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Polyhedra in chemistry

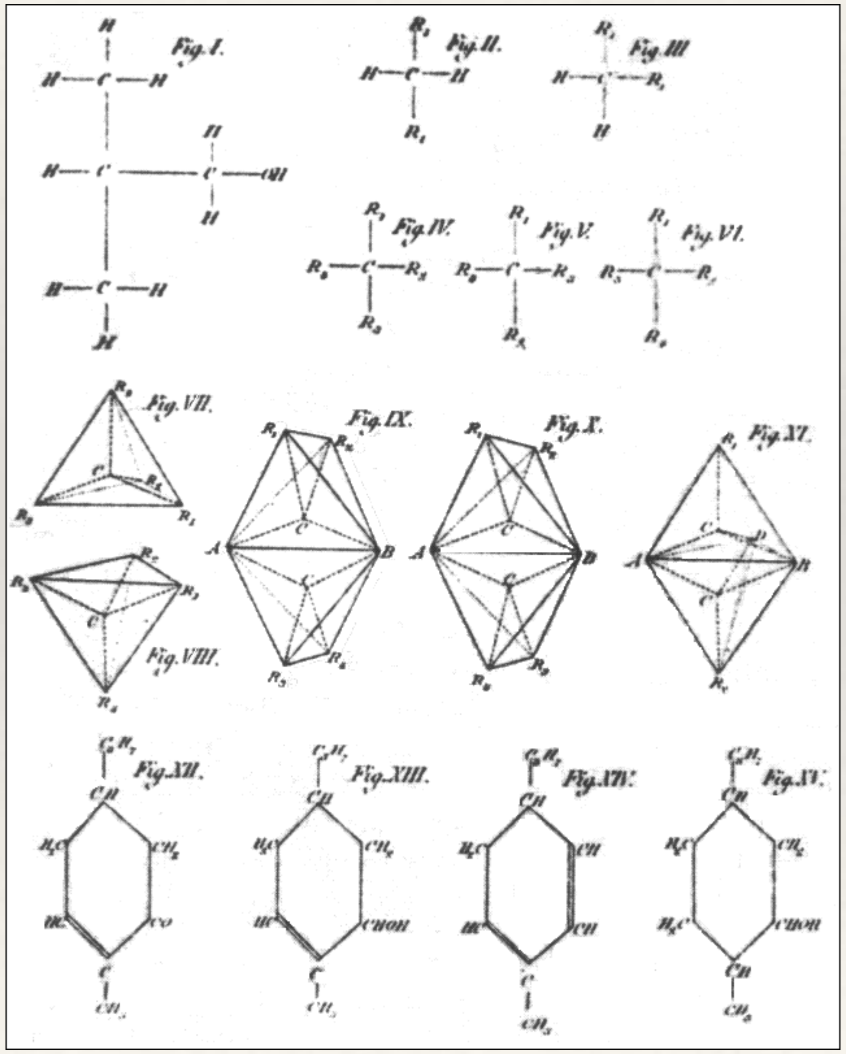
Pere Alemany
Universitat de Barcelona

Organic chemistry is tetrahedral

Physical properties of molecules (optical rotation) depend on the spatial distribution of atoms (and on the symmetry of this distribution)

Jacob H. van’t Hoff (1852 – 1911)

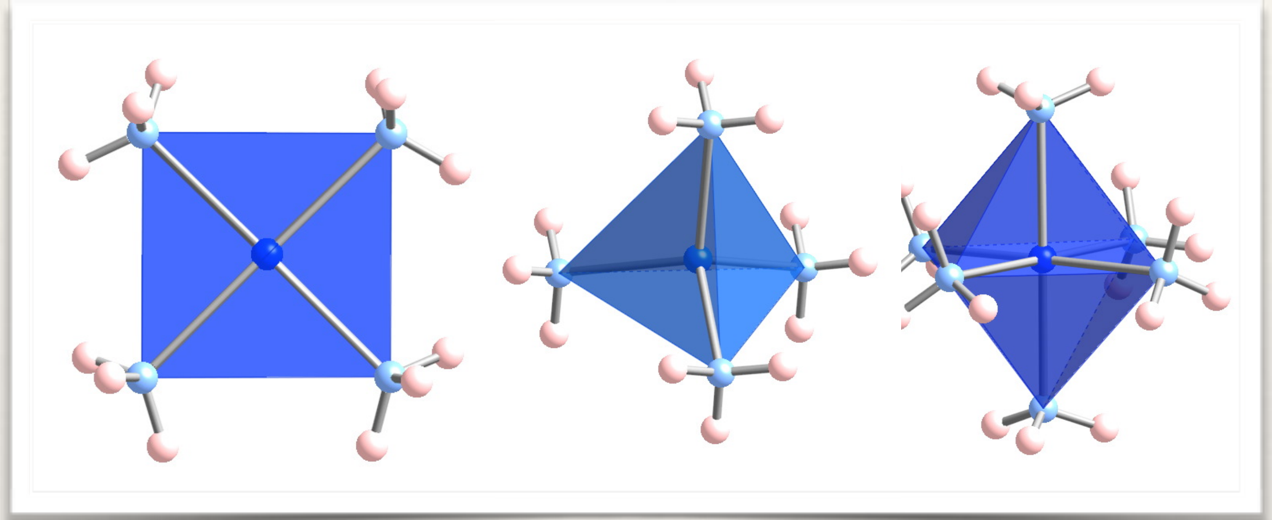
Joseph le Bel (1847 – 1930)



J. H. van’t Hoff: La chimie dans l'espace (1874)

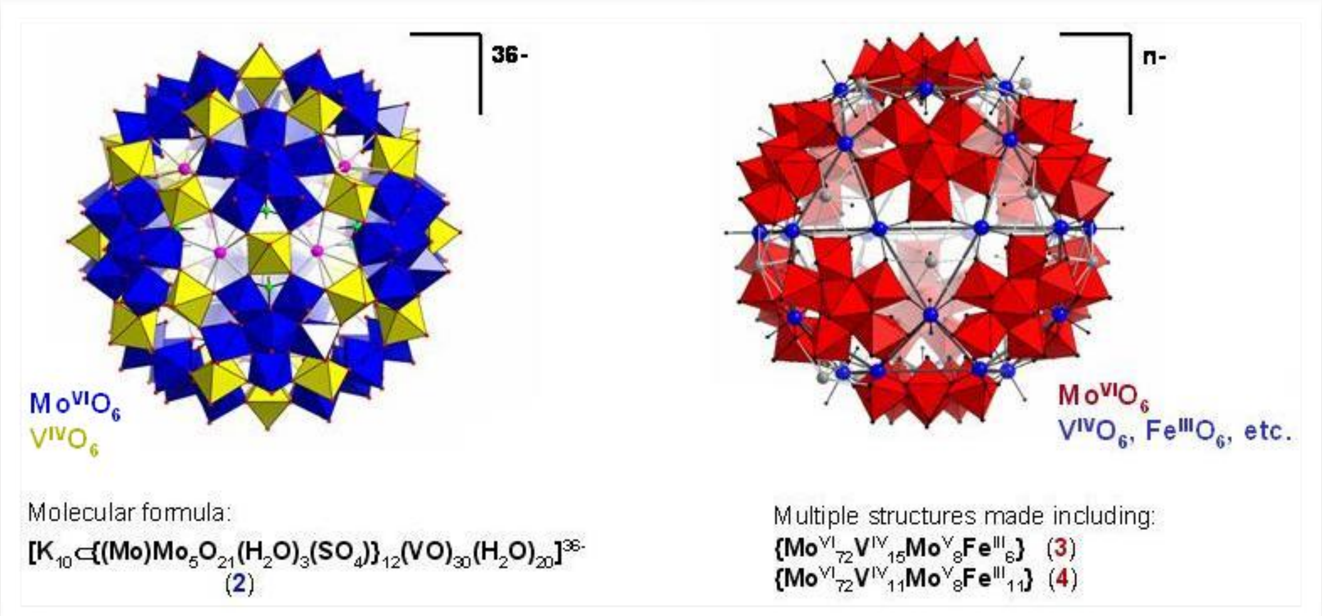
Polyhedra in chemistry

In 1893 Werner suggests to describe the **coordination environment** of transition metal atoms in coordination compounds by ideal polyhedra



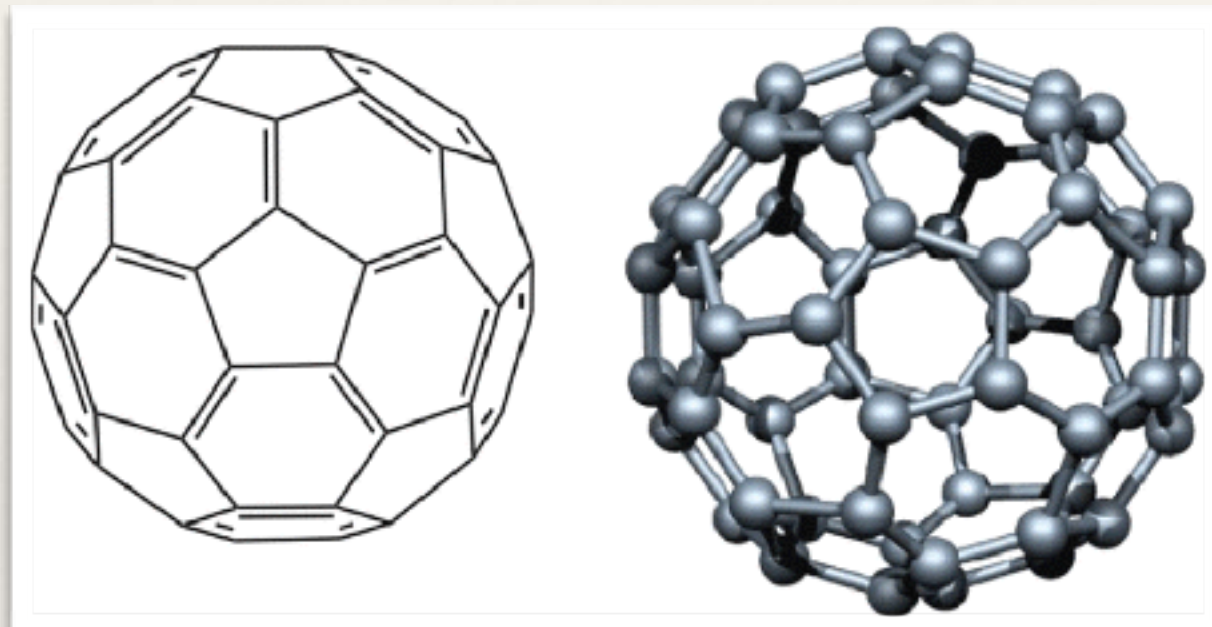
Alfred Werner (1866 – 1919)

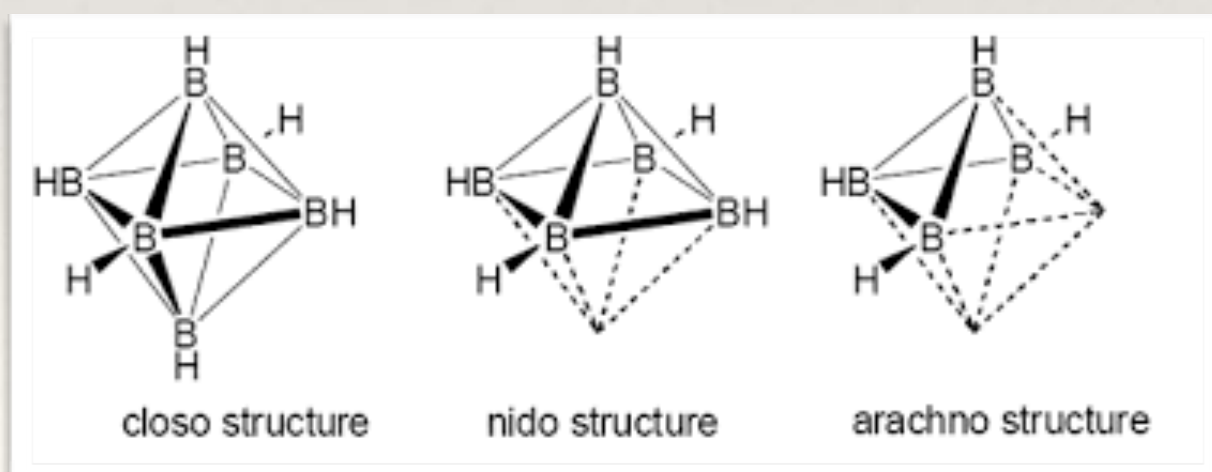
The shape and symmetry of complex molecules (solids) is often discussed as that of an **ordered ensemble of connected polyhedra**

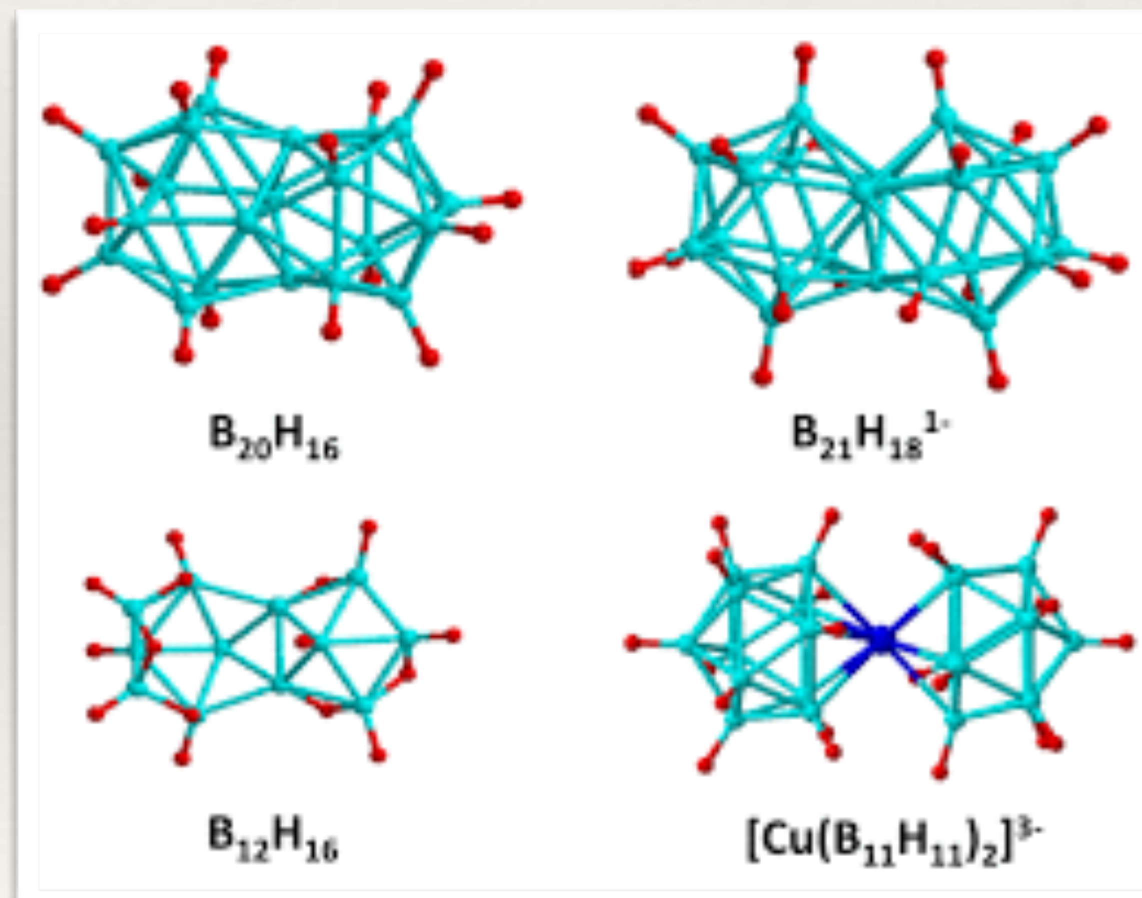


Polyhedral molecules

Besides coordination geometries, polyhedra play also an important role in the structural chemistry of **cage molecules**

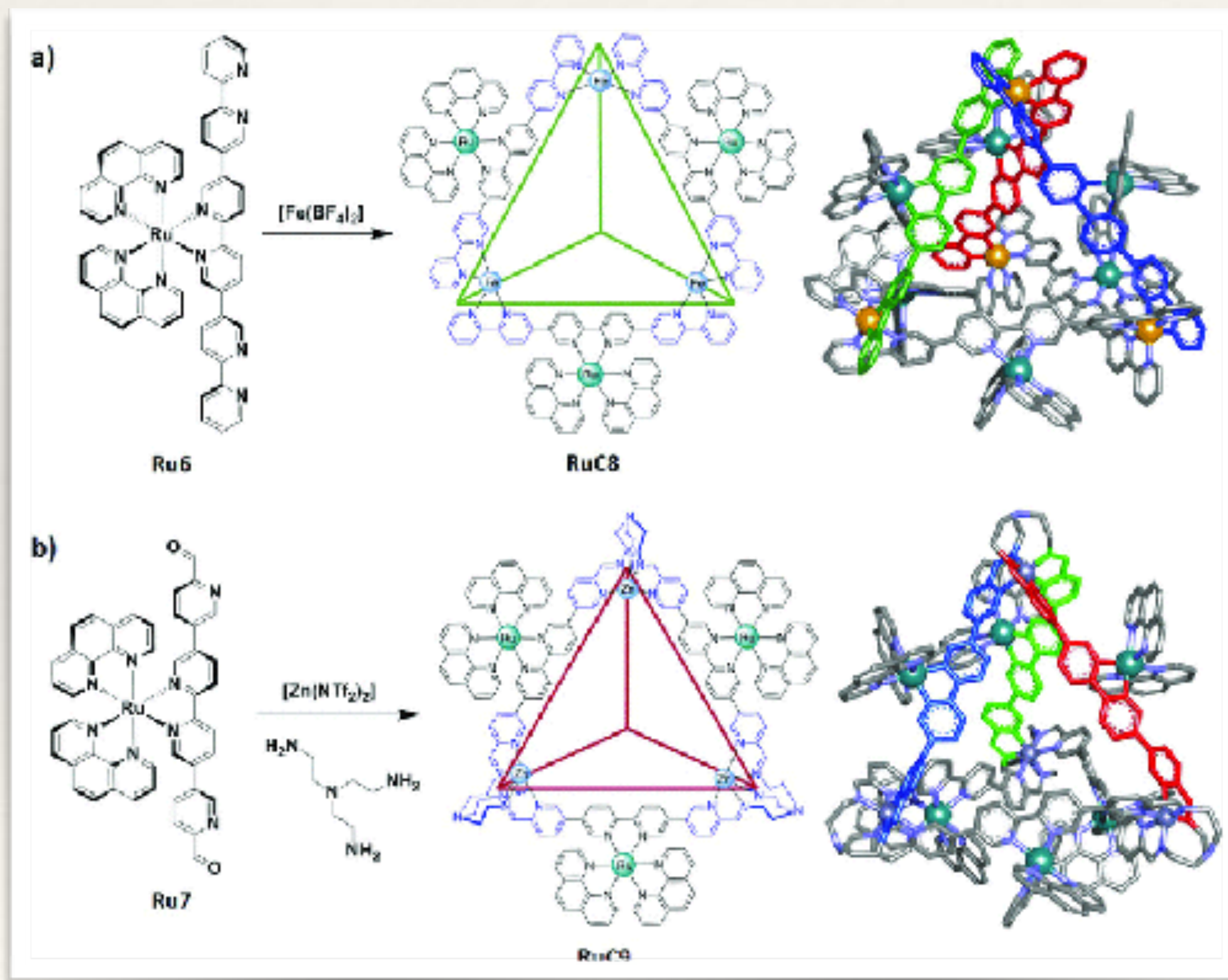


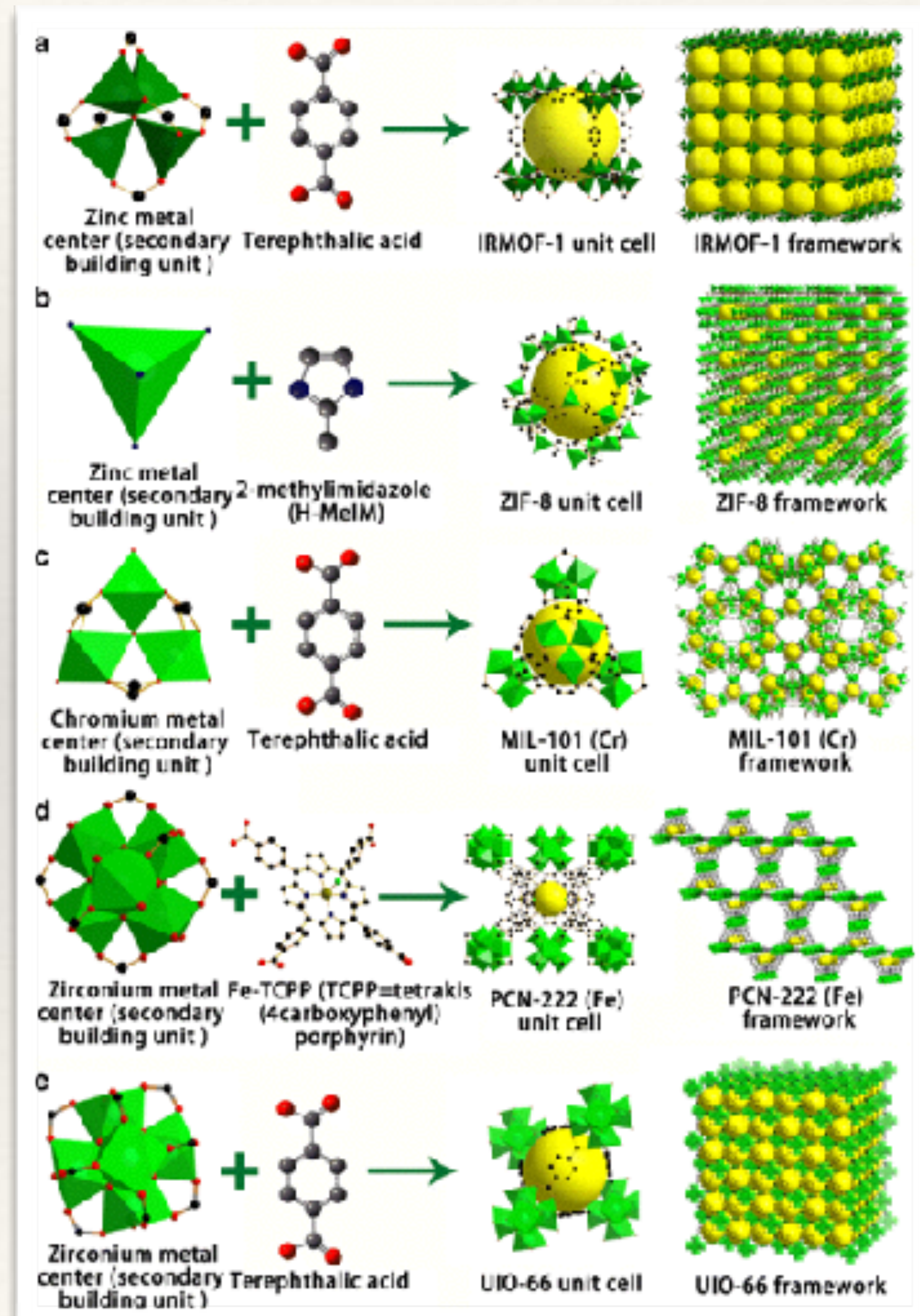




Polyhedra in supramolecular architectures

Polyhedral models are helpful in rationalizing the structure of complex supramolecular assemblies such as cage molecules or metal organic frameworks (MOFs)



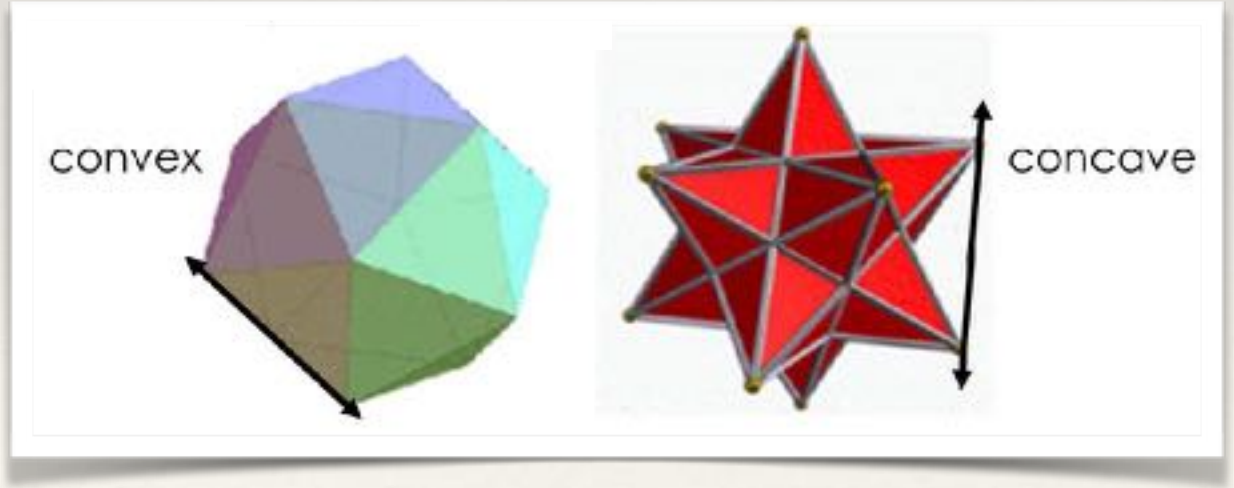


Mathematical definition of polyhedron

A polyhedron is a **three-dimensional shape** with **flat polygonal faces**, **straight edges** and **sharp corners** or vertices. Its shape is determined by a set of points (the vertices) in space. Besides the set of vertices, one can describe the polyhedron as a solid or as a surface.

The **number of faces** is often used to classify polyhedra: tetrahedron, octahedron, …

A polyhedron is **convex** if any line connecting any two (non-coplanar) points on the surface always lies in the interior of the polyhedron.



Euler's formula for convex polyhedra

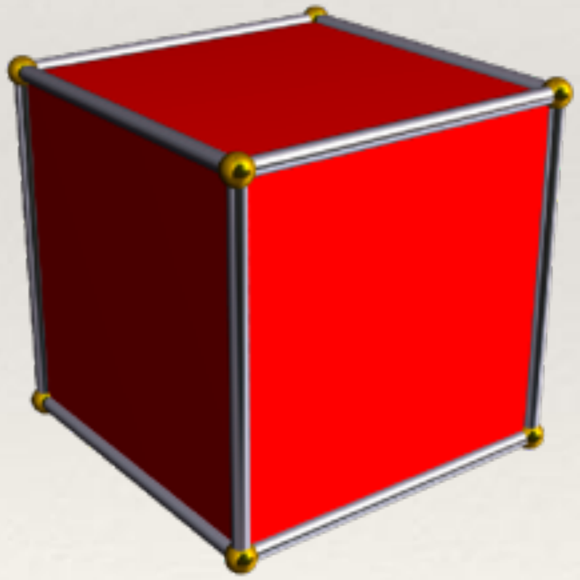
$$F + V - 2 = E$$

Example: cube F = 6, V = 8, E = 12

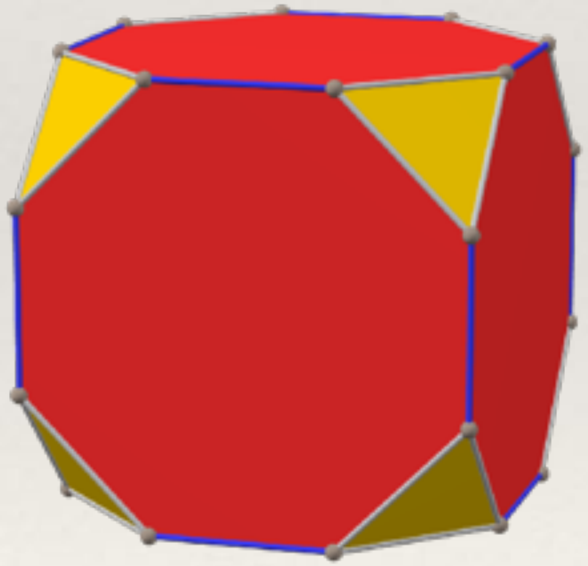
Symmetry of polyhedra

The most studied polyhedra are highly symmetrical. Each such symmetry may change the location of a given vertex, face, or edge, but the sets of all vertices, faces and edges are unchanged.

All elements (vertices, faces or edges) that can be superimposed on each other by symmetries form a **symmetry orbit**. If all the elements of a given feature, say all faces, lie in the same orbit, the figure is said to be **transitive** on that orbit.



Cube: vertex, face & edge transitive

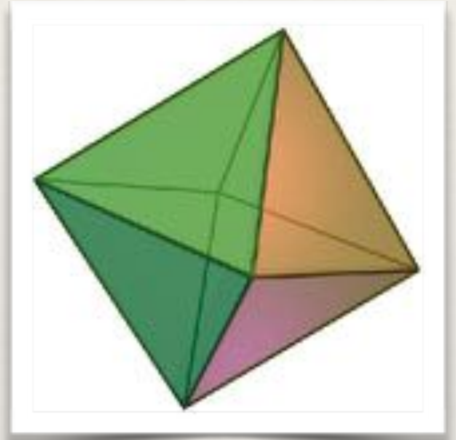


Faces in 2 different orbits

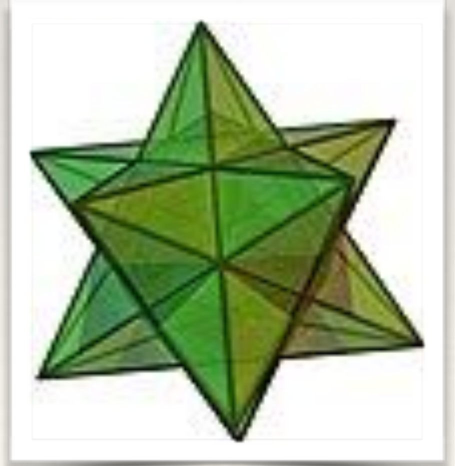
Truncated cube: vertex & edge transitive

Symmetric polyhedra

Regular:
vertex, edge & face-transitive



Octahedron

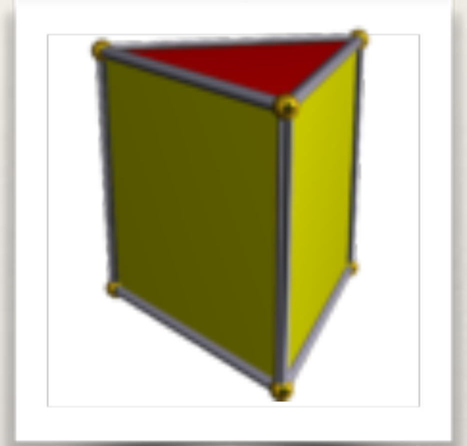


Small stellated
dodecaedron

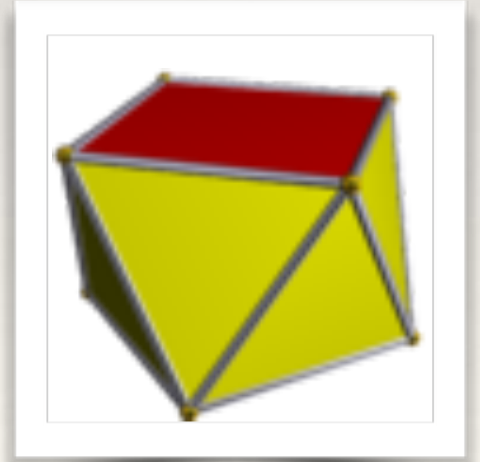
Quasi-regular:
vertex & edge-transitive

Cuboctaedron

Semi-regular: vertex-transitive,
All faces are regular polygons

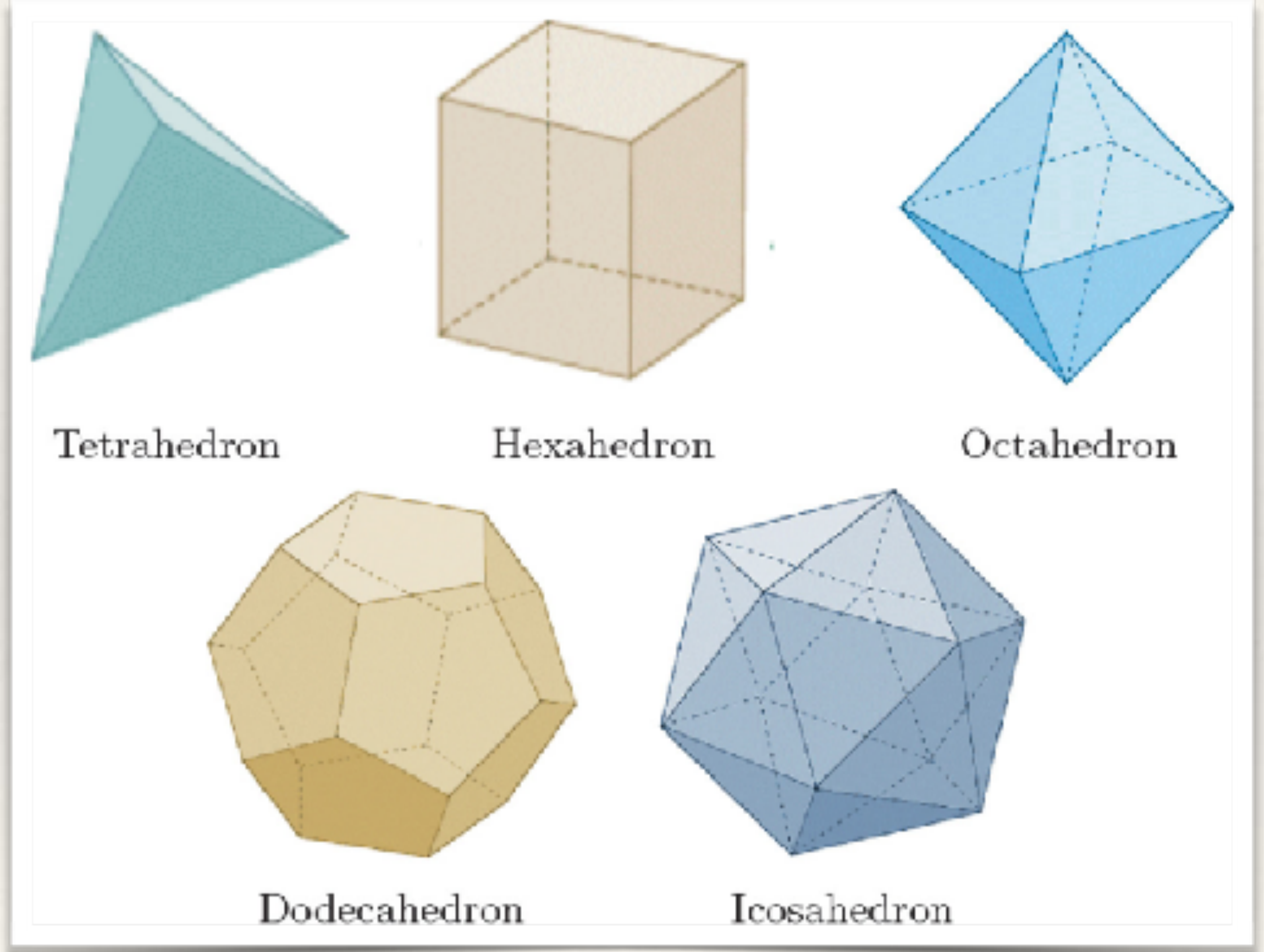


Triangular
prism



Square
antiprism

Platonic solids



The five possible **regular convex** polyhedra are also known as Platonic solids

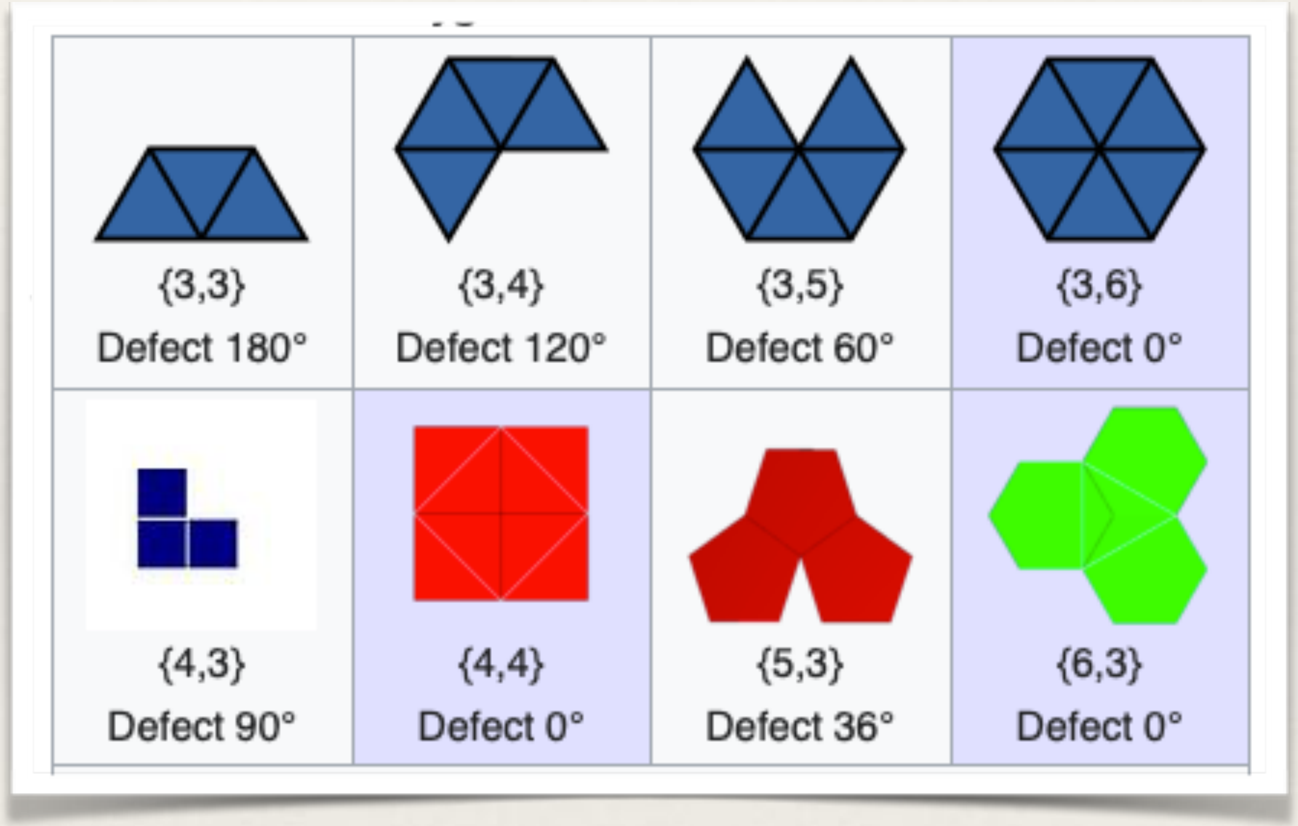
	V	E	F	Symmetry
tetrahedron	4	6	4	T_d
cube	8	12	6	O_h
octahedron	6	12	8	O_h
dodecahedron	20	30	12	I_h
icosahedron	12	30	20	I_h

Why are there only five platonic solids?

Each vertex of the solid must be a vertex for at least three faces.

At each vertex the total of the angles between adjacent sides must be strictly less than 360°. The amount less than 360° is called an angle defect.

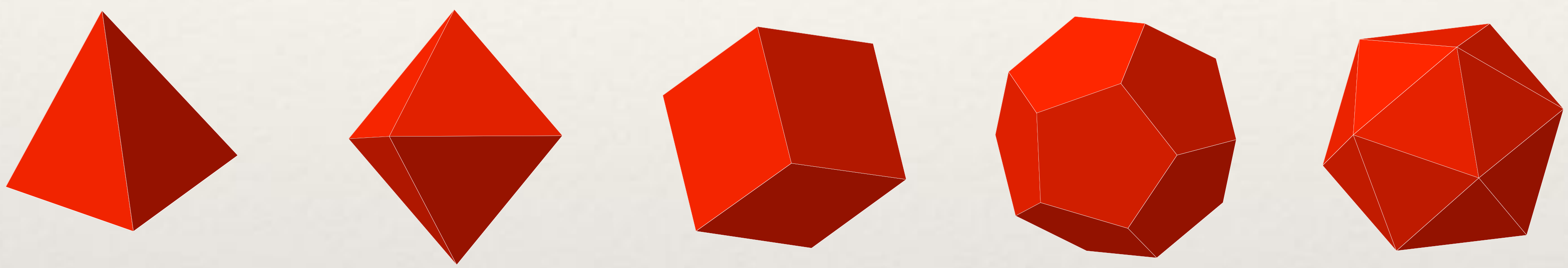
Regular polygons of six or more sides have only angles of 120° or more, so the common face must be the triangle, square, or pentagon.



Shape and Symmetry

Platonic Solids

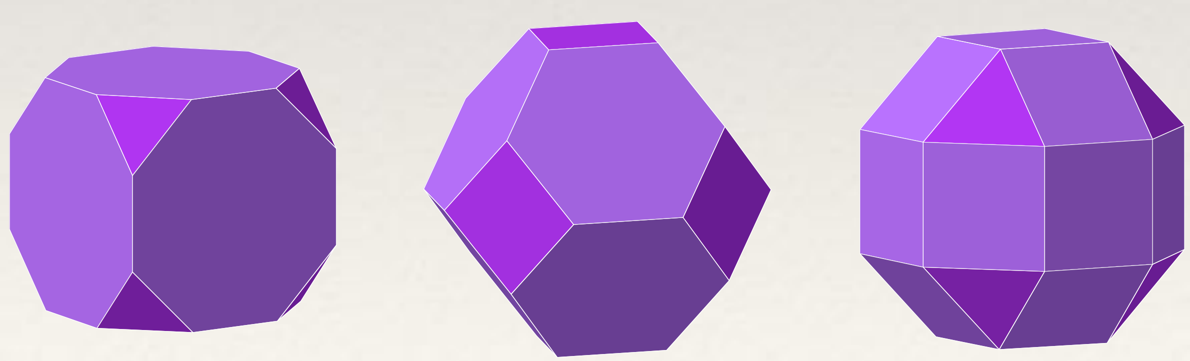
Univocal shapes for a given symmetry



T_d O_h O_h I_h I_h

General Polyhedra

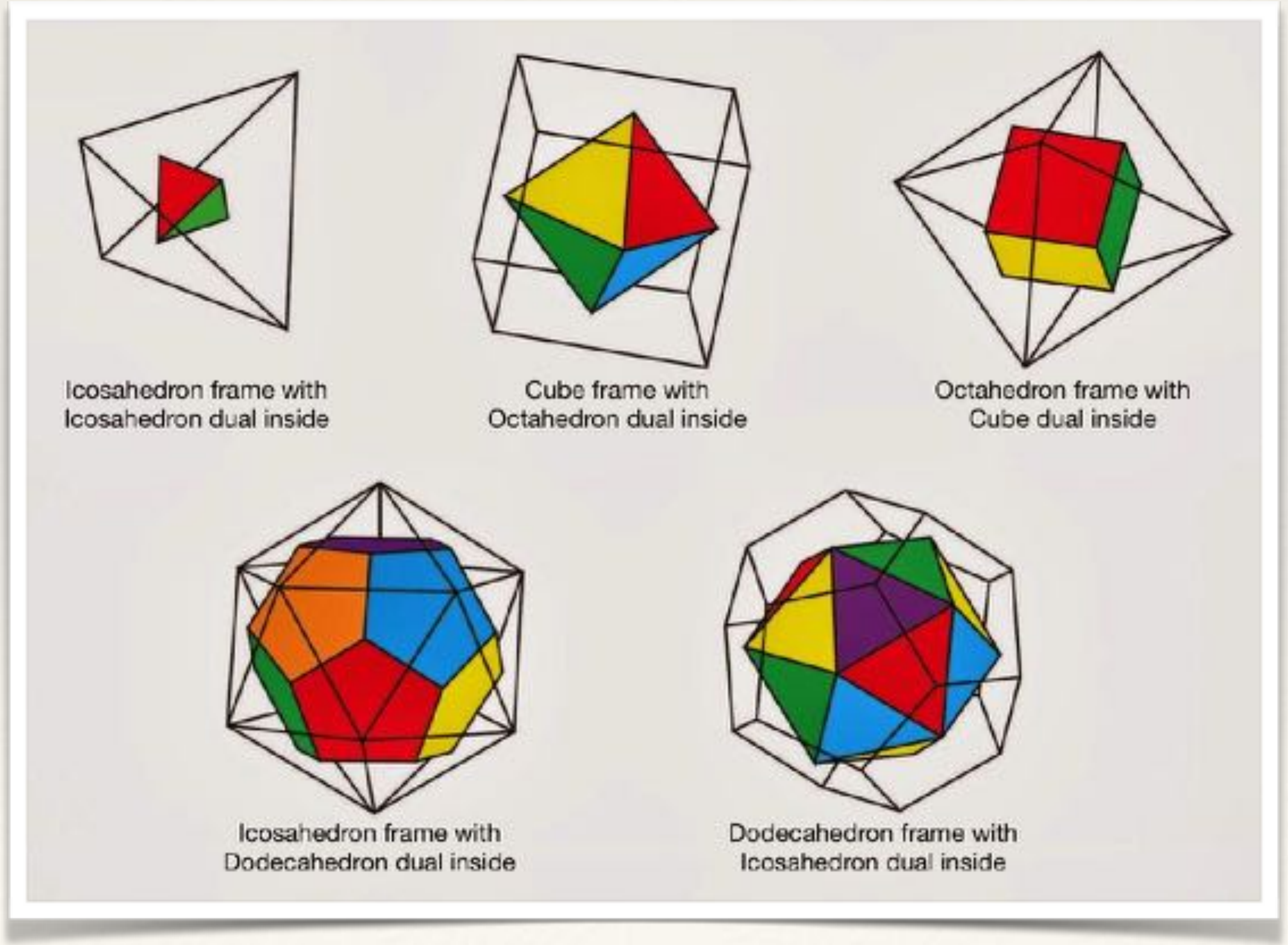
Different shapes for the same symmetry (O_h)



Three polyhedra with 24 vertices and O_h symmetry

Dual polyhedra

Every polyhedron is associated with a second **dual** structure, where the **vertices of one correspond to the faces of the other**. Duality preserves the symmetries of a polyhedron, hence all symmetry elements are symmetry elements of the two polyhedra.

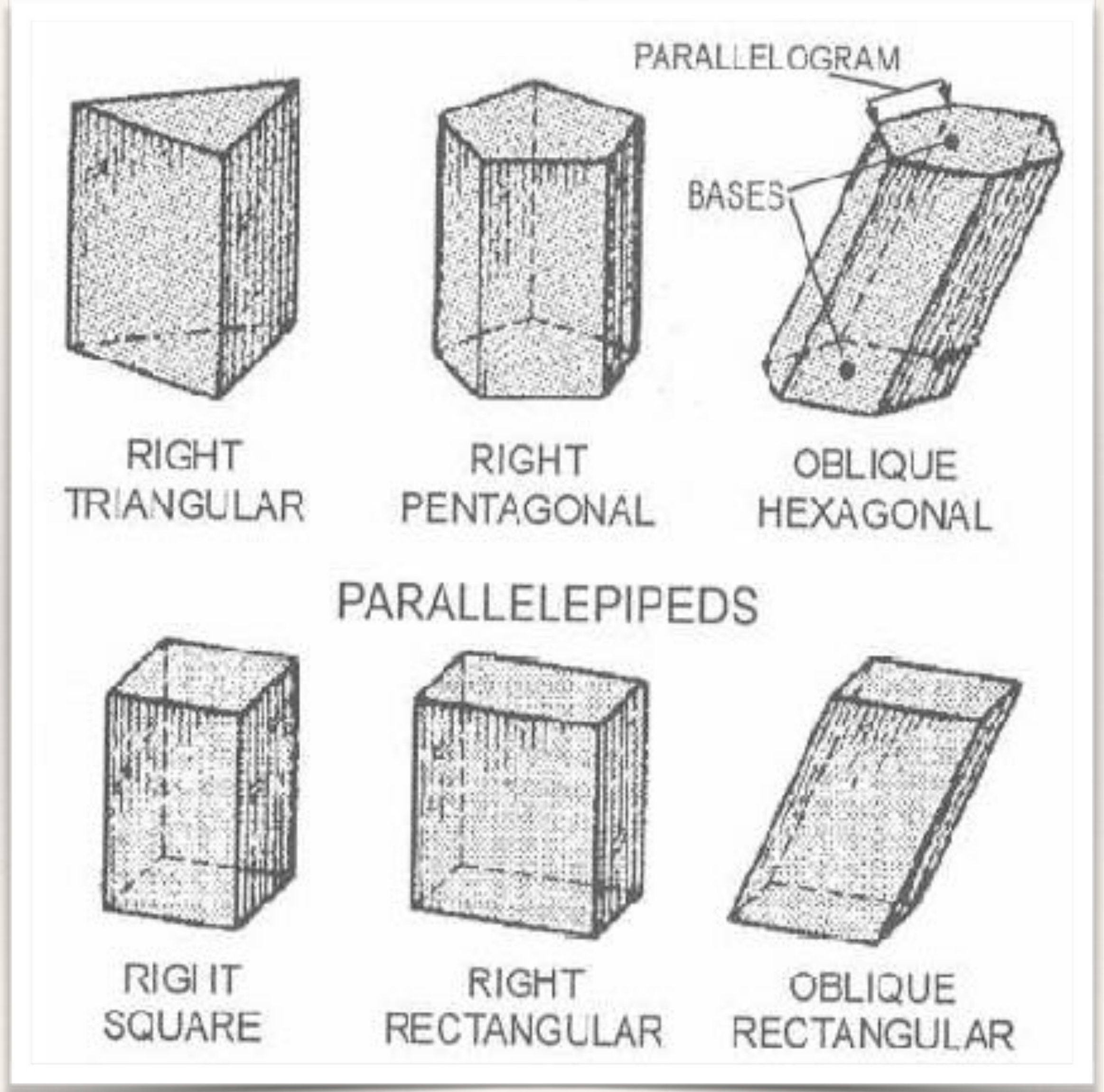


Prisms

A **prism** is a polyhedron comprising **two n-sided polygonal bases** and **n other faces**, necessarily all parallelograms, joining corresponding sides of the two bases.

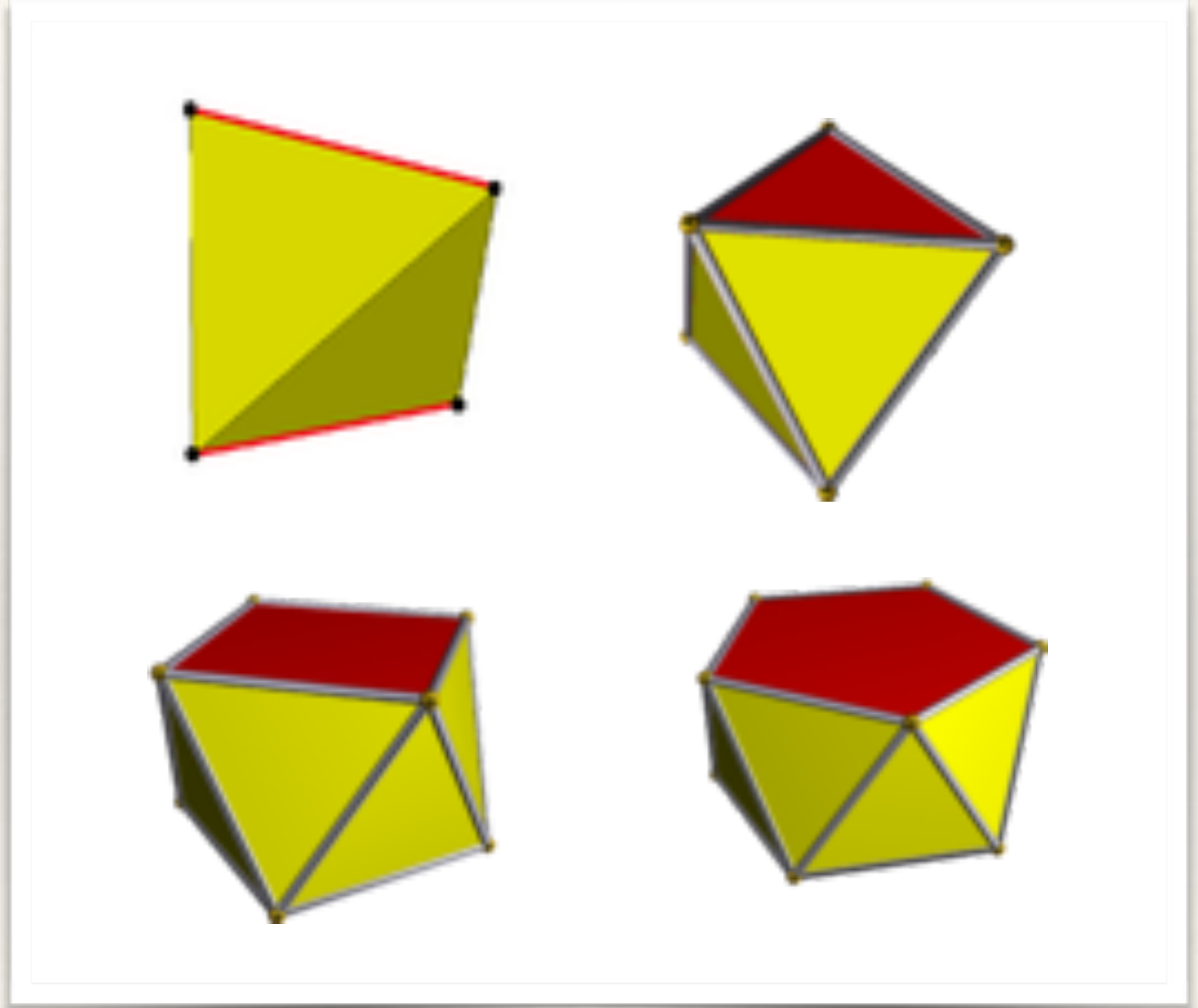
Right prisms with regular n-gon bases have $\mathbf{D_{nh}}$ symmetry. D_{nh} contains the inversion for even values of n.

A **uniform** prism is a prism with regular faces and all edges of the same length.



Antiprisms

A n-gonal **antiprism** or n-antiprism is a polyhedron composed of two parallel direct copies (not mirror images) of an n-sided polygon, connected by an alternating band of 2n triangles.



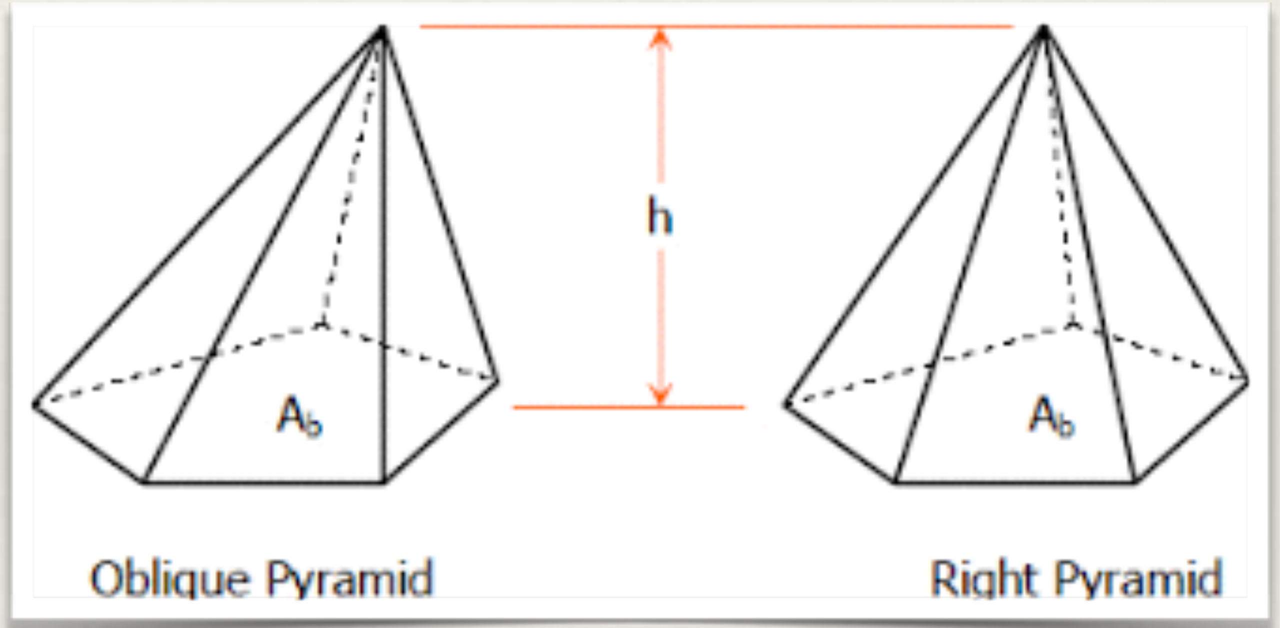
The symmetry group of a right n-antiprism (i.e. with regular bases and isosceles side faces) is $\mathbf{D_{nd}}$ except for n = 2 (tetrahedron) and n = 3 (octahedron)

Pyramids

A **pyramid** is a polyhedron formed by connecting a polygonal base and a point, called the **apex**. Each base edge and the apex form a triangle, called a lateral face.

A right pyramid has its apex directly above the centroid of its base. A regular pyramid has a regular polygon base and is usually considered to be a right pyramid.

A **right pyramid with a regular base** has isosceles triangle sides, with symmetry is **C_{nv}**.

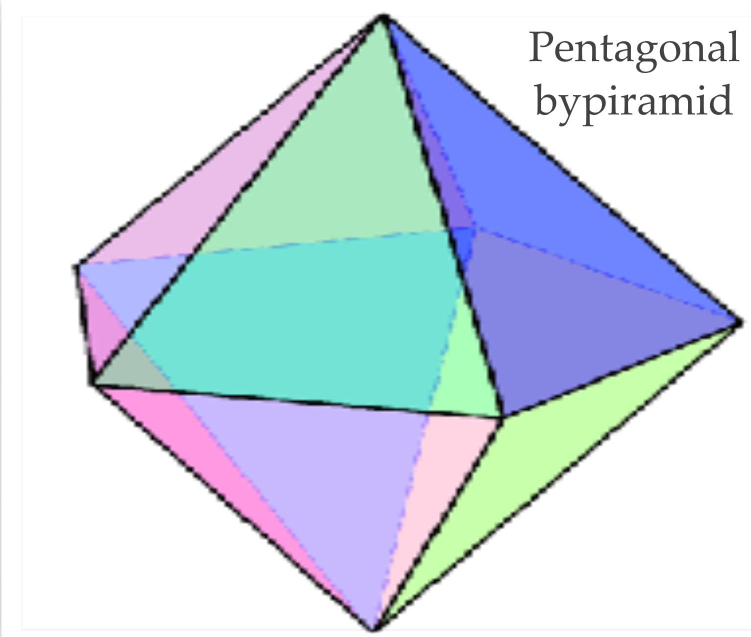


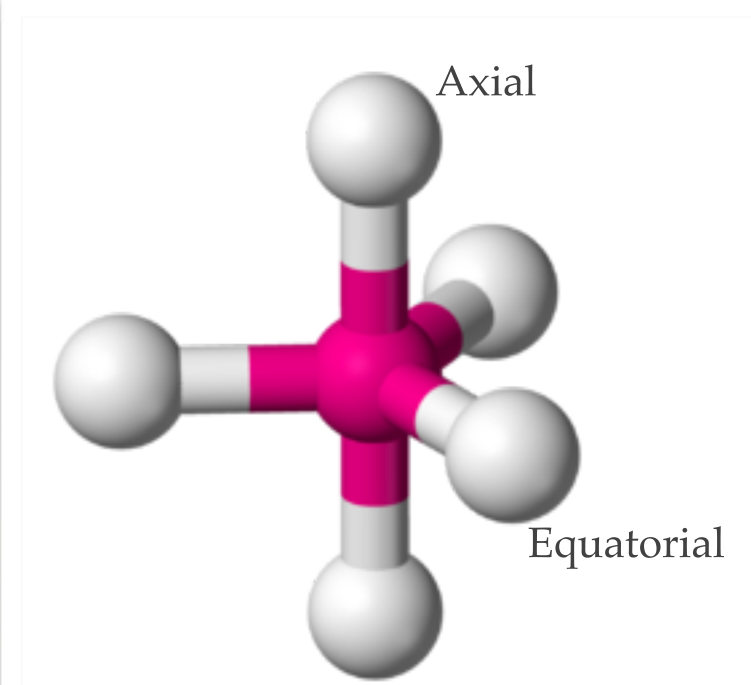
Bipyramids

A (symmetric) n-gonal bipyramid is a polyhedron formed by joining an n-gonal pyramid and its mirror image base-to-base.

A **"regular" n-bipyramid** has a regular polygon base. It is usually implied to be also a right bipyramid. Its symmetry class is $\mathbf{D_{nh}}$ except when n=4 (octahedron)

Bipyramids are not edge and vertex-transitive, one can distinguish **axial** and **equatorial** positions





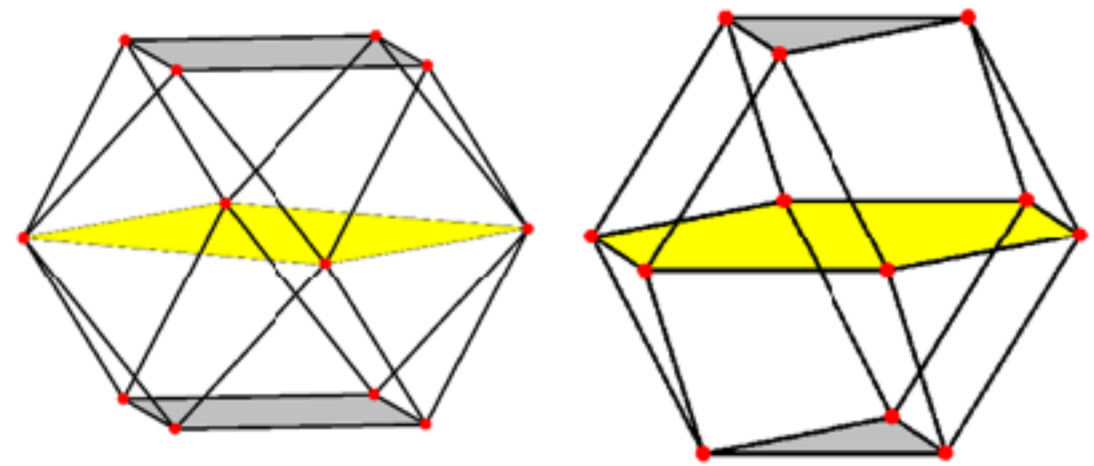
Sphere packings

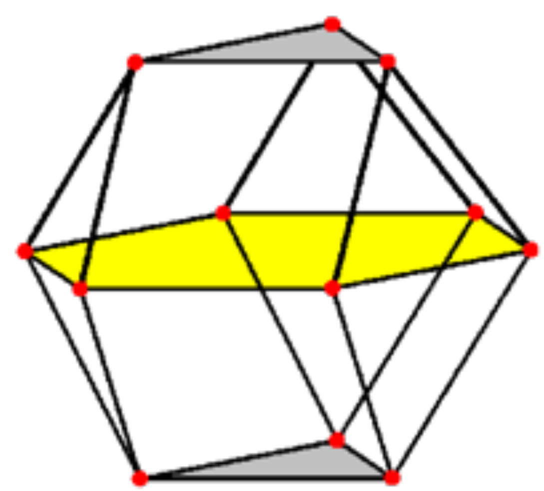
Many crystal structures are based on a **close-packing** of a single kind of atom, or a close-packing of large ions with smaller ions filling the spaces between them.

There are two simple regular lattices that achieve the highest average density. They are called **face-centered cubic** (FCC) (also called cubic close packed) and **hexagonal close-packed** (HCP), based on their symmetry.

Both closest packings are based on **12 vertex polyhedra**, the cuboctahedron and the triangular orthobicupola

FCC: cuboctahedron





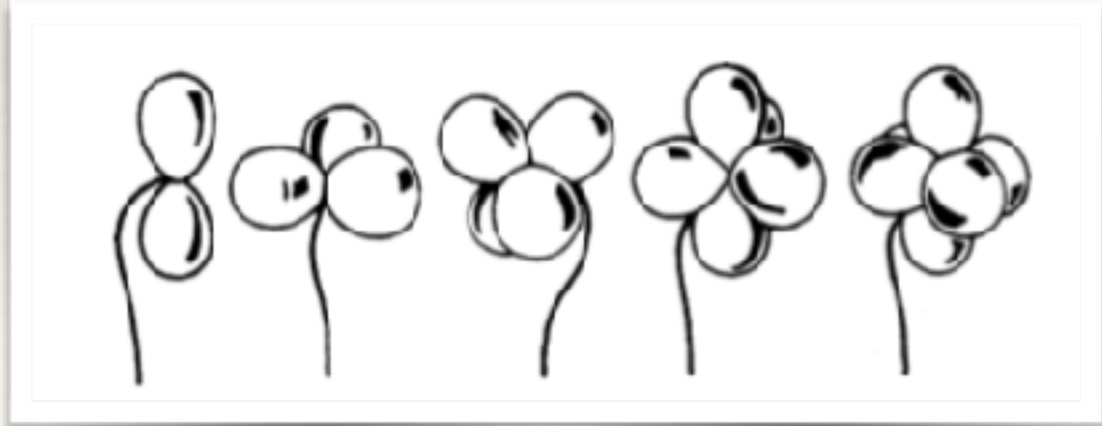
BCC:
triangular orthobicupola

Polyhedra in coordination environments

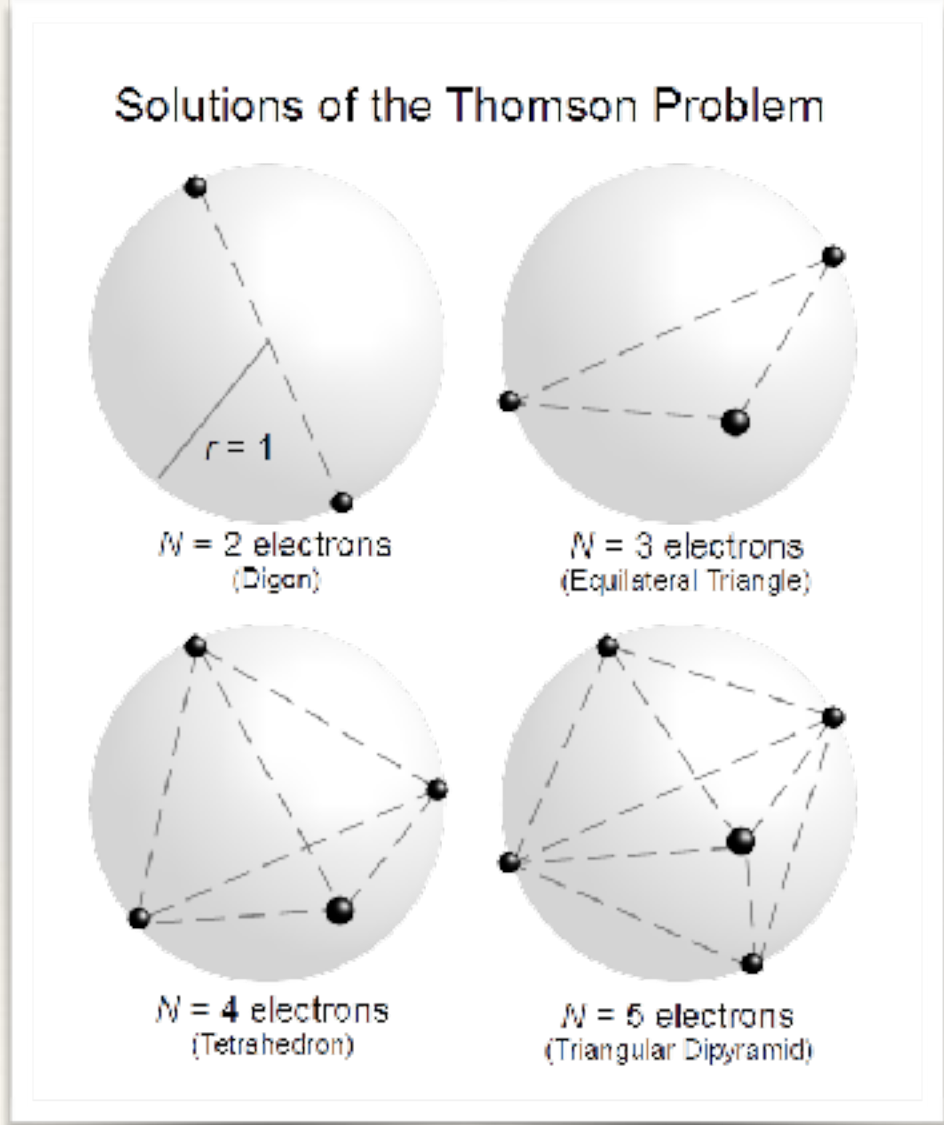
Polyhedra used in the description of coordination environments arise usually from **maximizing the distances between ligands** (minimizing repulsions)

The Thompson problem

Determine the minimum electrostatic potential energy configuration of n electrons constrained to the surface of a sphere that repel each other with a force given by Coulomb's law.



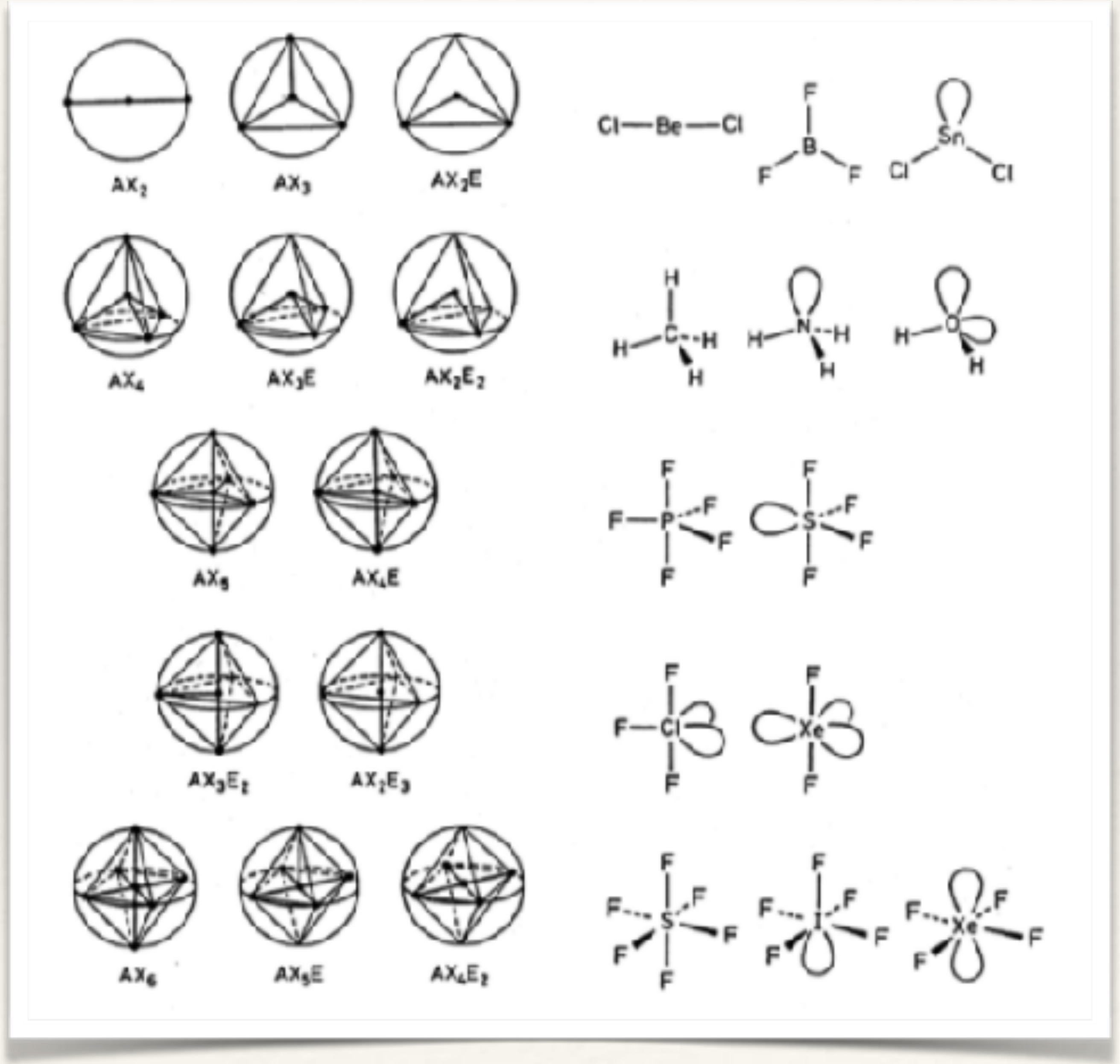
Analogy: packing of balloons



VSEPR theory

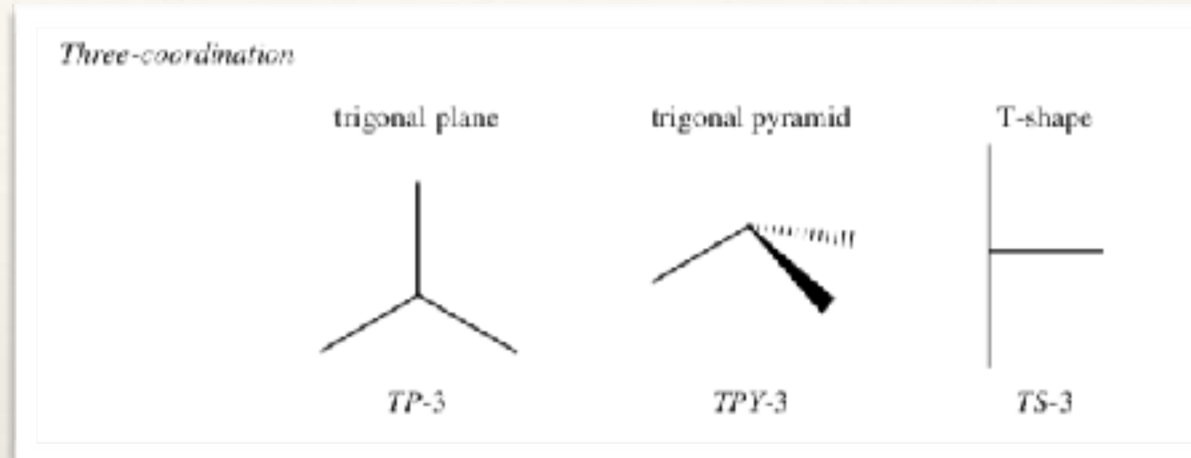
Valence shell electron pair repulsion (VSEPR) theory is a model used in chemistry to predict the geometry of individual molecules from the number of electron pairs surrounding their central atoms. It is also named the Gillespie-Nyholm theory after its two main developers.

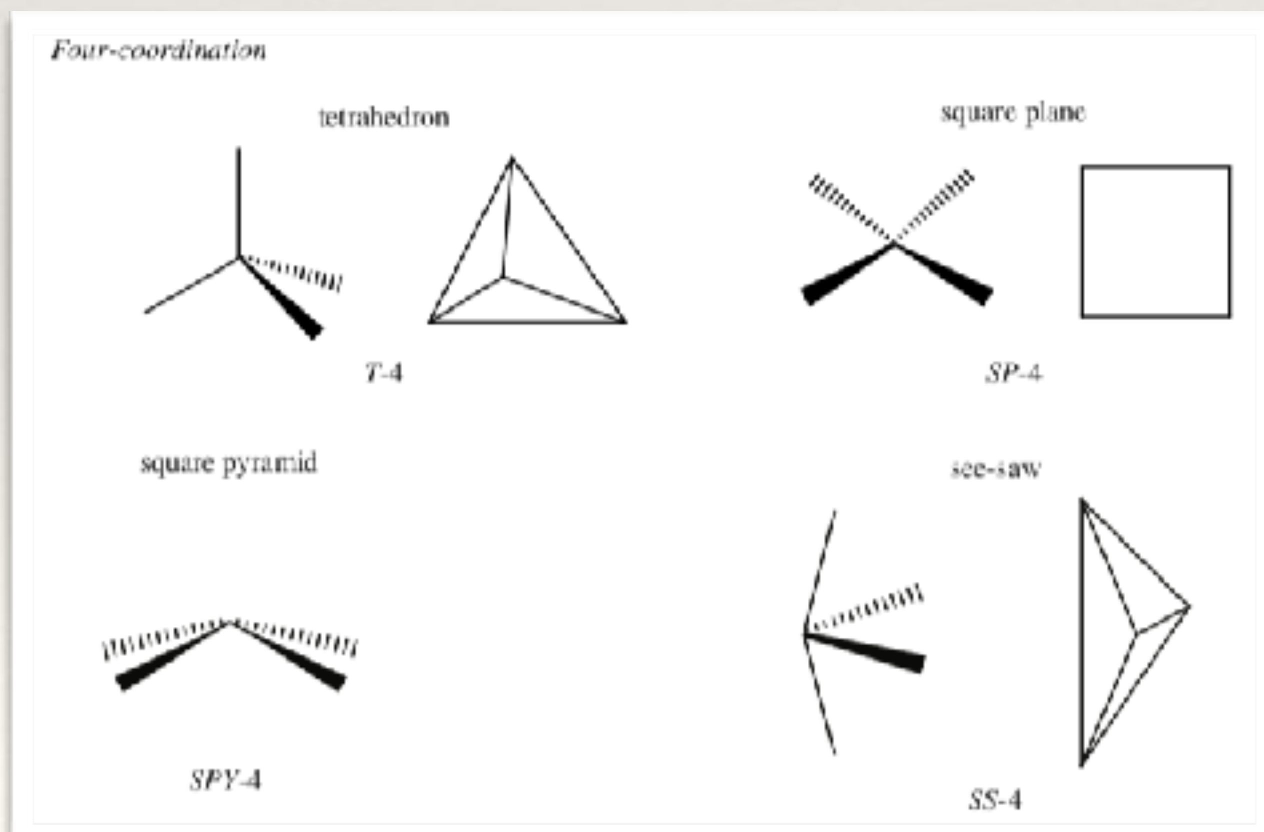
The premise of VSEPR is that the **valence electron pairs** surrounding an atom tend to **repel each other** and will, therefore, adopt an arrangement that **minimizes this repulsion**.

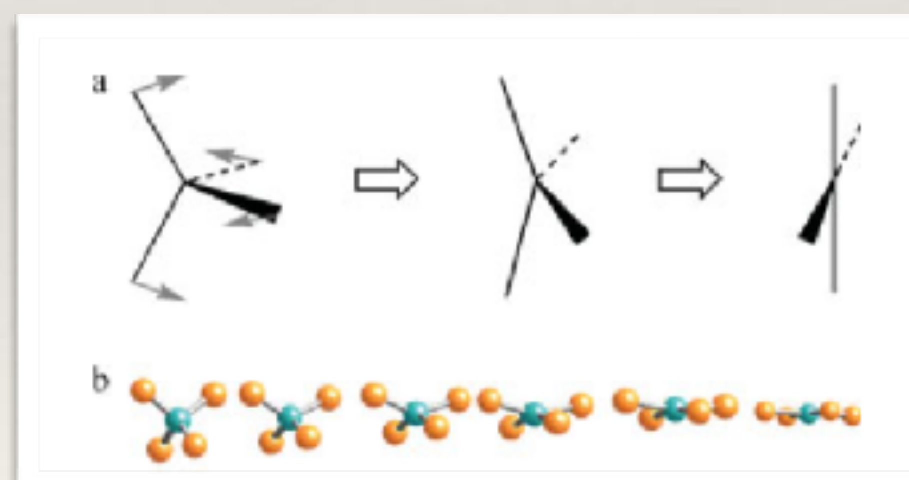


Polyhedral symbols

Polyhedral symbols include a **standard label**, LA, and the **number of coordinating atoms**, N: LA-N



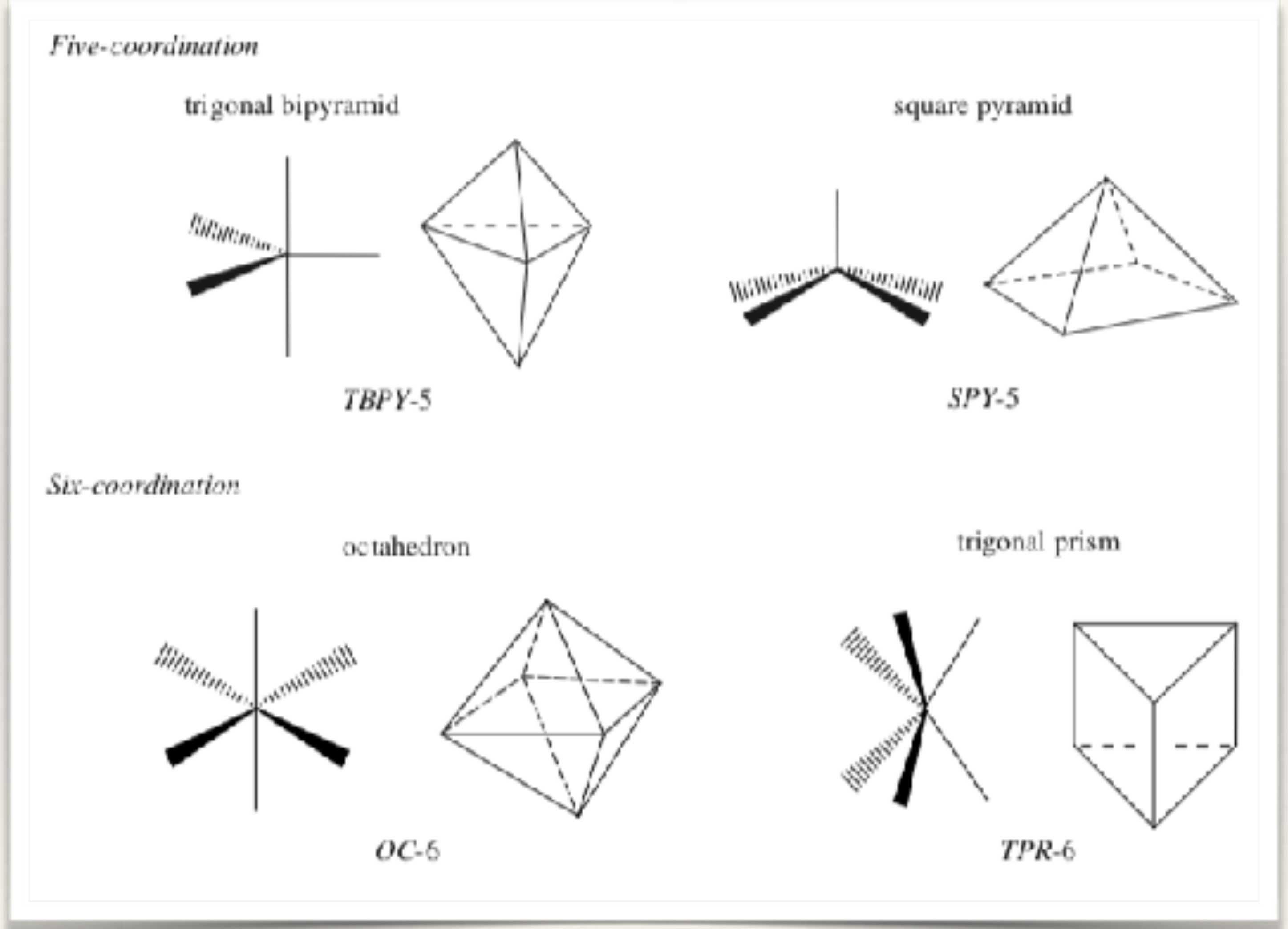




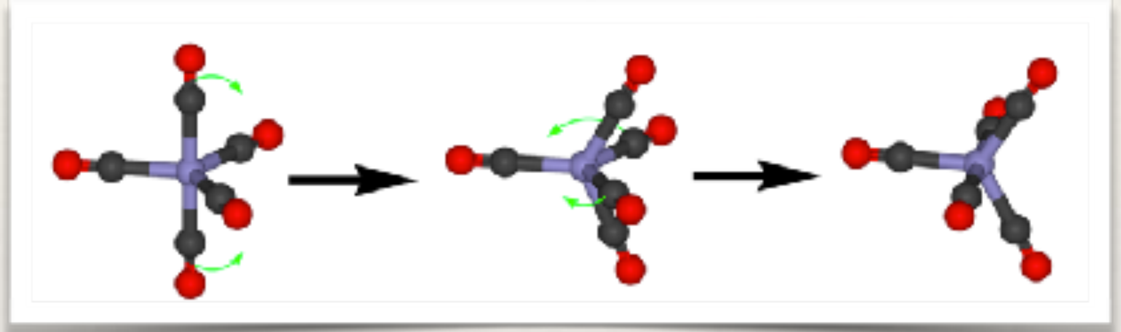
Spread path

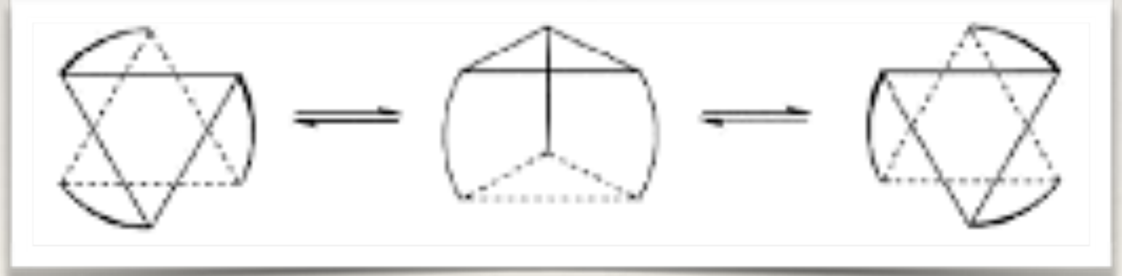
$T_d \rightarrow D_{2d} \rightarrow D_{4h}$

Polyhedral symbols



Berry pseudorotation mechanism





Bailar mechanism

Polyhedral symbols