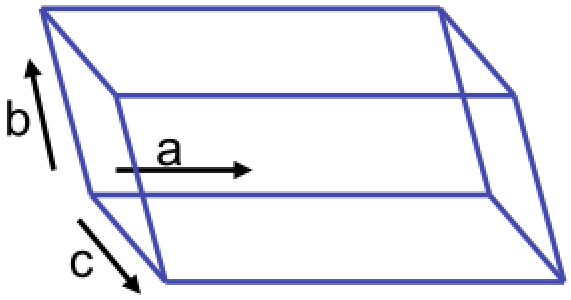
Supramolecular and Structural Inorganic Chemistry

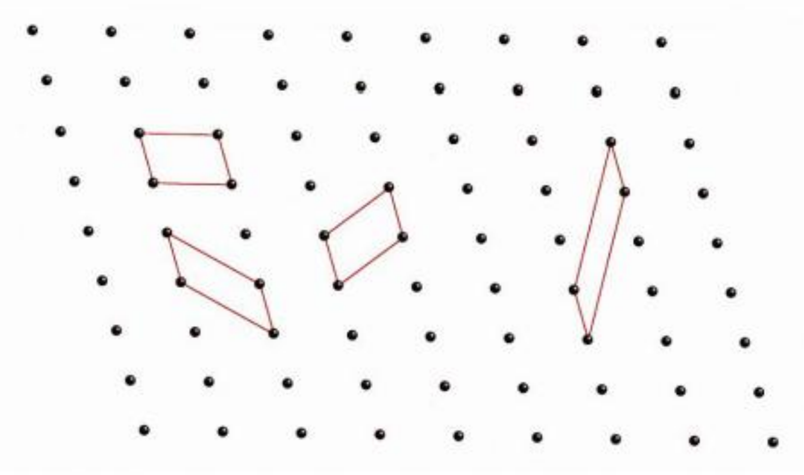
X-Ray Crystallography

Unit Cell

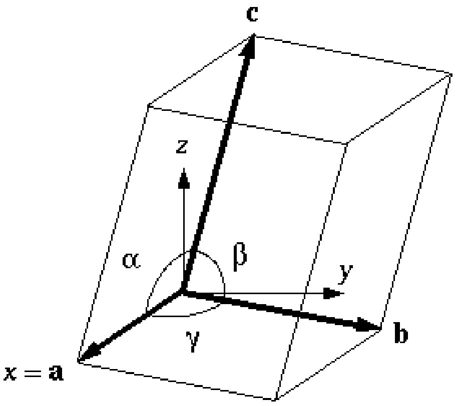
A regular parallelepiped with edge lengths a, b and c and angles α, β, γ. The whole crystal is generated by continuous replication and translation of the unit cell.

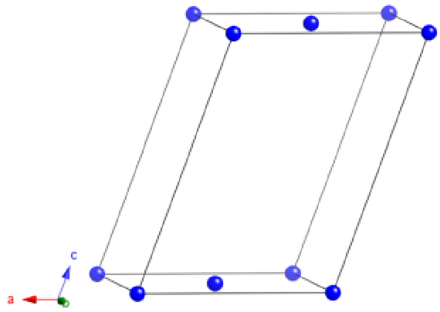


By convention the unit cell with angles closest to 90° is selected as the unit cell.

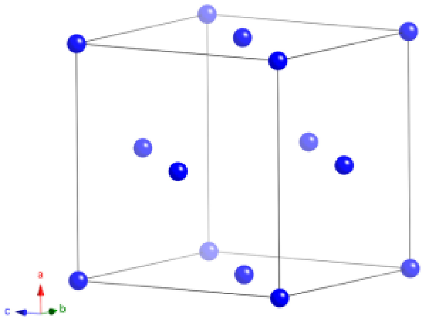


Body-centred and face-centred cells can also be identified.

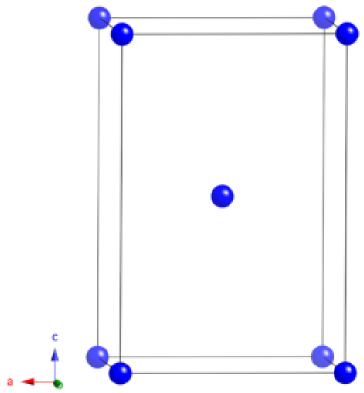




C-centered monoclinic cell



Face-centred cubic cell

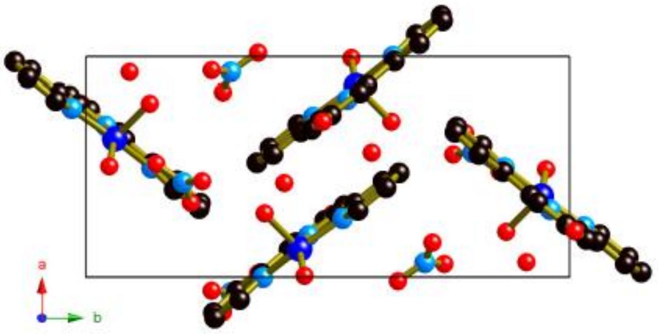


Body-centred tetragonal cell

Space groups

Within a crystal structure the largest unit that possesses no symmetry is referred to as the asymmetric unit. A series of symmetry operations may be applied to this unit to generate the full contents of the unit cell. The series of symmetry operations that are applied, correspond to one of 230 " space groups ".

The asymmetric unit

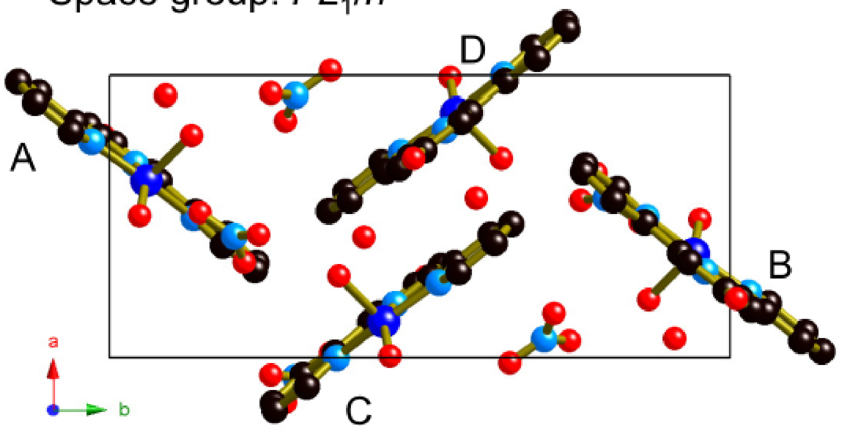


The unit cell

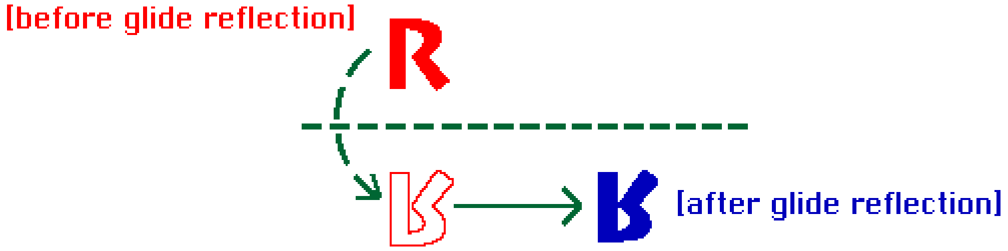
Symmetry operations:

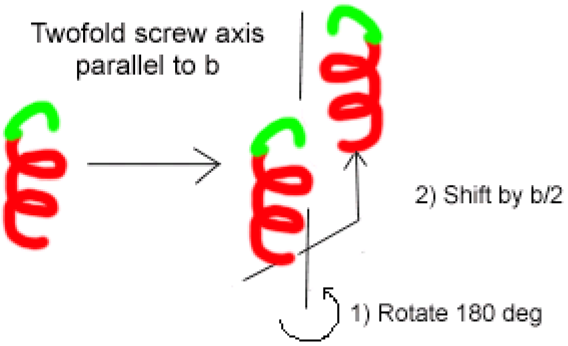
- Reflection across a mirror plane: m
- Rotation around an axis: indicated by a single integer n (2, 3, 4 or 6)
- Inversion: indicated by $\bar{1}$
- Rotation coupled with inversion: indicated by $\bar{n}$ $(\bar{3}, \bar{4}, \bar{6})$
- Glide planes: combination of a reflection followed by a translation parallel to the plane of the reflection, the letter indicates whether the glide is in the a, b or c direction
- Screw axes: combination of rotation followed by translation along the direction of the axis, indicated by a subscripted integer $2_1, 3_1, 3_2, 4_1, 4_2, 4_3$

Space group: $P2_1/n$



A is related to B by an inversion.
A is related to C by an *n*-glide.
A is related to D by a 2-fold screw.
B is related to C by a 2-fold screw.
B is related to D by an *n*-glide.
C is related to D by an inversion.

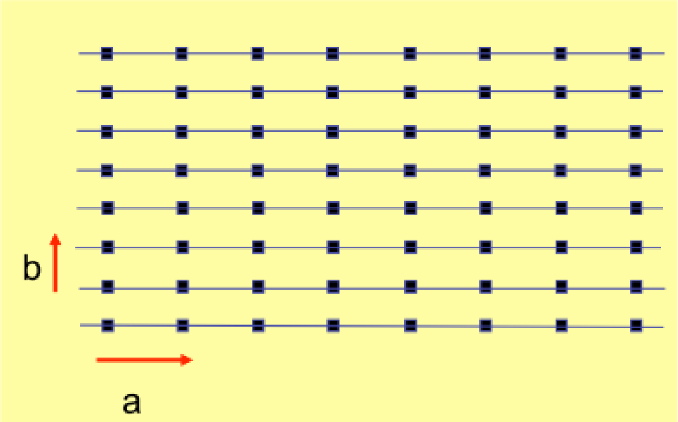




A proper symmetry operation moves an object but does not change its handedness, e.g. rotations, screws. An improper symmetry operation moves an object and changes its handedness, e.g. reflections, inversions.

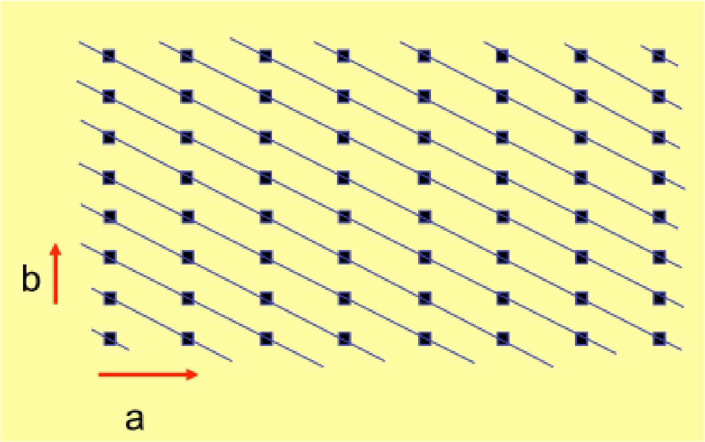
Miller Indices

A family of lattice planes is determined by three integers *h*, *k*, and *ℓ*, the *Miller indices*, written (hkℓ).



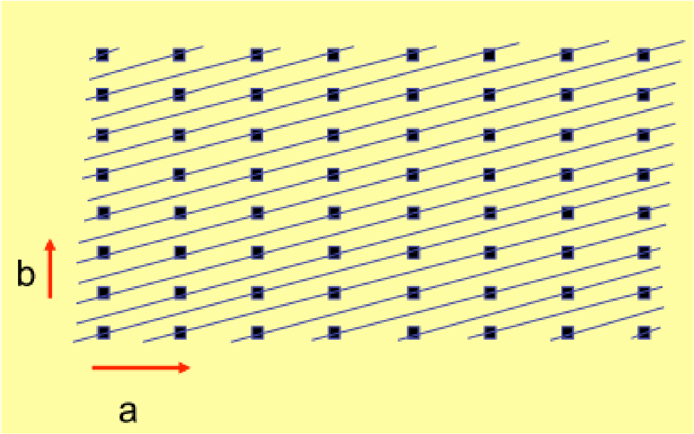
The lines represent planes (viewed edge-on) within an infinite family of planes, and parallel to the *a*- and *c*-axes.

These planes intersect the b axis at intervals of 1b, while they intersect the a and c axes at all points. Thus the Weiss indices are $(\infty, 1, \infty)$. The Miller indices (h, k, l) are obtained by taking the reciprocals and clearing any fractions. So here the Miller indices are $(0,1,0)$.



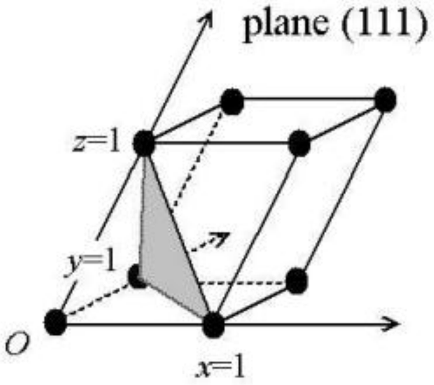
Consider the family of lattice planes shown on the left (infinite in the *c*-direction).

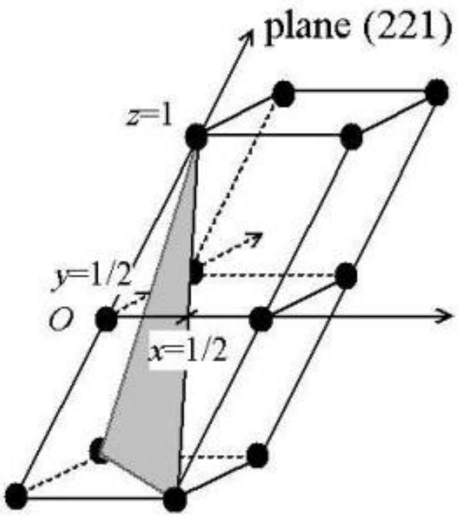
These planes intersect the a axis and the b axis are intervals of 1, while it intersects the c axis at every point. Thus the Weiss indices are $(1,1,\infty)$ and the Miller indices are $(1,1,0)$.



Consider the family of regularly spaced parallel lattice planes shown on the left (infinite in the *c*-direction).

These planes intersect the a-axis at 1a intervals and intersect the b axis at 0.5b intervals. Thus the Weiss indices are $(-1,1/2\,,\infty)$ and the Miller indices are $(-1,2,0)$.

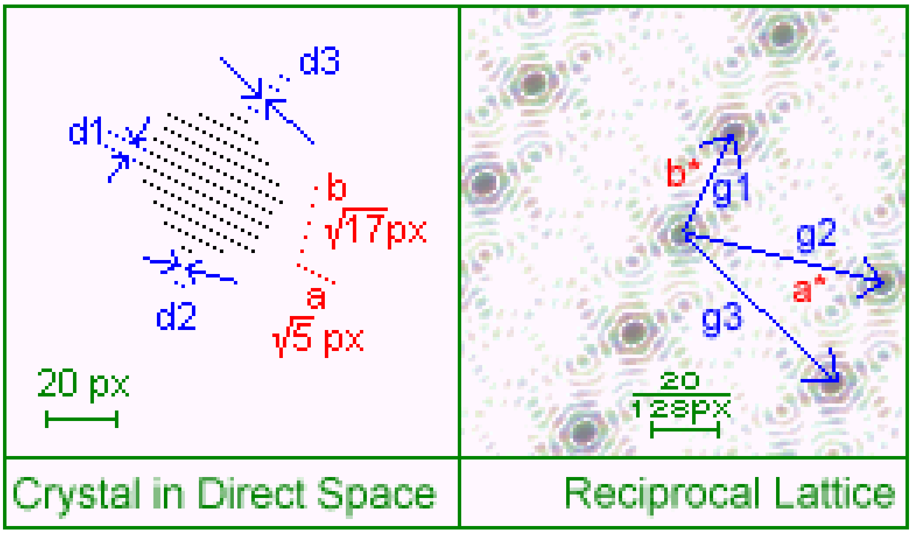




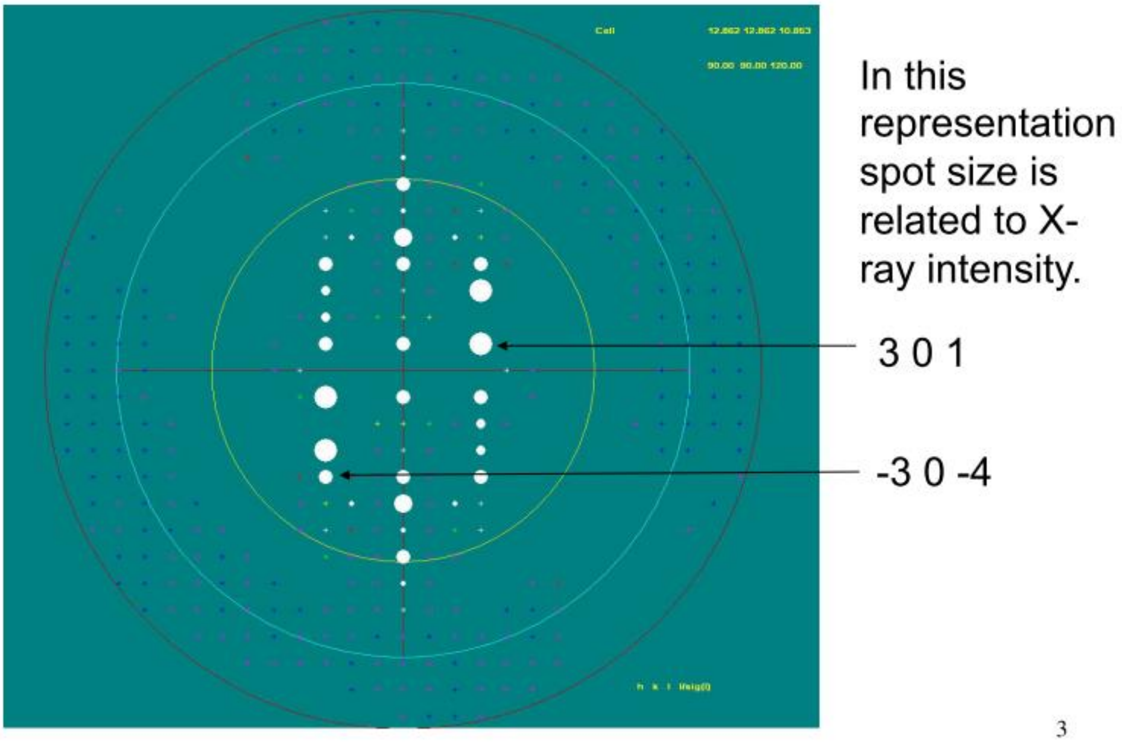
An important point to note is that the smaller the value of one of the indices, the closer it is to being parallel to the axis direction to which it corresponds.

Reciprocal Lattice

The reciprocal lattice represents the Fourier Transform of another lattice (usually a Bravais lattice). While the direct lattice exists in real-space and is what one would commonly understand as a physical lattice, the reciprocal lattice exists in reciprocal space.



The symmetry with respect to reflection intensity in a reciprocal lattice is related to the symmetry in the real crystal.



In this representation spot size is related to X-ray intensity.

3

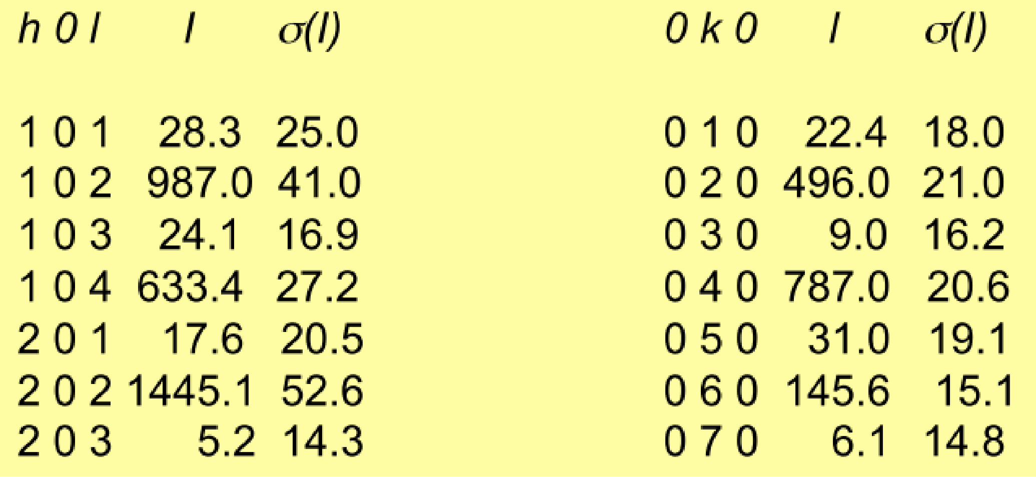
The pattern of symmetries in a reciprocal lattice reflects symmetries of the underlying lattice. If a crystal is orthorhombic then it is has Laue symmetry of mmm. Therefore the reflection 4 5 6 will be:

-4 5 6
-4 -5 6
4 -5 6
4 -5 -6
4 5 -6
-4 -5 -6

We can take advantage of the Laue symmetry in the diffraction pattern and measure only a fraction of the reflections.

Space Group Determination

Once the reflection data has been collated we are then in a position to decide upon the space group. At this point we look for systematic absences in the data.



h 0 l	I	σ(I)	0 k 0	I	σ(I)
1 0 1	28.3	25.0	0 1 0	22.4	18.0
1 0 2	987.0	41.0	0 2 0	496.0	21.0
1 0 3	24.1	16.9	0 3 0	9.0	16.2
1 0 4	633.4	27.2	0 4 0	787.0	20.6
2 0 1	17.6	20.5	0 5 0	31.0	19.1
2 0 2	1445.1	52.6	0 6 0	145.6	15.1
2 0 3	5.2	14.3	0 7 0	6.1	14.8

Systematic absences in hkl reflections arise when symmetry elements containing translational components are present, such as in the following cases. The presence of certain symmetry operations in a crystal can result in some reflections suffering from complete destructive interference.

While analysis of systematic absences can narrow down the choice of space groups it does not always lead to a single space group. In many cases a number of space groups will have the same systematic absences. Under these circumstances we generally choose the highest symmetry space group that provides a sensible solution.

Phase Problem

In order to solve a crystal structure for each reflection we need: reflection position (indicated by the Miller indices), intensity (measured by the detector), phase angle. There is no straightforward way to determine the phase angle, and so this is known as the phase problem.

Patterson method: A Patterson map is a series of atom-to-atom vectors. When the position of heavy atoms are known along with the cell symmetry, the assignment of reflections becomes possible.

Direct methods: these make use of relationships between the phase and the intensities of reflections. It is also makes the assumption that the electron density can never be negative in the unit cell and takes advantage of the fact that the electron density of a crystal is concentrated within atoms. Considerable computing power is required for such methods to work.

Structure Refinement

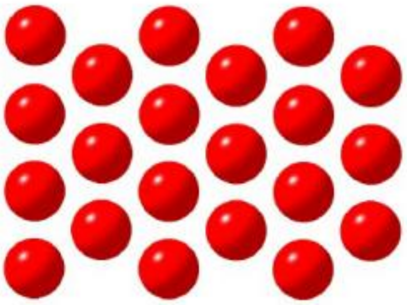
In the process of refinement, a model of the crystal structure is generated and the diffraction pattern of the model is then calculated. This theoretical pattern is then compared to the real diffraction pattern. An agreement factor, the R value (often expressed as a percentage) provides an indication of the accuracy of our model.

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

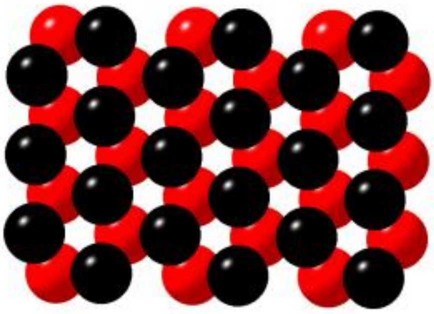
Sphere Packing

Close Packing

A single layer of spheres.

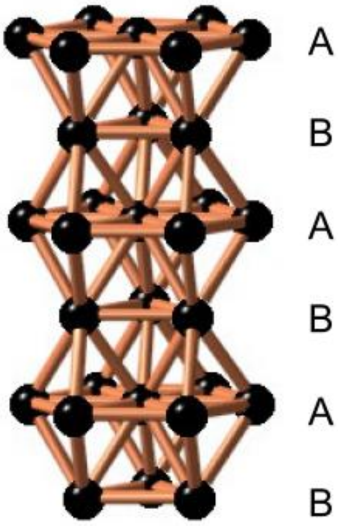


2 layers of spheres.



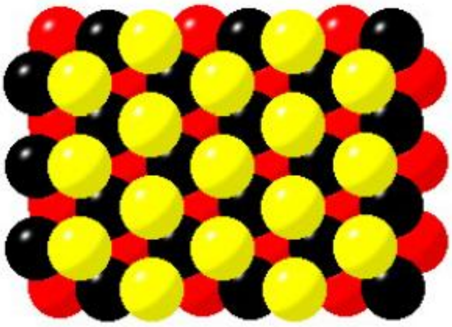
Hexagonal Close Packing

If the 3rd layer stacks above the 1st and the 4th above the 2nd and this process is continued then we have ABAB stacking, which is known as hexagonal close packing (HCP).



Cubic Close Packing

If the 3rd layer is offset from both the red layer and the black layer and this stacking sequence is continued then we have ABC stacking, which is known as cubic close packing (CCP) or face-centered cubic (FCC).

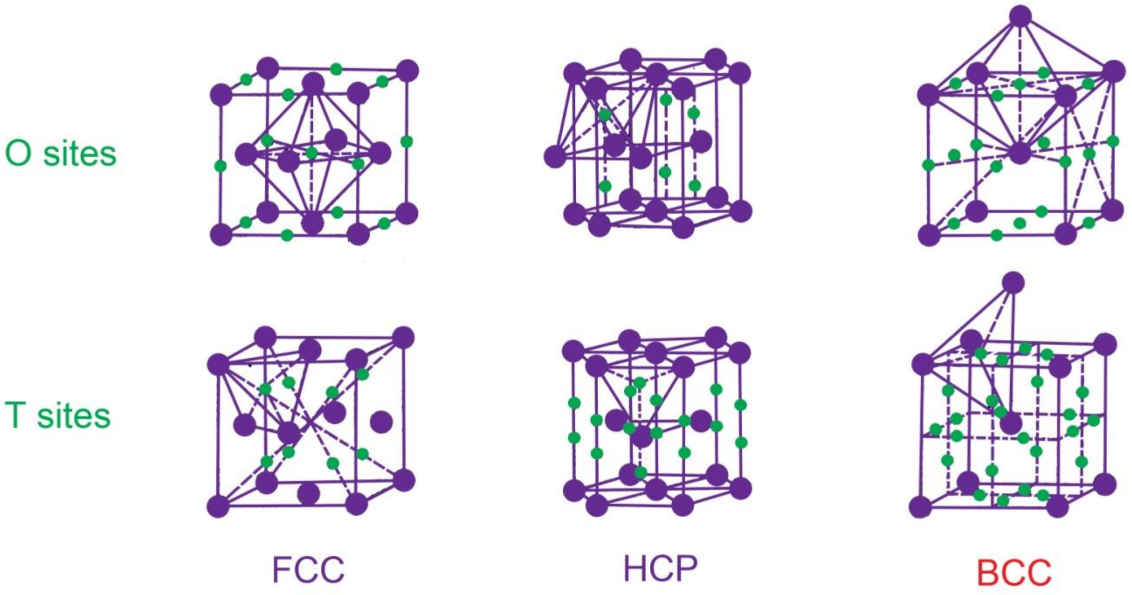


Red spheres - A layer
Black spheres - B layer
Yellow spheres -C layer

In both arrangements (CCP and HCP) the spheres occupy 74 % of the volume of the structure

Interstitial Sites

Two types of interstitial sites (holes) are formed between the 2 layers. Octahedral sites - Sites surrounded by six spheres arranged at the corners of an octahedron. Tetrahedral sites - Sites surrounded by four spheres arranged at the corners of a tetrahedron.



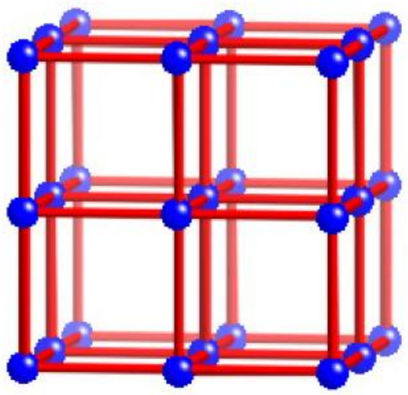
In both HCP and CCP there are 6 octahedral sites around each sphere and 6 spheres around each octahedral site. The ratio of octahedral sites to spheres is therefore 1:1.

In both HCP and CCP there are 8 tetrahedral sites around each sphere and 4 spheres around each tetrahedral site. The ratio of tetrahedral sites to spheres is therefore 2:1.

An octahedral site is considerably larger than a tetrahedral site and both are much smaller than the spheres.

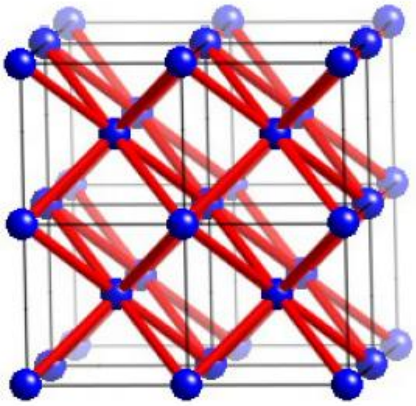
Simple Cubic Packing

Spheres arranged at the vertices of a cube. Each sphere makes contact with six other spheres. The spheres (when touching) occupy 52.4 % of the volume of the structure.



Body-Centred Cubic

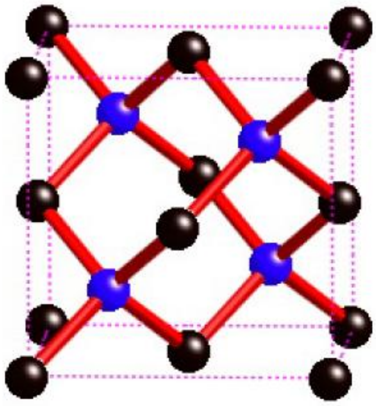
Spheres are arranged at the vertices AND at the centre of a cube. The spheres occupy 68 % of the volume of the structure.



Carbon allotropes

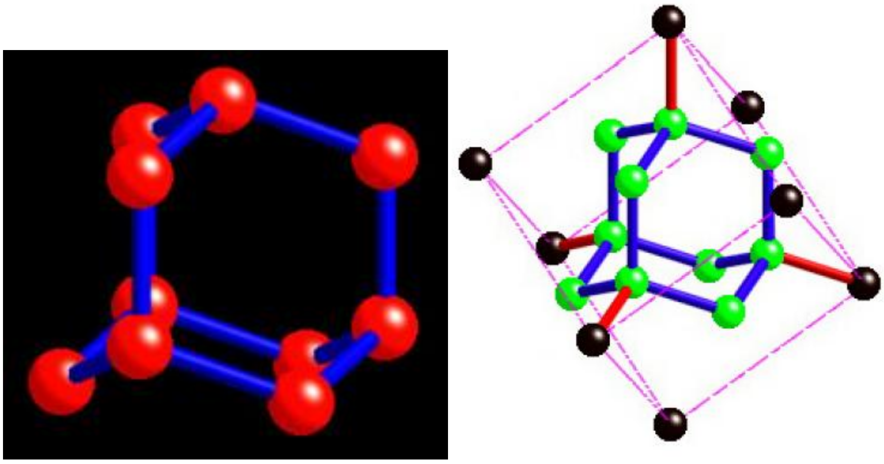
Diamond

A CCP arrangement with every second tetrahedral site of the cube filled with a carbon atom.



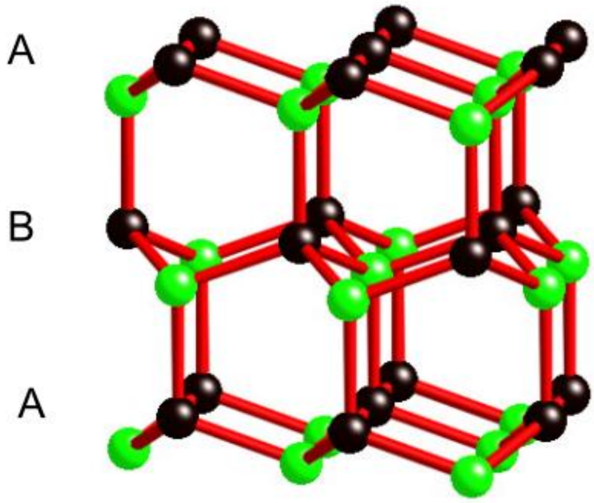
Adamantane Unit

Found in the centre of the diamond unit cell



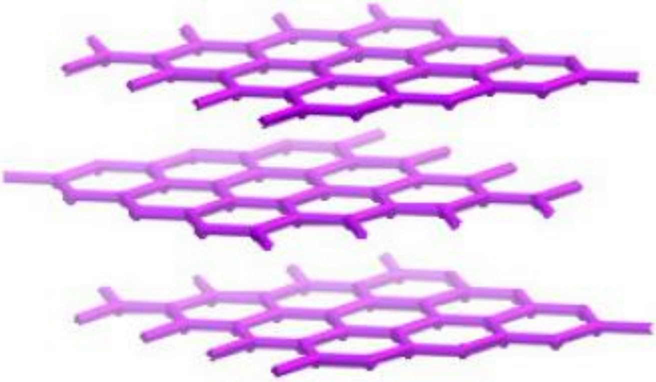
Lonsdaleite

HCP arrangement of carbon atoms, with half the tetrahedral sites filled with carbon atoms (green).



Graphite

Forms a 2-dimensional hexagonal grid structure. No carbon atom is directly above another in adjacent layers.



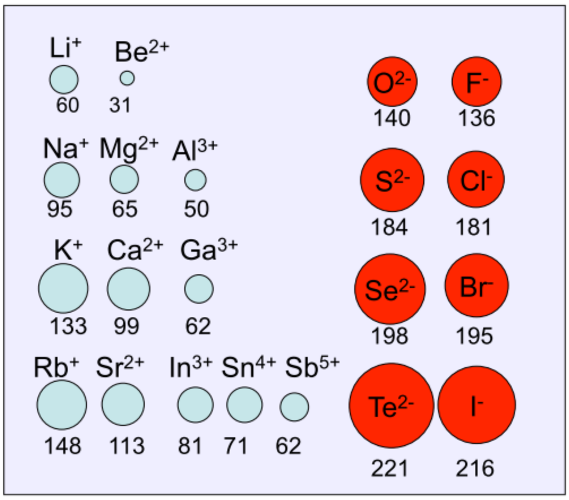
It is possible to place molecules or ions between the layers; this is known as intercalation. Intercalation is possible because of the weak attraction between layers.

Intercalculation

Addition of K to graphite produces a paramagnetic copper-coloured compound, $K^+[C_8]$. K^+ lies in between sheets and causes the staggered sheets to become eclipsed. The interlayer separation increases from 3.35 to 5.40 Å. Electrical conductivity is significantly enhanced with additional electrons added to the delocalised system. Alkali metal intercalates are highly reactive and will be removed by heating or exposure to air or water.

Ion Sizes

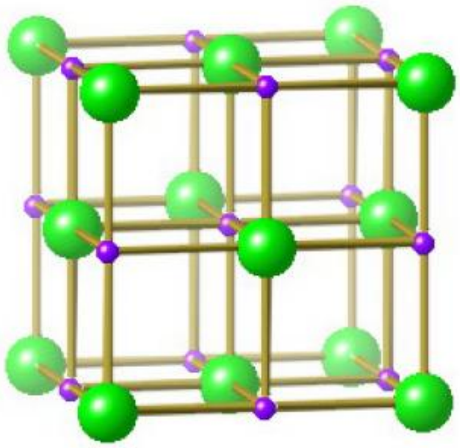
Generally (not always) anions are bigger than cations. Therefore ionic structures are often described in terms of the packing arrangement of anions. The smaller cations fill interstitial sites (holes).



AX Solids

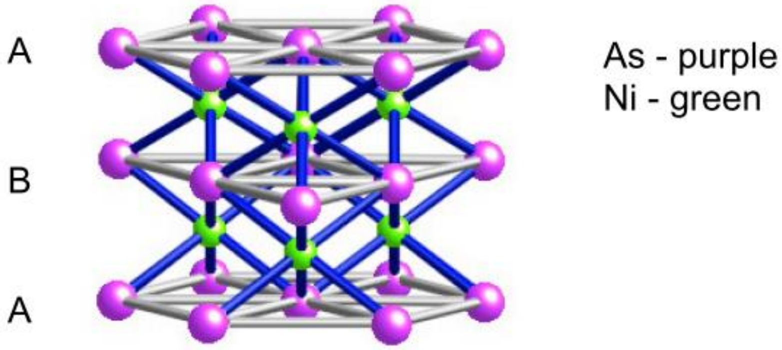
Rock Salt

An FCC (CCP) arrangement of anions with cations occupying the octahedral sites



NiAs Structure

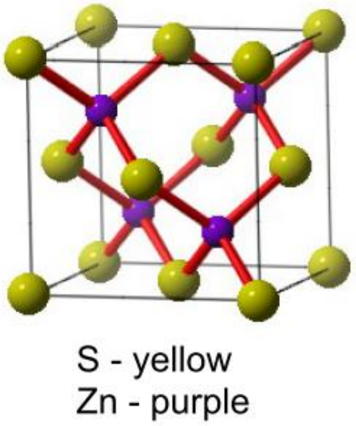
HCP arrangement of arsenic atoms with nickel atoms in all the octahedral sites.



The arrangement of Ni atoms is not HCP. This contrasts with NaCl where the arrangement of is Cl - FCC and the arrangement of Na + is also FCC.

Zinc Blende

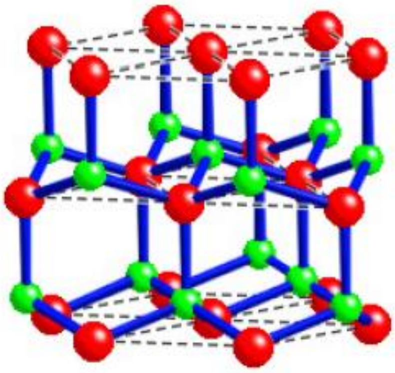
FCC (or CCP) arrangement of sulfide anions with Zn 2+ in half the tetrahedral holes.



Note that if all the centres were identical, the structure would be the same as diamond.

Wurtzite

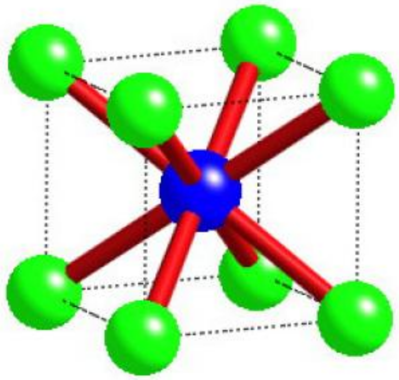
HCP arrangement of S ions with Zn ions in half the tetrahedral holes.



If all the centres were identical, the structure would be the same as Lonsdaleite.

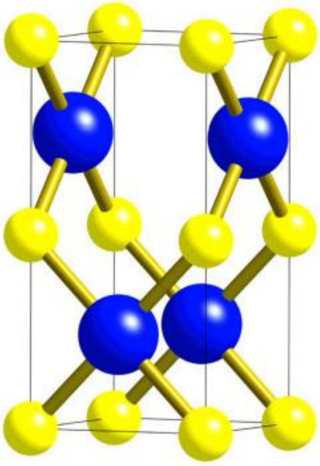
Cesium Chloride

Primitive cubic arrangement of chloride anions with cesium ions in cubic sites.



Platinum Sulfide

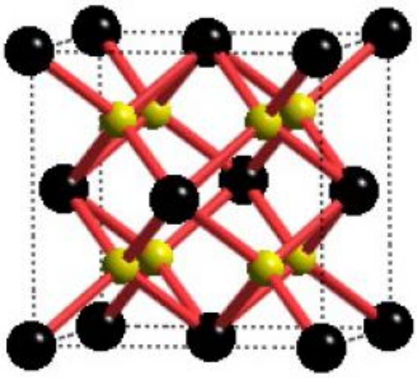
The Pt centre is in a square planar environment, while the sulfide ion is in a tetrahedral environment. S – yellow Pt - blue



AX2 Solids

Fluorite Structure

FCC arrangement of calcium centers with all the tetrahedral sites occupied by fluorides.

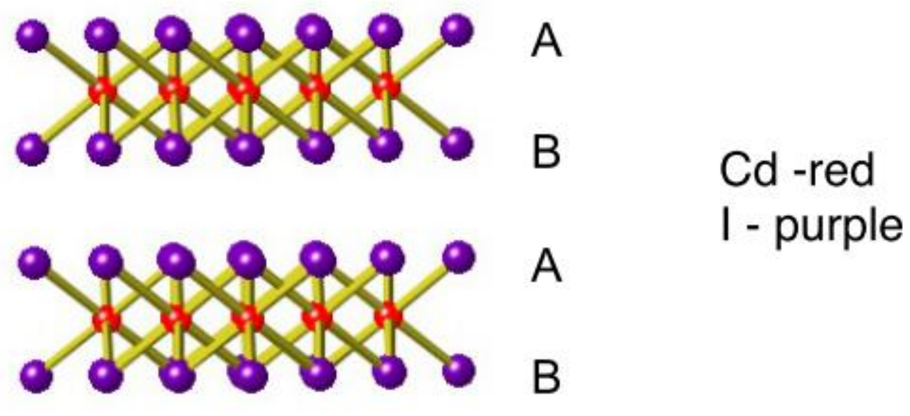


Anti-Fluorite Structure

The anti-fluorite structure is geometrically the same as fluorite but now the anions (-2) make the FCC lattice and the cations (+1) occupy all the tetrahedral holes.

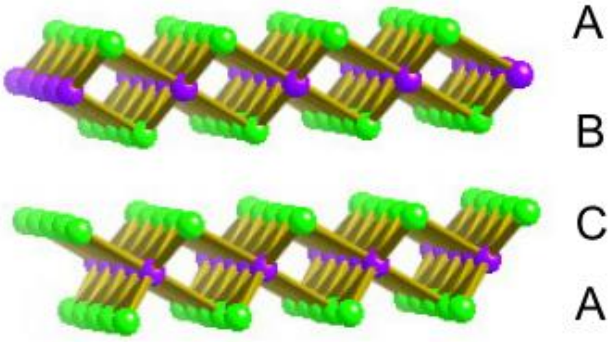
CdI2 Structure

HCP arrangement of I- ions with half the octahedral holes occupied by Cd2+ centers. Alternate sheets of octahedral holes are fully occupied and fully unoccupied.



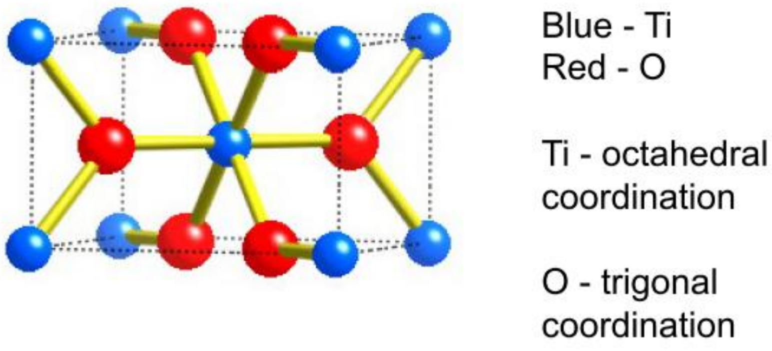
CdCl2 Structure

CCP arrangement of chloride anions with 1/2 the octahedral sites filled with Cd ions.



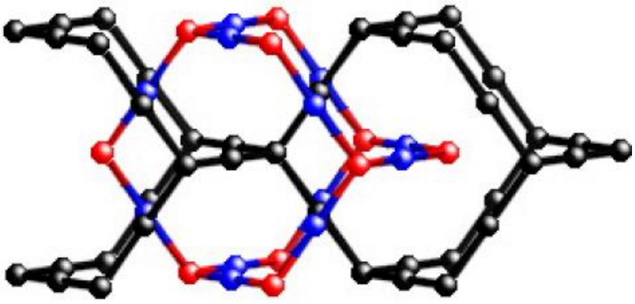
Rutile TiO2

Rutile has a body-centred tetragonal unit cell, with half the octahedral holes occupied by titanium.



Cuprite Cu2O

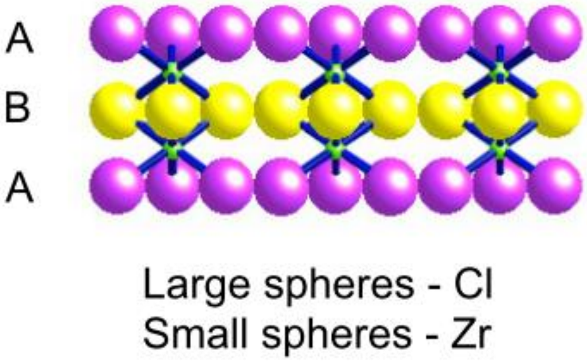
A diamond-like network is thereby generated with tetrahedral oxygen nodes connected together by linear O-Cu-O “ rods ”. The increase in rod length leaves cavities so large that a second identical BUT INDEPENDENT diamond type network can interpenetrate the first.



AX3 Solids

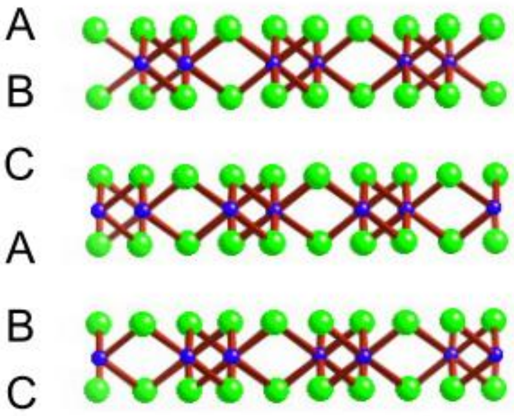
β-ZrCl3 Structure

HCP arrangement of Cl ions with Zr ions occupying 1/3 of octahedral sites in between any pair of chloride layers.



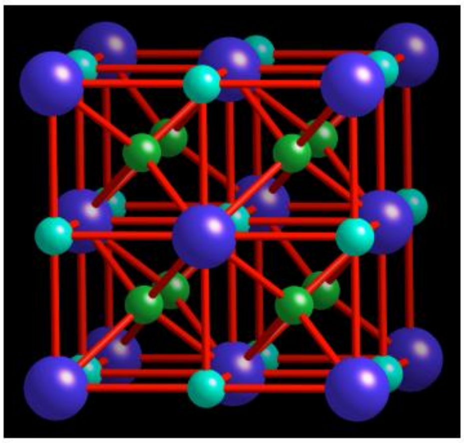
CrCl3 and BiI3 Structures

Same as above, but one layer of octahedral holes is 2/3 filled and the next layer of octahedral holes is completely empty and so on.



Li3Bi Structure

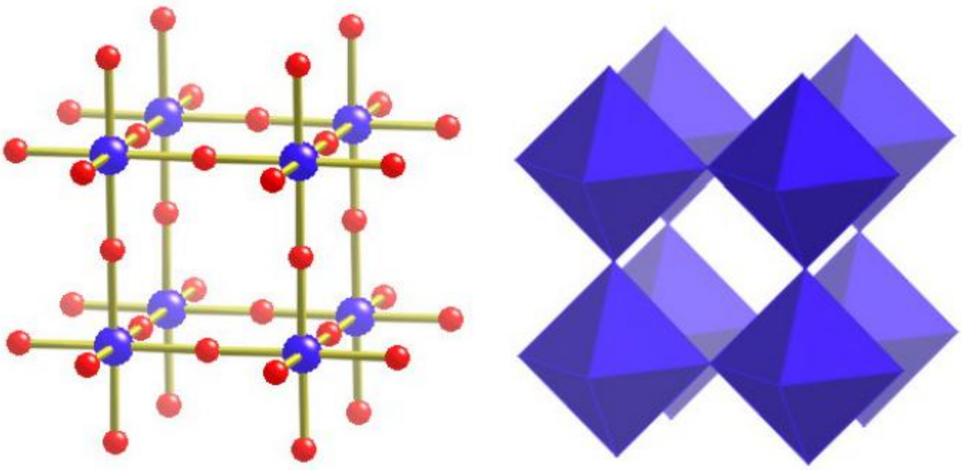
FCC arrangement of Bi atoms with Li atoms occupying all the octahedral and all the tetrahedral sites.



Other Structures

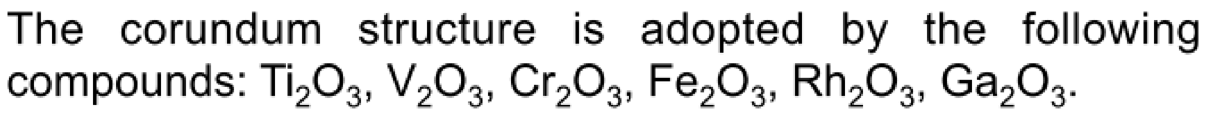
ReO3 Structure

Can be considered as a 3D structure formed by corner sharing of ReO6 octahedra.

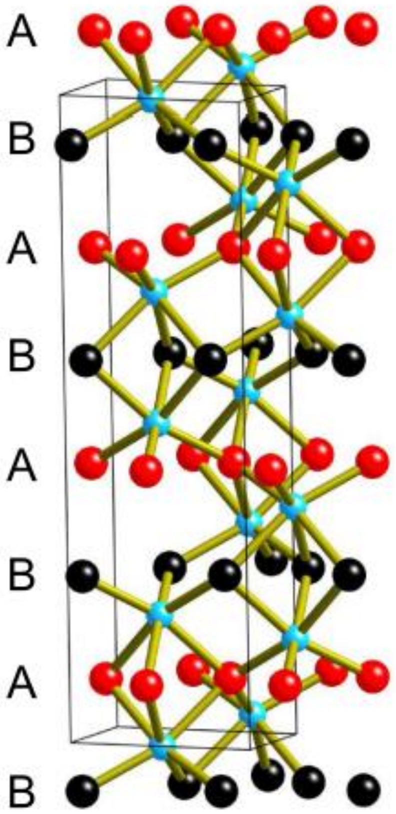


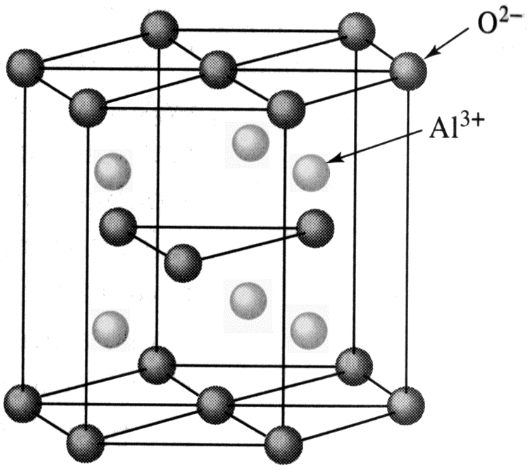
Aluminium Oxide - Al2O3

The structure may be considered as a HCP arrangement of oxide ions with A 3+ ions occupying 2/3 of the octahedral holes. Note that the Al3+ ions do not all lie in the same plane between oxide sheets.



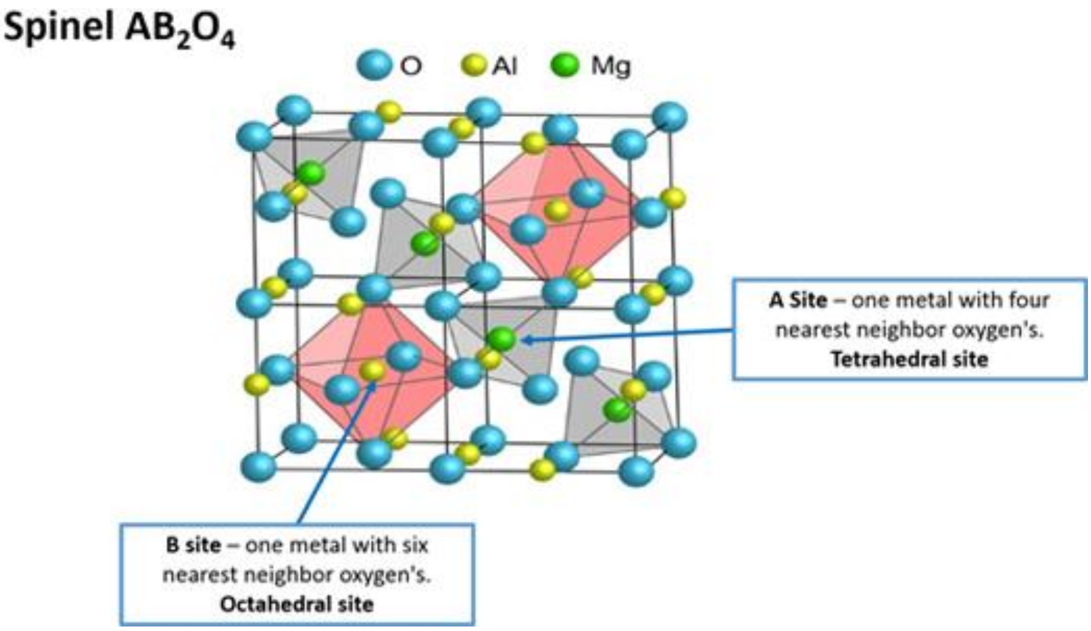
The corundum structure is adopted by the following compounds: Ti_2O_3, V_2O_3, Cr_2O_3, Fe_2O_3, Rh_2O_3, Ga_2O_3.





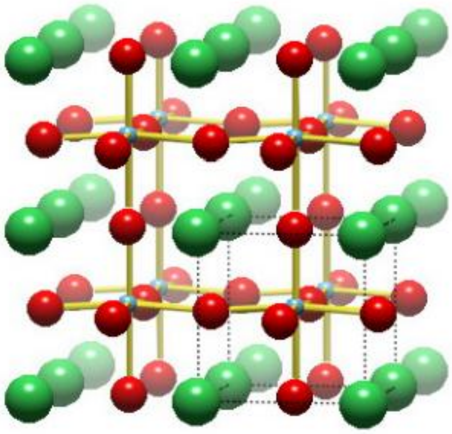
Spinels

Spinels are a large group of minerals with the general formula AB2X4 . Generally “X” is oxide and metals “A” and “B” are +2 and +3 ions respectively. The structure may be considered as a CCP arrangement of oxide ions with 1/2 the octahedral sites occupied by the B3+ ions and 1/8 of the tetrahedral sites occupied by the A2+ ions.



Perovskites

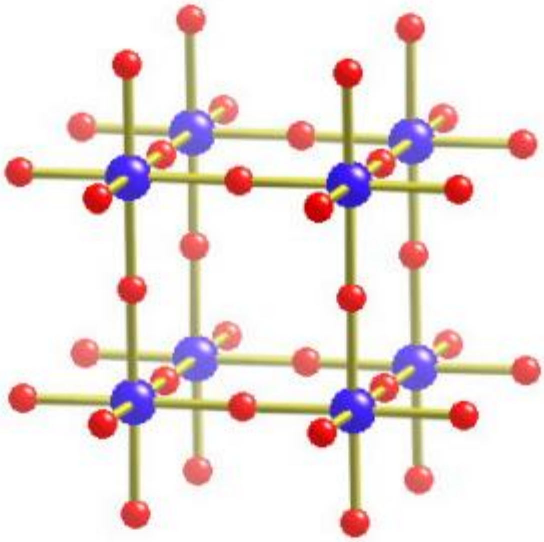
The perovskite ($CaTiO_3$) structure is closely related to that of ReO_3. The difference is that the large Ba^{2+} ion expands the lattice to a state where the Ti^{4+} ion is too small for its octahedral interstice. This leads to ferroelectric and piezoelectric properties with important applications in capacitorsand transducers in devices such as microphones. In piezoelectric materials a mechanical stress can result in the generation of an electric field (develops charges on opposite faces of the crystal).



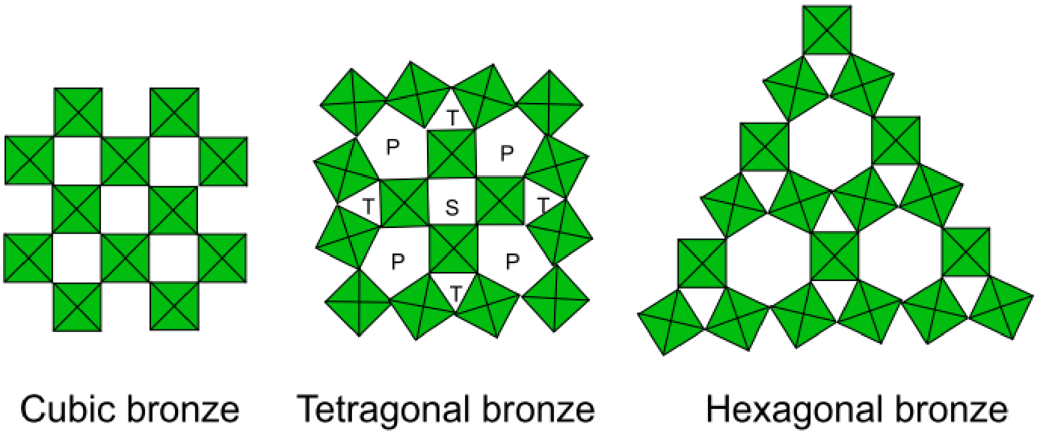
Ball and stick $BaTiO_3$
Ba - green; O - red; Ti - blue

Tungsten Bronzes

The tungsten bronzes are a group of compounds made up of tungsten trioxide, WO_3, and an alkali metal, such as sodium (Na) , potassium (K), rubidium (Rb) , or cesium (Cs). The general chemical form is M_xWO_3. They are not related to bronze except in colouration. Other metal ions (group 1 and 2 and f-block) may also be included into the WO_3 network if some of the W(VI) is reduced to W(V).



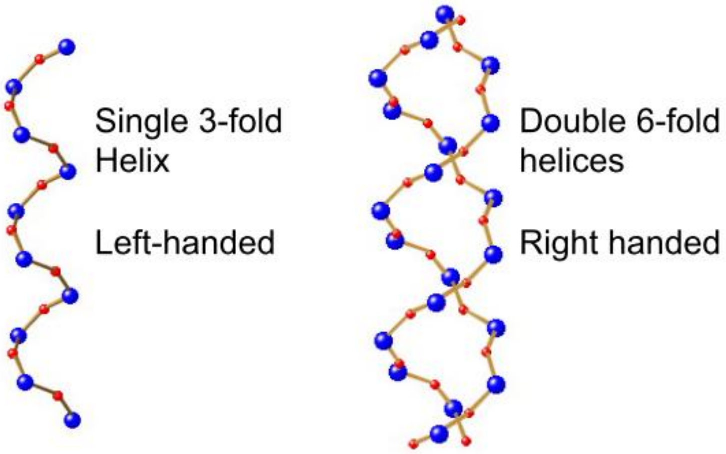
The preceding structure is a perovskite (cubic) bronze. It is also possible to have tetragonal and hexagonal bronzes.



Silicates

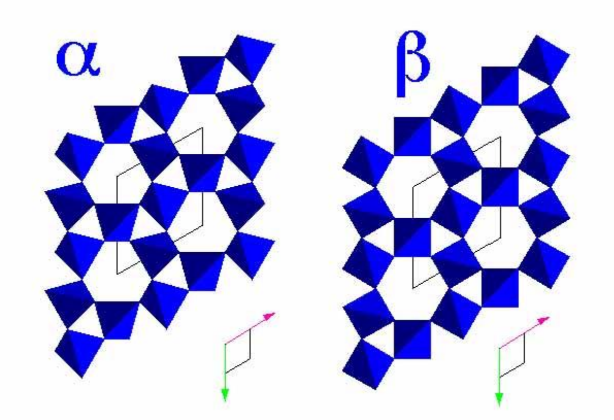
Alpha-Quartz

Thermodynamically the most stable form of silica at room temperature is α-quartz. Both enantiomeric forms of quartz crystals exist.



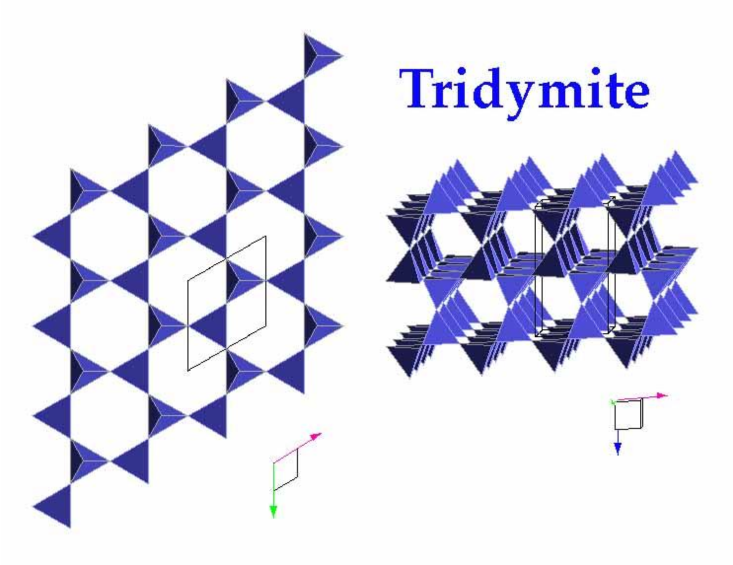
Beta-Quartz

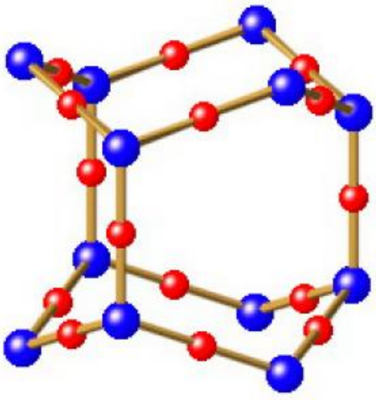
At 573 °C α-quartz transforms to β-quartz. This has same general structure but more linear Si-O-Si connections.



Tridymite

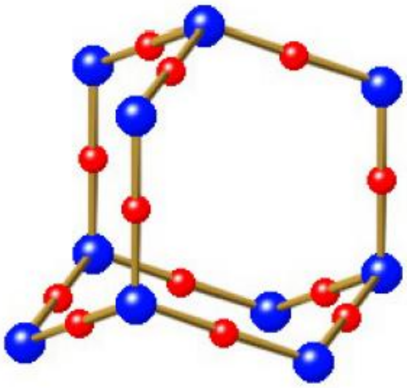
At 867°C β -quartz is transformed into β-tridymite. This process requires breaking and reforming Si-O bonds.

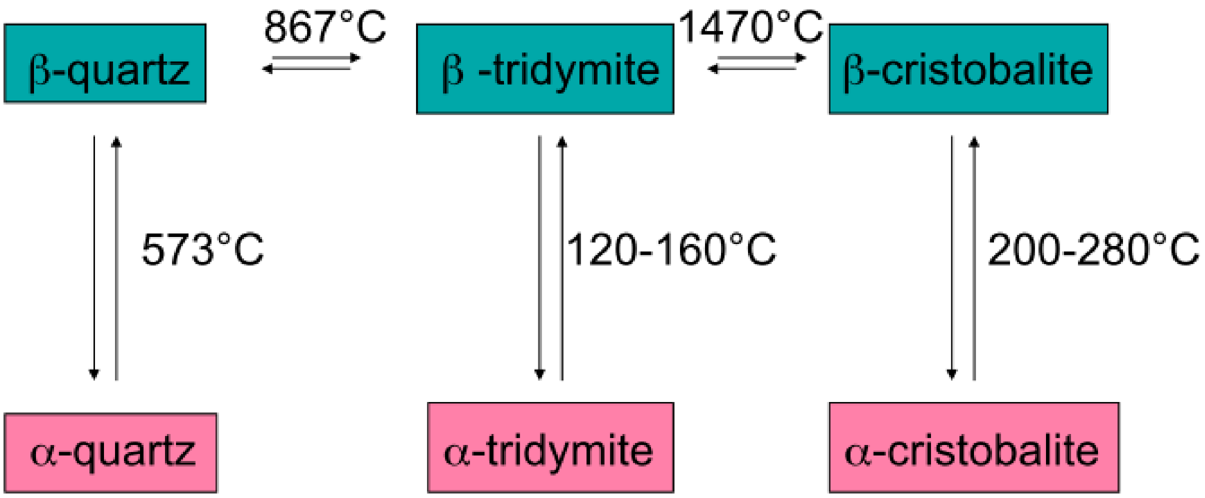




Cristobalite

At 1470°C β -tridymite is transformed into β-cristobalite. Cristabolite has a structure that may be related to diamond.





Aluminosilicates

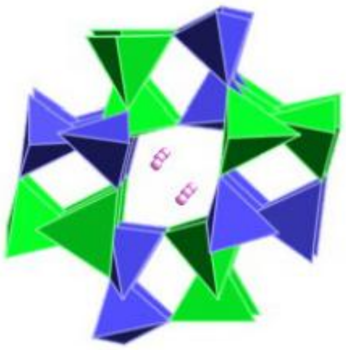
When Al atoms replace some Si atoms in infinite SiO2 structures, aluminosilicate minerals result - feldspars, zeolites and sodalites. The 3D framework is now negatively charged and cations are required for electrical neutrality.

Feldspars

Feldspars are the most abundant of all minerals, comprising 60% of Earth's crust.

Most feldspars can be classified chemically as members of the ternary system:
$NaAlSi_3O_8$ - $KAlSi_3O_8$ - $CaAl_2Si_2O_8$

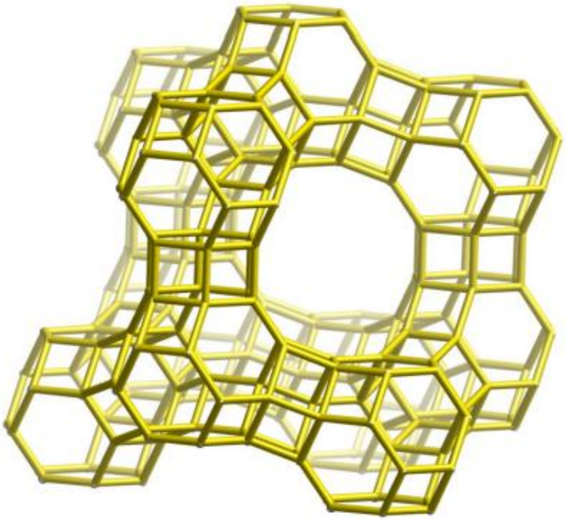
Polyhedron



AlO_4 green, SiO_4 blue
Ca purple

Zeolites

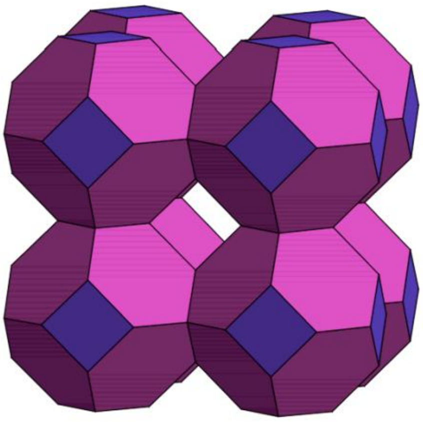
Zeolites possess a much more open framework than feldspars. They can take up small molecules such as water in their structure. Zeolites possess large open channels or systems of interconnected cavities. The great interest in zeolites arises mainly from their molecular sieving properties and their ability to function as very effective microporous heterogeneous catalysts. In faujasite, the truncated octahedra are linked by hexagonal prisms.



Faujasite $NaCa_{0.5}(Al_2Si_5O_{14}).10.H_2O$

Sodalites

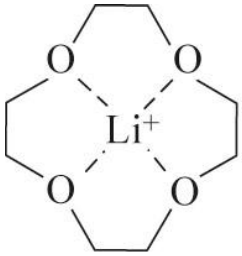
Similar to zeolites except that the truncated octahedral are completely space-filling, so no micropores are present.

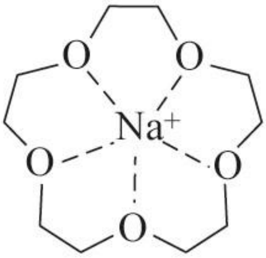


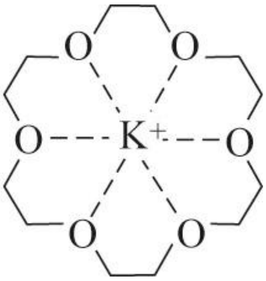
Cation Binding Systems

Crown Ether Ligands

A relationship exists between cavity size, cationic radius and stability of the resulting complex - the better the fit of the cation into the crown ether, the stronger the complex.

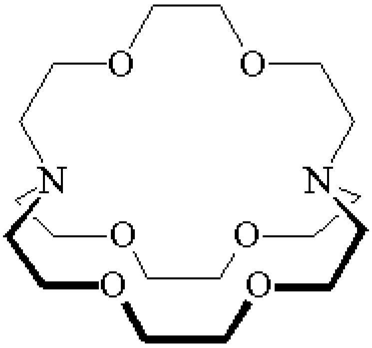






Cryptands

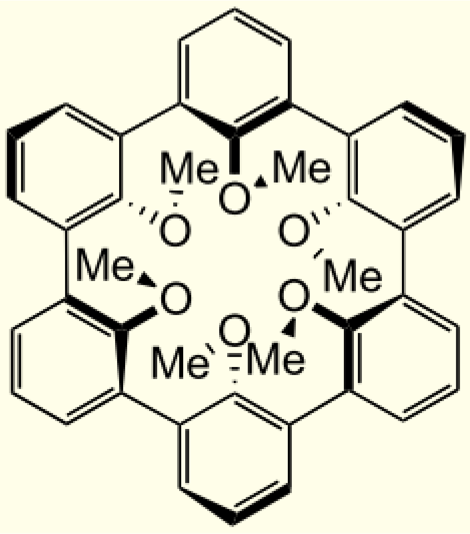
Cryptand complexes are several orders of magnitude more stable than those of crowns, and show big differences in preference even for small differences in cation size. The term cryptand implies that this ligand binds substrates in a crypt, interring the guest as in a burial.



2,2,2-crypt

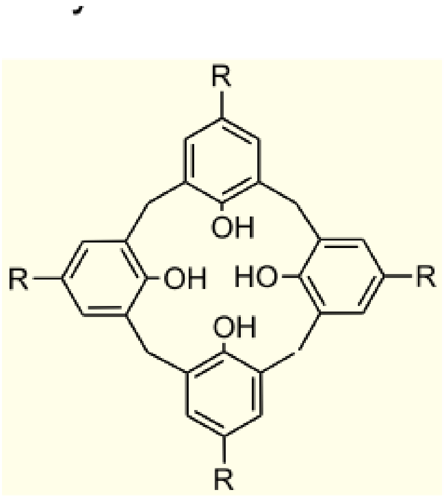
Spherands

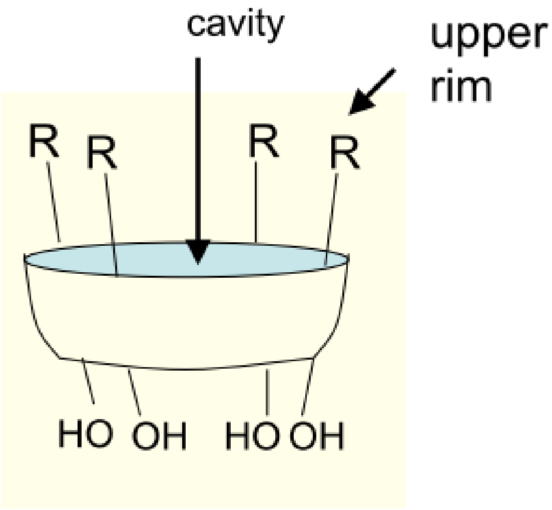
Designed to be a ligand with an enforced spherical cavity



Calixarenes

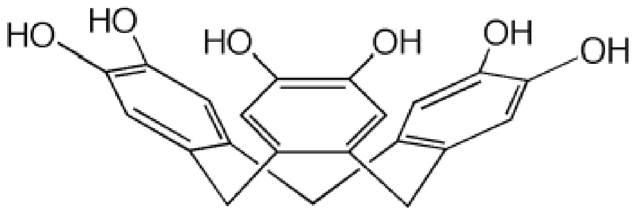
Synthetic macrocyclic receptors with cyclic arrays of n-phenol moieties linked by methylene groups. Can serve as a model for potassium channel proteins.

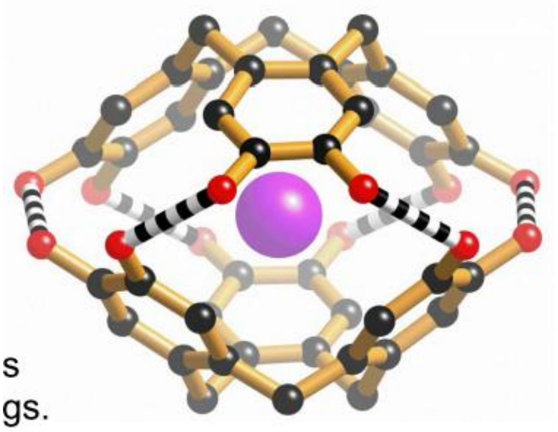




Clams

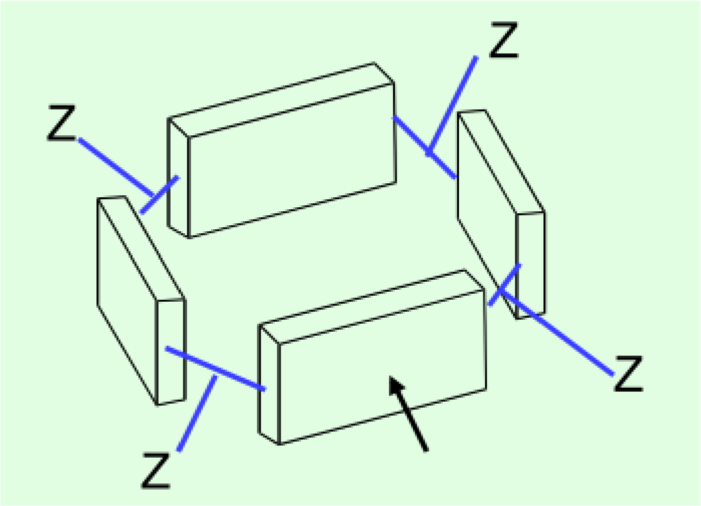
Deprotonate to form a closed cage-like structure around cations like Cs+ and Rb+, which interact only with the aromatic rings. Smaller cations are too small to promote such a cage. Larger cations still can yield partially open cages.

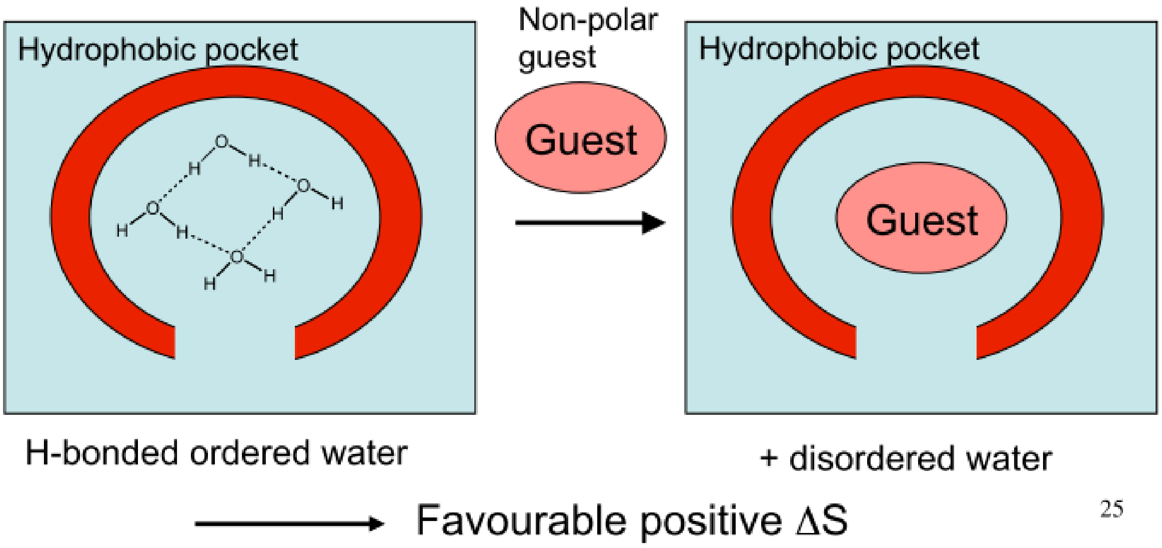




Cyclophanes

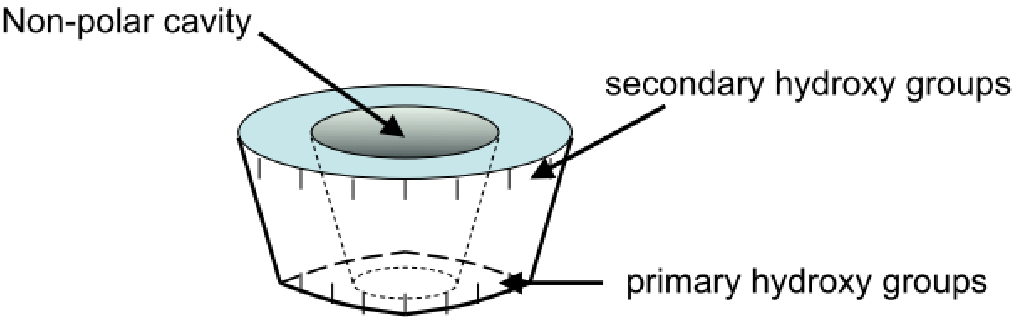
Macrocycles containing aromatic units generally oriented "face-on" to the cavity. Take advantage of the hydrophobic effect with Polar side chains (Z).

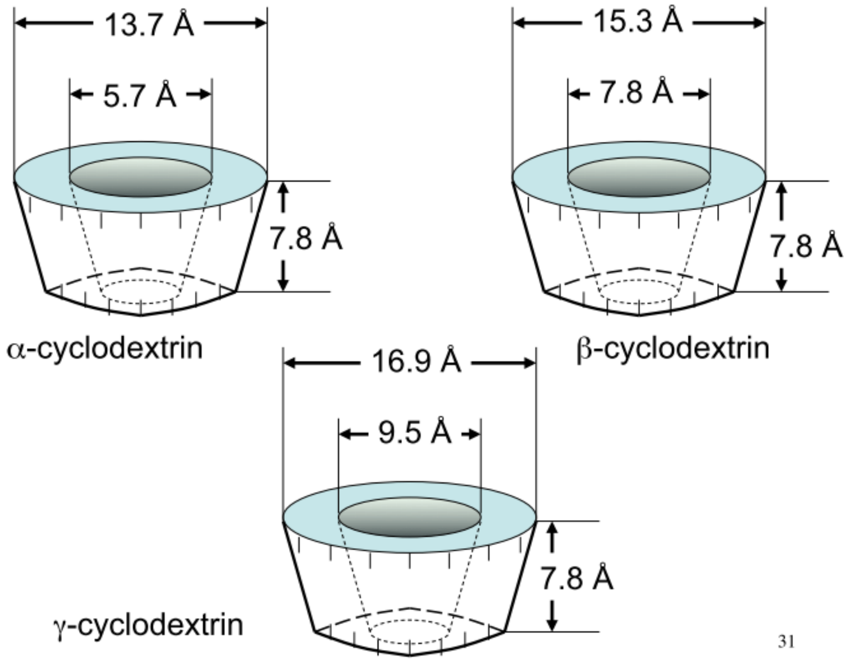




Cyclodextrins

Cyclodextrins are naturally occurring macrocycles composed of sugar units. A non-polar guest molecule can reside in the central cavity.

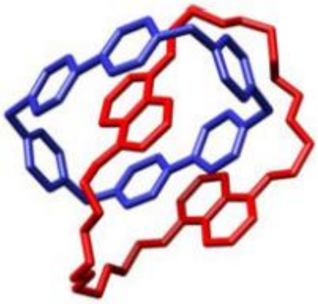


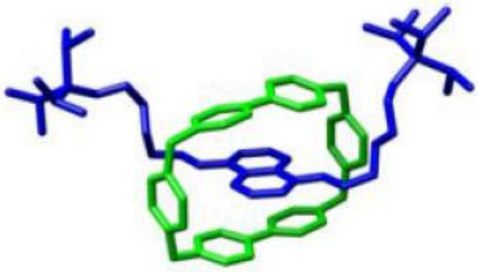


Catenanes and Rotaxanes

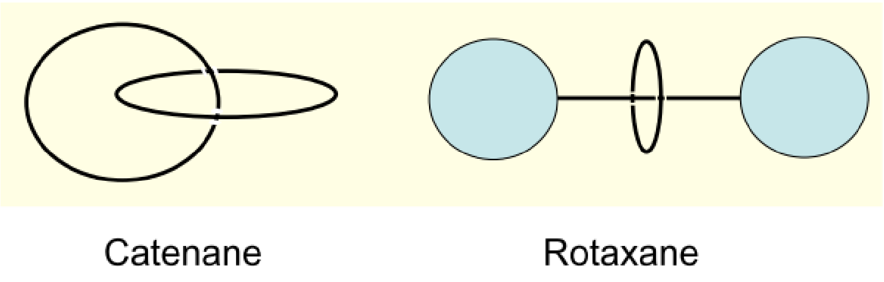
Overview

Synthesis of molecular units which are interlinked but not covalently bound represents a special challenge for supramolecular chemists. A catenane is a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles.



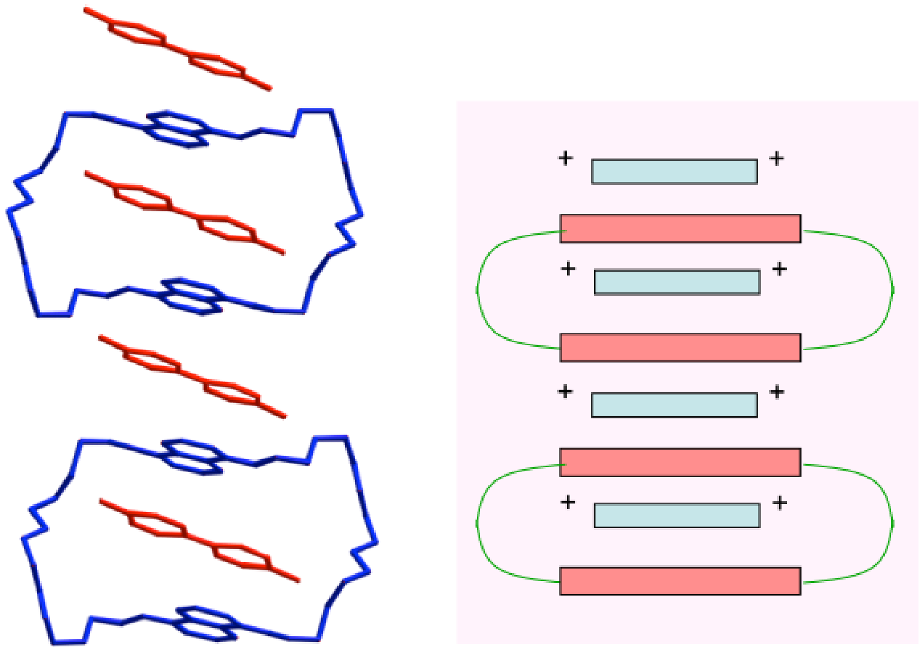


A rotaxane is a mechanically interlocked molecular architecture consisting of a "dumbbell shaped molecule" which is threaded through a macrocycle. The two components of a rotaxane are kinetically trapped since the ends of the dumbbell are larger than the internal diameter of the ring and prevent dissociation of the components since this would require significant distortion of the covalent bonds.



Paraquat Approach

Inspired by stacks of the Paraquat- BPP34C10 complex



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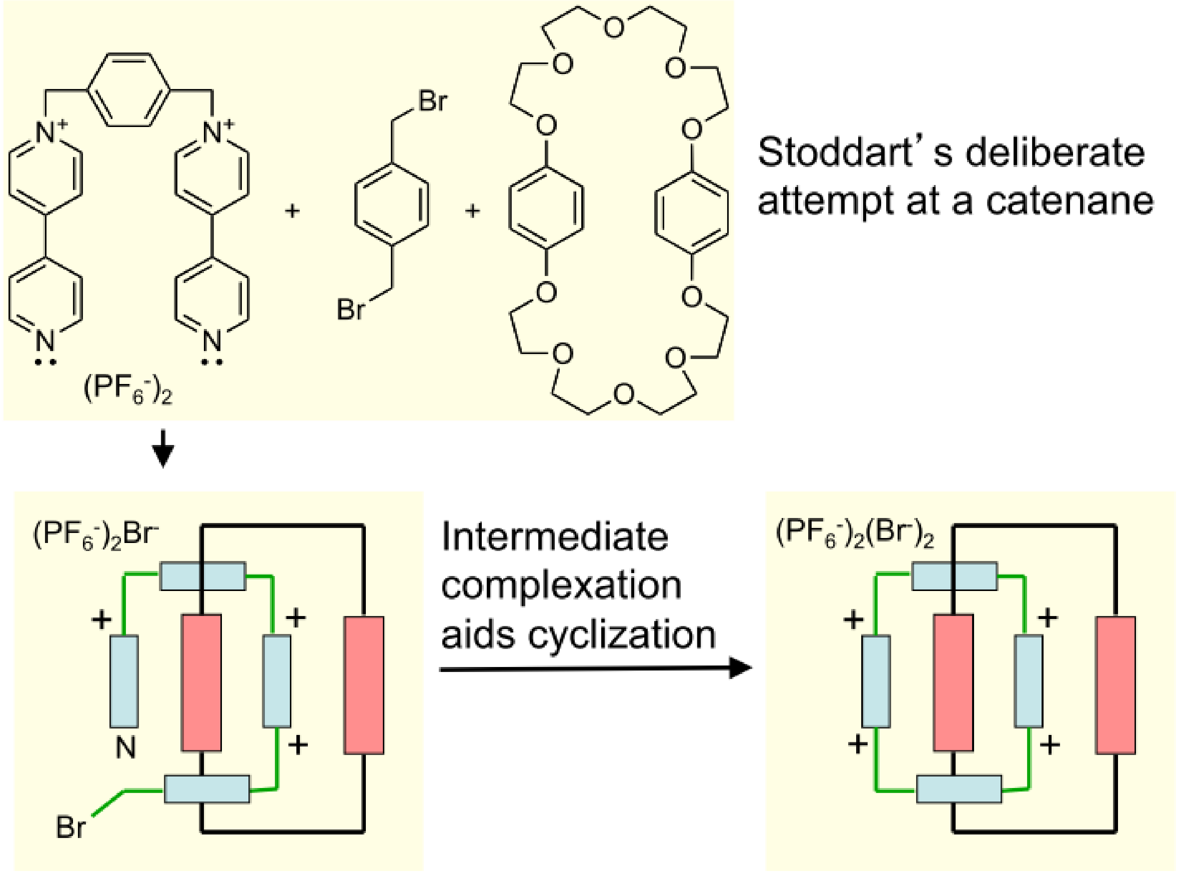
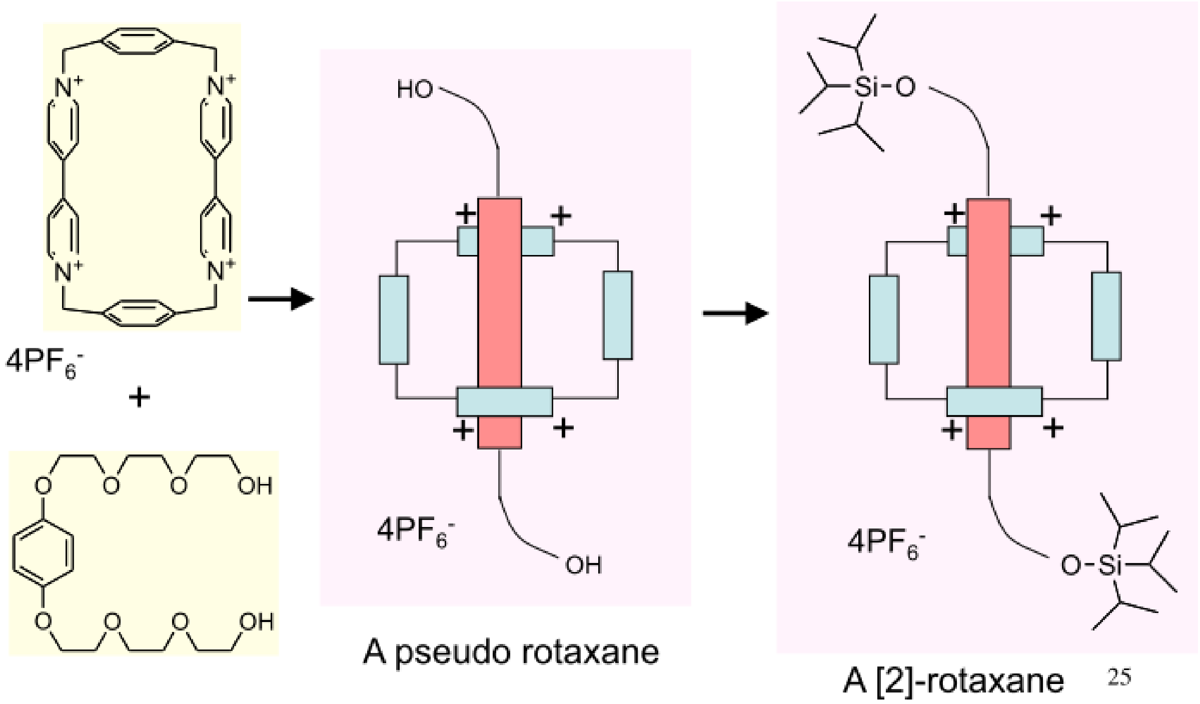
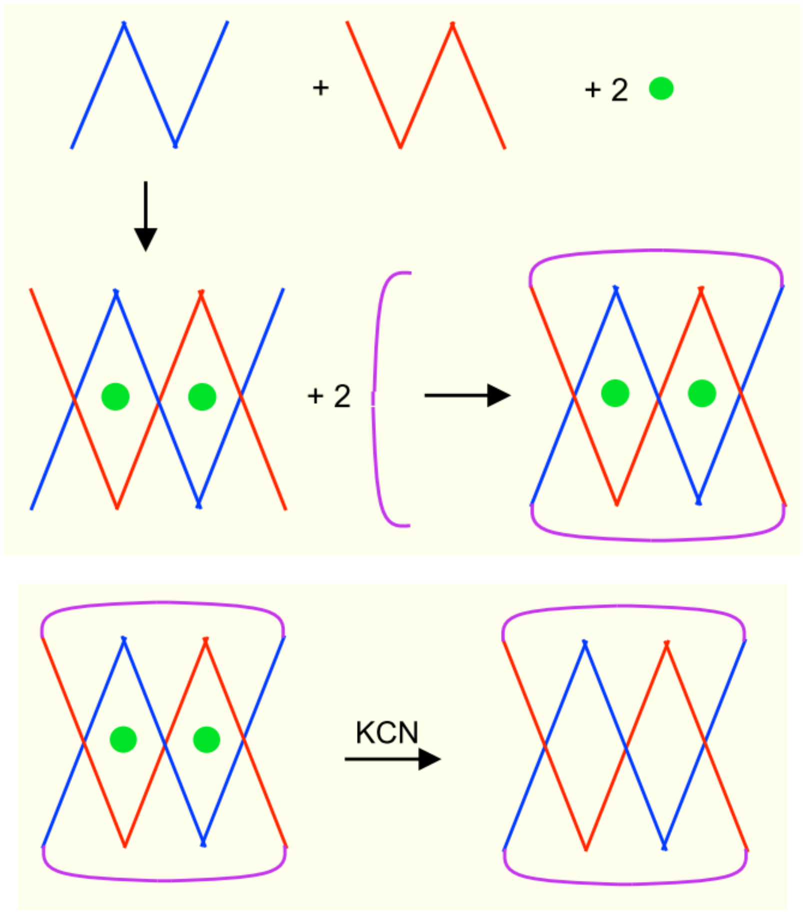
Stoddart devised a deliberate attempt to produce a catenane

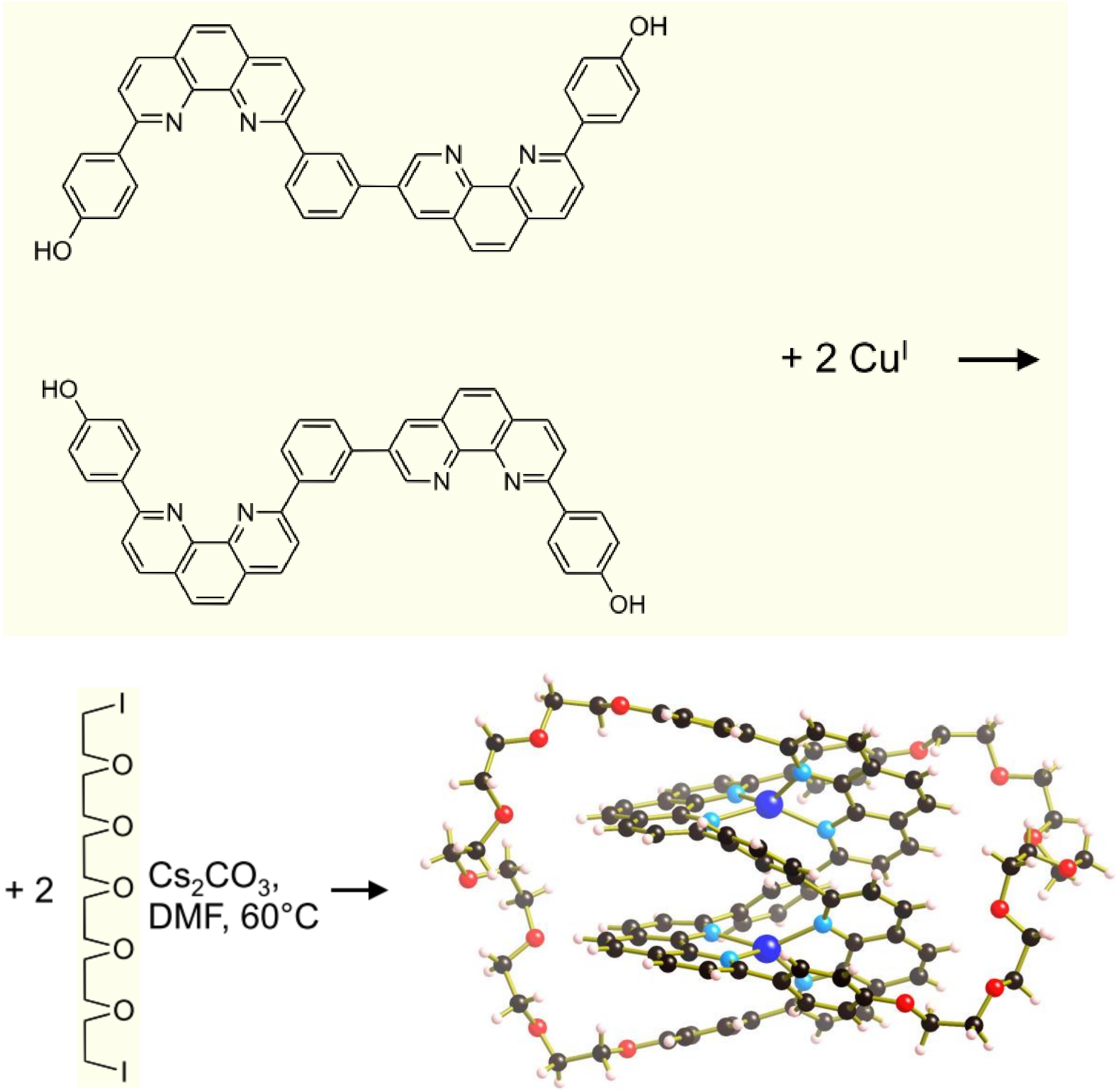


Threading Approach to Rotaxanes



Trefoil Knot

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Cs$_2$CO$_3$,
DMF, 60°C

- Rock Salt
- Diamond
- Londsdalite
- Cuprite
- Zinc Blende
- Wurtzite
- Fluorite
- Corundum
- CdCl2
- CdI2
- CsCl
- Rutile
- PtS
- ReO3
- Spinel
- Tungsten Bronze
- Perovskites
- Feldspar
- Zeolites
- Sodalites
- Quartz
- Tridymite
- Cristobalite
- Crown Ether
- Cryptands
- Spherands
- Calixarenes
- Clams
- Cyclophanes
- Cyclodextrins