flu

1 2 0 0 0
1 3 0 0 0
1 2 1 0 0
1 3 -1 0 0
1 2 0 1 0
1 3 0 -1 0
1 2 0 0 1
1 3 0 0 -1

But most nets in crystal chemistry have tens or even hundreds of vertices in the repeat unit.

Systre (O. Delgado-Friedrichs)

vector representation

↓

Barycentric (center of mass) coordinates

↓

symmetry

↓

canonical form

↓

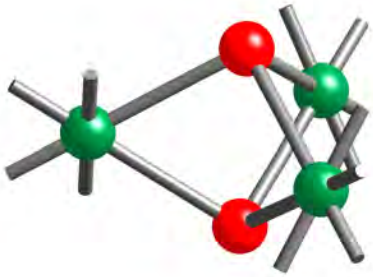
equal edge, minimal density embedding

O. Delgado-friedrichs & M. O'Keeffe, *Acta Crystallogr.* **A59**, 351 (2003)

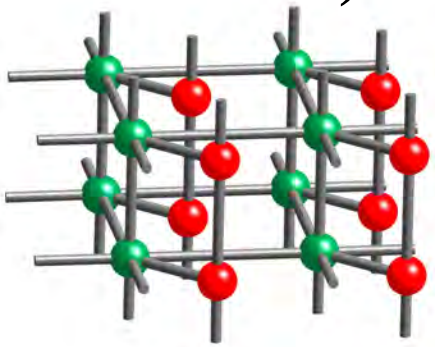
barycentric coordinates
(equilibrium placement,
Olaf Delgado-Friedrichs 2005 after Tutte 1960)

once one vertex fixed, rest unique
rational, hence exact, using integer arithmetic

problem: there may be collisions (two or more vertices with the same coordinates)



vertices with common neighbors



“dangling” vertices & ladders

collisions rare in crystal nets!

barycentric coordinates, example of diamond

dia

from	to	in unit cell
1	2	0 0 0
1	2	1 0 0
1	2	0 1 0
1	2	0 0 1

let vertex 2 be at 0,0,0 and vertex 1 at *x*, *y*, *z* then coordinates of neighbors of 1 are

0 0 0
1 0 0
0 1 0
0 0 1

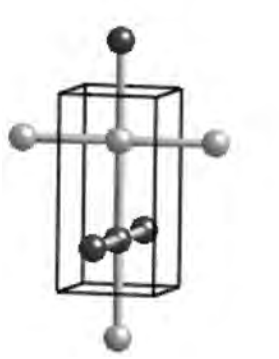
average 1/4, 1/4, 1/4

thus $x = 1/4$, $y = 1/4$, $z = 1/4$

barycentric coordinates, example of $CdSO_4$

cds

from	to	in unit cell
1	2	0 0 0
1	1	1 0 0
2	2	0 1 0
1	2	0 0 1



let vertex 2 be at 0,0,0 and vertex 1 at *x*, *y*, *z* then coordinates of neighbors of 1 are

0 0 0

1+*x* *y* *z* sum 2*x*, 2*y*, 1 + 2*z*

-1+*x* *y* *z* average *x*/2, *y*/2, 1/4+*z*/2

0 0 1

thus $x = x/2$, $y = y/2$, $z = 1/4+z/2$

i.e. $x = 0$, $y = 0$, $z = 1/2$

Systre

Olaf Delgado-Friedrichs

Symmetry

Once Systre has determined a placement (barycentric coordinates) the automorphisms of the net (including translations) can be found. For nets without collisions these correspond to operations of a space group which is identified.

Systre first looks for translations. If any found a reduced cell is determined.

Then find matrices **A** and translations **t** such that $\mathbf{A}\mathbf{x}_1 + \mathbf{t} = \mathbf{x}_2$ where $\mathbf{x}_1$ and $\mathbf{x}_2$ are coordinate triples.

A,t can be identified with a symmetry operation.

Symmetry operations must map vertices and edges.

Two important results (Olaf Delgado-Friedrichs)

1. 3-periodic nets without collisions have an automorphism group isomorphic with a space group (also J.-G. Eon).

If this group is chiral, the net is chiral
If not, not.

2. The graph-isomorphism problem is solved for nets without collisions.

Systre finds the symmetry and "Systre key" (unique signature)

Canonical form of vector representation

Olaf Delgado-Friedrichs

The vector representation of a net is a string of digits that codes exclusively for that net. But:

(a) there are $n!$ ways of numbering the vertices in the unit cell (n can easily be > 100, $100! = 10^{159}$)
(b) there is an essentially infinite number of choices of basis vectors

Systre solves these problems to find a unique canonical form for each topology.

Number vertices in order of barycentric coordinates
$x_i < x_j$; if $x_i = x_j$ then $y_i < y_j$; if $y_i = y_j$ then $z_i < z_j$

We have gone from $n!$ to n possible numbering schemes

Basis vectors must be 100 010 001

Write out all possible representations (not so many) as a string of digits
e.g. (1 2 0 0 0 1 2 0 0 1 1 2 0 1 0 1 2 1 0 0)

Keep the lexicographically smallest as canonical form

It has been proved that this is unique and can be done in polynomial time

Systre

structure

Once we have the canonical form for a new net, we can compare it to those of known structures. If it matches one, we know that the new net is isomorphic with that one. If there are no matches, the net is different from those known structures. Thus, for the first time, one can determine without ambiguity whether two nets are isomorphic or not!

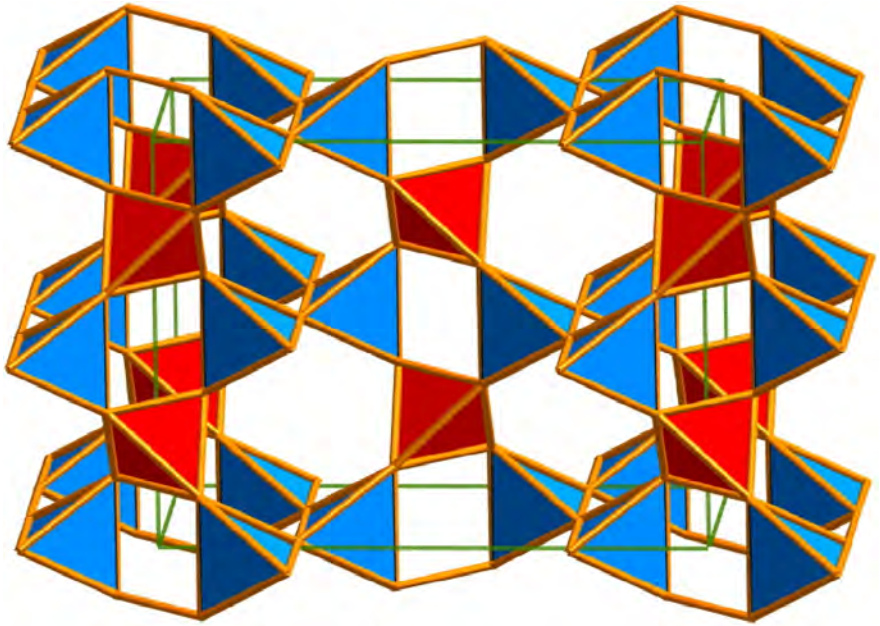
Systre
realization

The final step in Systre is finding a maximum symmetry realization, which may, or may not, be an embedding.
If possible all edges are constrained to be equal (e.g. to 1.0)
The, subject to that constraint, the volume is maximized (density minimized).

Something that happens very rarely,
but to be aware of. The maximum symmetry embedding may not permit the coordination figure you want. This if a 4-c site has symmetry *mmm* in maximum symmetry it cannot accommodate a tetrahedral atom. This is the case for the structure of moganite (a form of SiO_2):

anion net of moganite (a form of SiO_2 - also structure of BeH_2)

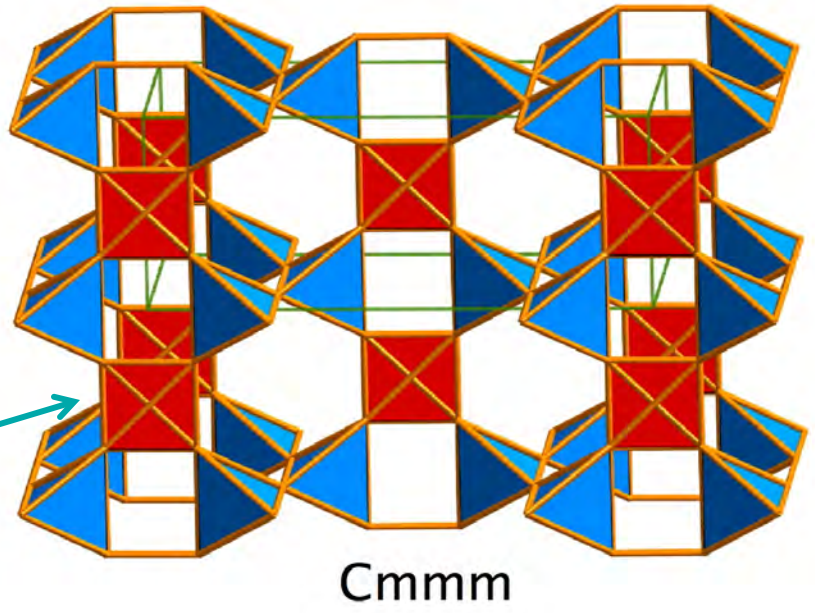
maximum symmetry for tetrahedral coordination



Ibam

maximum symmetry red quadrangles must be planar

rectangle, edges intersect



Cmmm

Get Systre at **www.gavrog.org**

requires Java (on Apple Macintosh and many others or free download, if not already installed)

Systre input for periodic graph:

```
PERIODIC_GRAPH
ID "diamond"
EDGES
1 2 0 0 0
1 2 1 0 0
1 2 0 1 0
1 2 0 0 1
END
```

Examples of Systre input

```
CRYSTAL
GROUP P6122
ATOM 1 4  0.28727 0.59679 0.02762
EDGE 1 0.69048 1.40321 -0.02762
EDGE 1 0.40321 0.71273 -0.19429
EDGE 1 0.59679 0.30952 -0.13905
END
```

Give symmetry and one of each kind of vertex ("atom") and edge.

```
CRYSTAL
ID 'banalsite'
GROUP Ibam
CELL 8.496 9.983 16.775 90.0 90.0 90.0
ATOM 1 4 0.2283 0.4429 0.4067
ATOM 2 4 0.0754 0.3095 0.1586
END
```

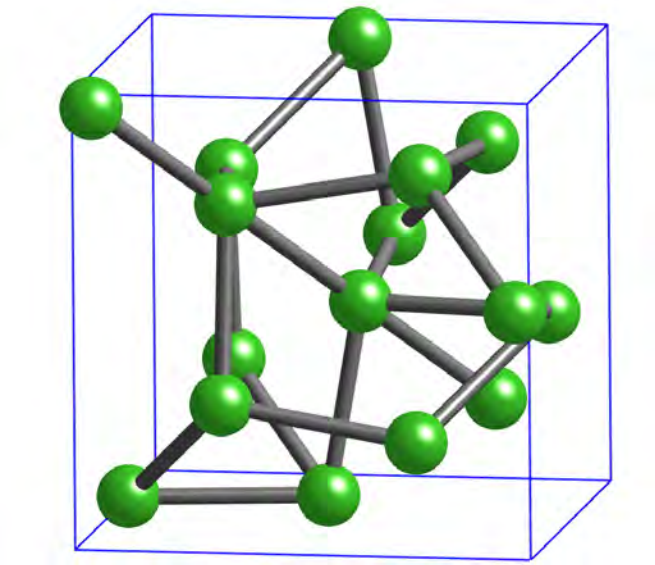
If no edges are given, Systre will take the n nearest neighbors of each atom of coordination number n. Now a unit cell is necessary.

Sphere Packings

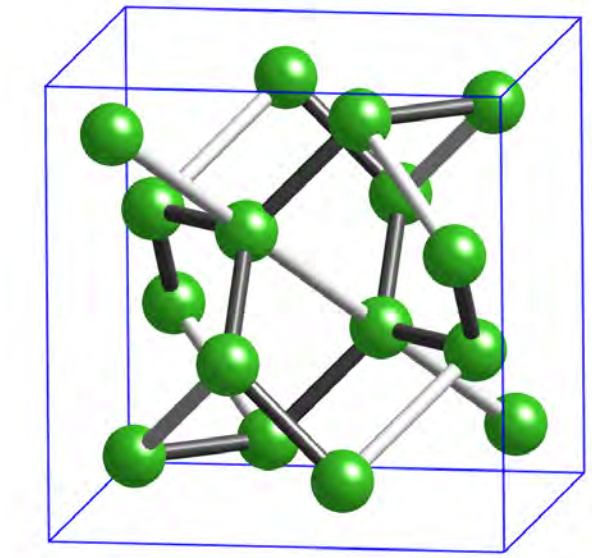
If an embedding of a net has all edges equal and these are the shortest distances between vertices we say that the structure is a sphere packing.
Many (most?) nets of interest in crystal chemistry have embeddings as sphere packings.
A lot is known about sphere-transitive (one kind of sphere) packings **(W. Fischer, E. Koch, H. Sowa)**

Not all sphere packings can be realized as sphere packings at full symmetry. (next slides):

Sphere packing 5/5/*c*1 (W. Fischer) symbol **fnm**



I-43*d* 0.0366, *x*, *x*
5 equidistant neighbors



x = 0.125. True symmetry
Ia-3*d*. 3 nearest neighbors

Fischer symbol for sphere packing

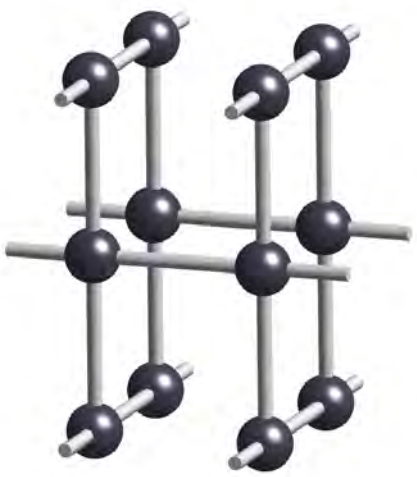
p/*q*/letter*n*

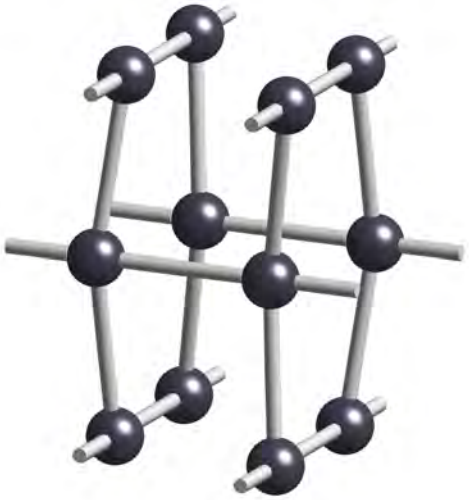
p is the coordination number
q is the size of the shortest ring
"letter" = *c* (cubic) or *h* (hexagonal)
or *t* tetragonal or *o* (orthorhombic)
or *m* (monoclic)
n is an arbitrary serial number

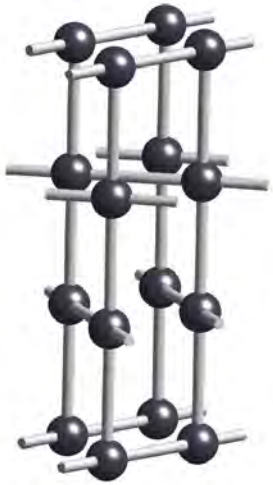
Examples of important 4-coordinated nets that are not 4-coordinated sphere packings in maximum symmetry embeddings

can be realized as
4-coordinated SP:

cannot be realized as
4-coordinated SP







cds

qzd

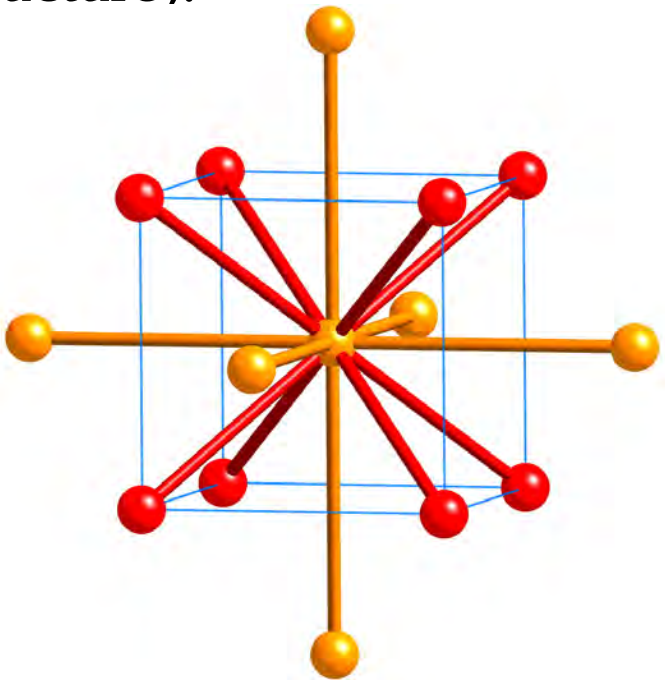
$P4_2/mmc$
6 equidistant
neighbors

$P4_2/mbc$ ($a' = 2a$)
4 equidistant
neighbors

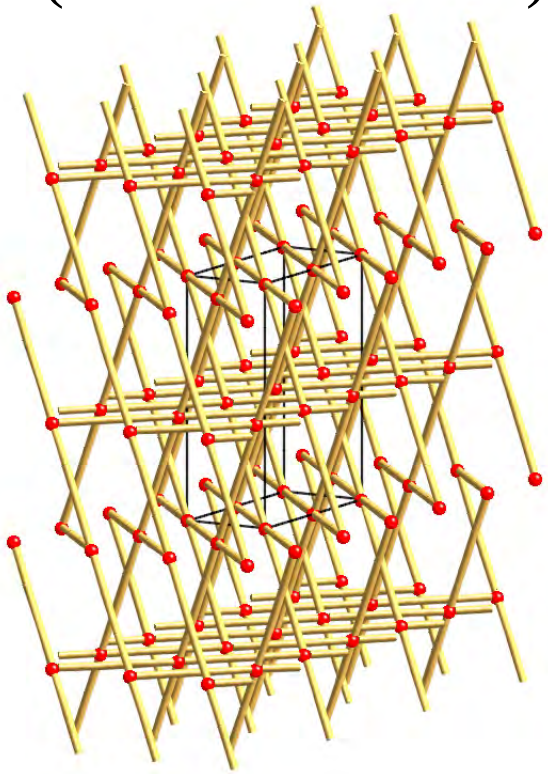
$P6_222$
8 equidistant
neighbors

Example of a structure for which there is no embedding with all edges equal. this is the body-centered cubic lattice with edges linking first- and second geometric neighbors. (for some purposes this is the ‘best’ way to consider this structure).

bcu-x
(the symbol **bcu** refers to 8-coordination)



Example of a net in which intervertex distances are always shorter than edges.
Minimum intervertex distance ~ 0.88 longest edge.
Such nets rare in crystal chemistry, but in principle very common (“almost” all nets?)



tcb a net with vertex symbol $8_2 \cdot 8_2 \cdot 8_5 \cdot 8_5 \cdot 8_5 \cdot 8_5$

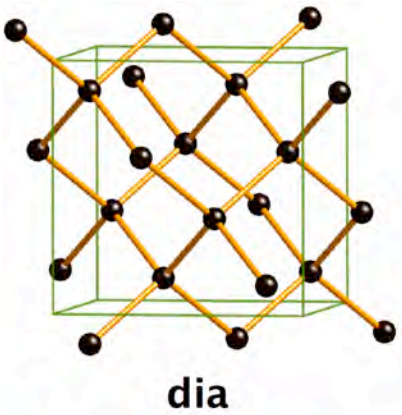
J.-F. Ma et al. 2003; M.-L. Tong et al. 2003

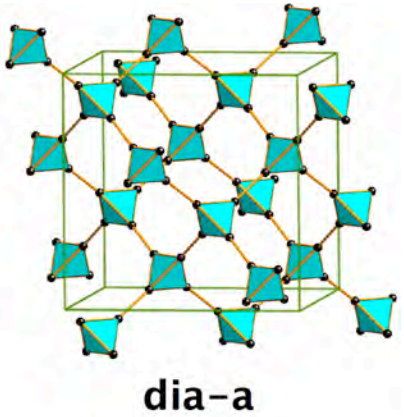
RCSR symbols for nets

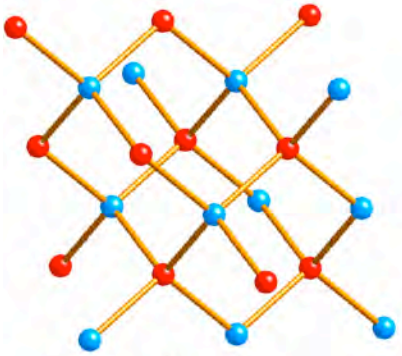
dia
typical three letter code
dor the diamond net

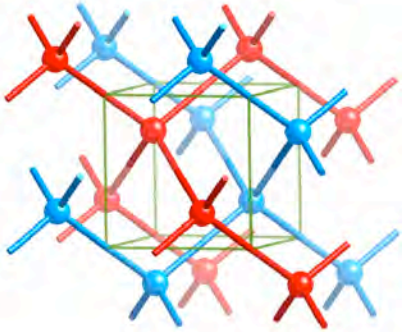
relateded net

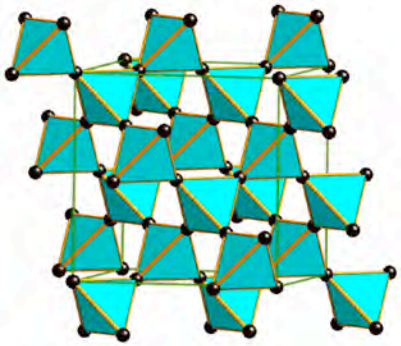
dia-a = **a**ugmented
dia-b = **b**inary version
dia-c = **c**atenated
dia-d = **d**ual
dia-e = **e**dge net
dia-x = e**x**tended coord.

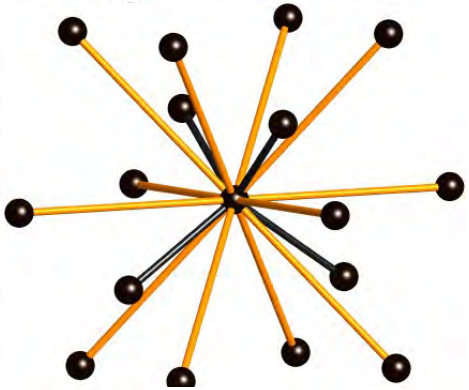

dia

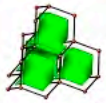

dia–a


dia–b


dia–c


dia–e


dia–x



dia

names: diamond, D, 4/6/c1
key words: regular net, uniform net, isohedral tiling, 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
1a	Fd-3m	12.3168	0.6495	3	981

unit cell:

a	b	c	alpha	beta	gamma
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	0.125	0.125	0.125	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	0.0	0.0	0.0	0, 0, 0	16 c	-3m

tiling:

tiling	dual	vertices	edges	faces	tiles	D-symbol
[6^4]	dia	1	1	1	1	2

Export 3dt input: dia.cgd

occurrences: [show|hide]

A page from the RCSR

rcsr.net

M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi
Accts. Chem. Res. **41**, 1782 (2008)

What nets are there?

It is convenient to discuss tiling first

end