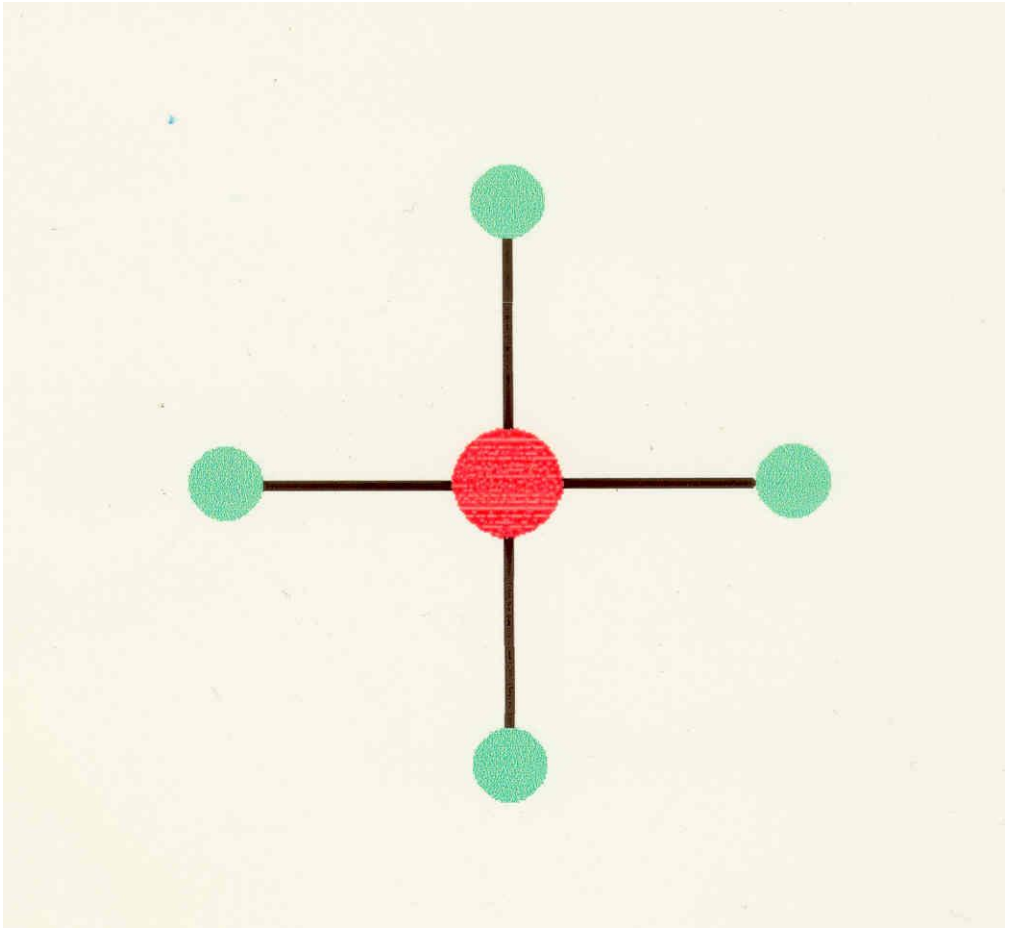
From Point Groups to Space Groups

- How to expand from a point group to a space group
- Special and General Positions.
- Complete Hermann-Maugin Notation

HOMEWORK

- **Why do biological macromolecules often crystallize in space groups of higher symmetry than small molecules?**
- **How many different isomers could exist for (a) $[en_2CoCl_2]^+$ and (b) $[en_2Co(\mu Cl)_2Coen_2]^{4+}$ (*en = ethylene diamine*, can bridge only *cis*-positions), what are their point groups (in both systems), and which of them are *optically active*? How could racemates containing such ions be resolved into optically pure components?**
- **Which symmetry elements are present in the following, and to which point groups (in both systems) should they be assigned: (a) S_8, (b) ferrocene $(C_5H_5)_2Fe$, rings parallel and eclipsed, (c) ferrocene, staggered?**

Start with $PtCl_4^{2-}$

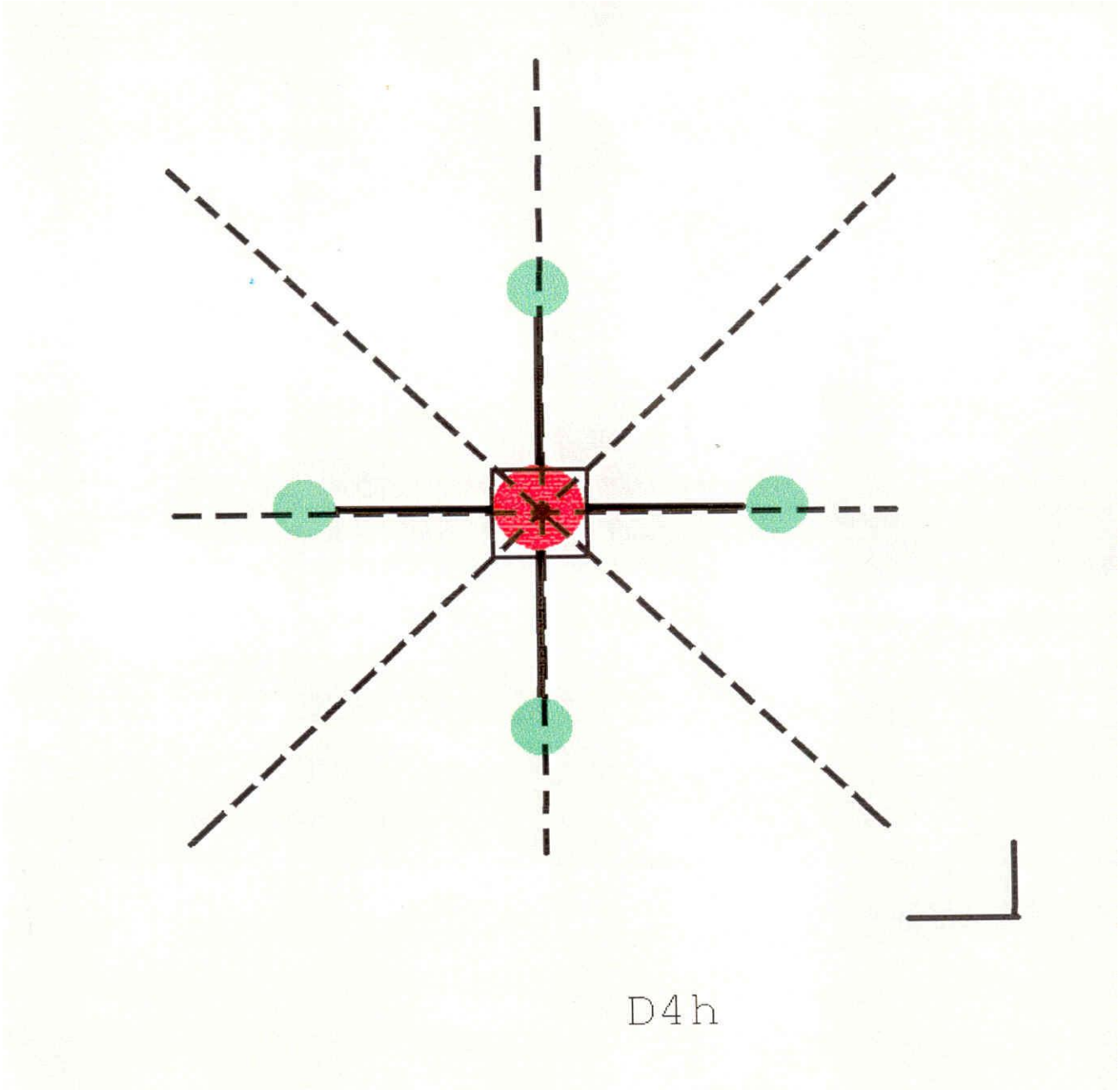


D4h Character Table

Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Add Unique Symmetry



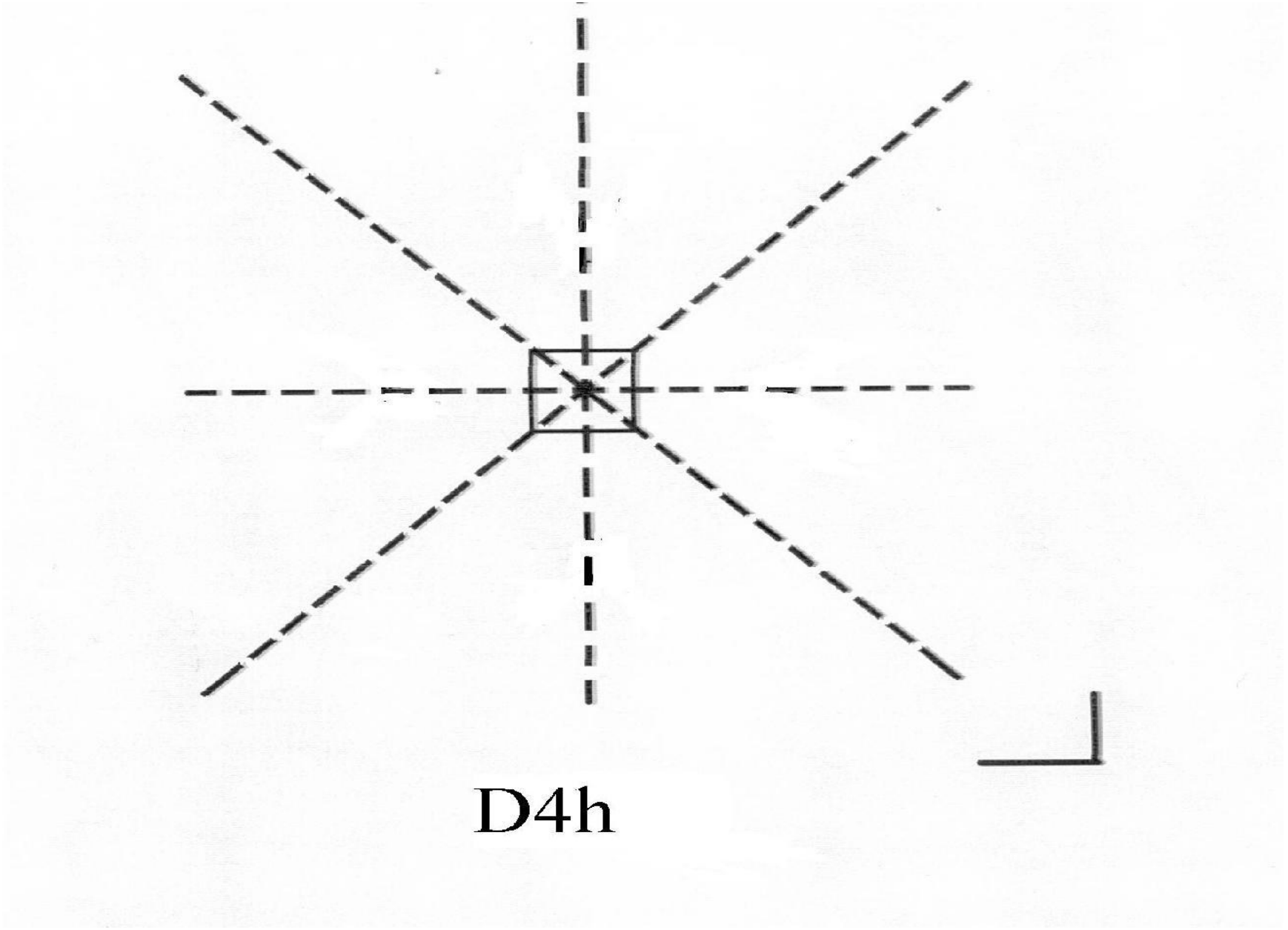
The Features

- The view is looking down the 4-fold axis
- The square in the mirror represents the 4-fold axis
- The bracket in the lower right corner is the horizontal mirror
- The dashed lines are out of plane mirror planes
- Anything that can be placed on this template has at least D4h symmetry

Comments on D4h

- There are 16 symmetry operations
- The two-fold rotations perpendicular to the 4-fold are generated by the mirrors.
- The 4-fold and the horizontal mirror are unique
- The H-M name is 4/mmm

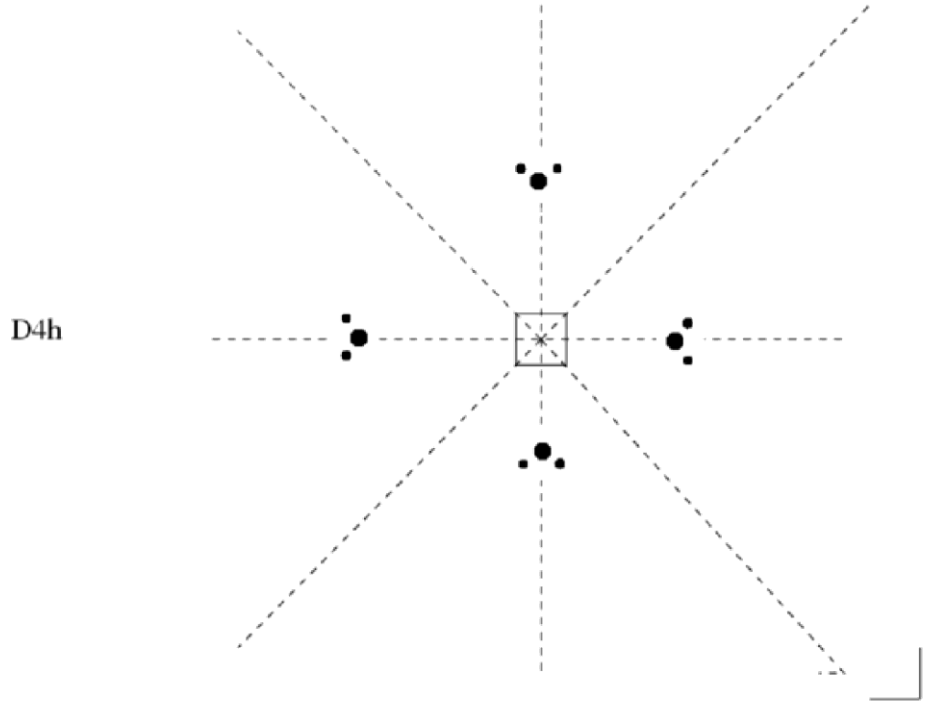
Getting Rid of $PtCl_4$



Question

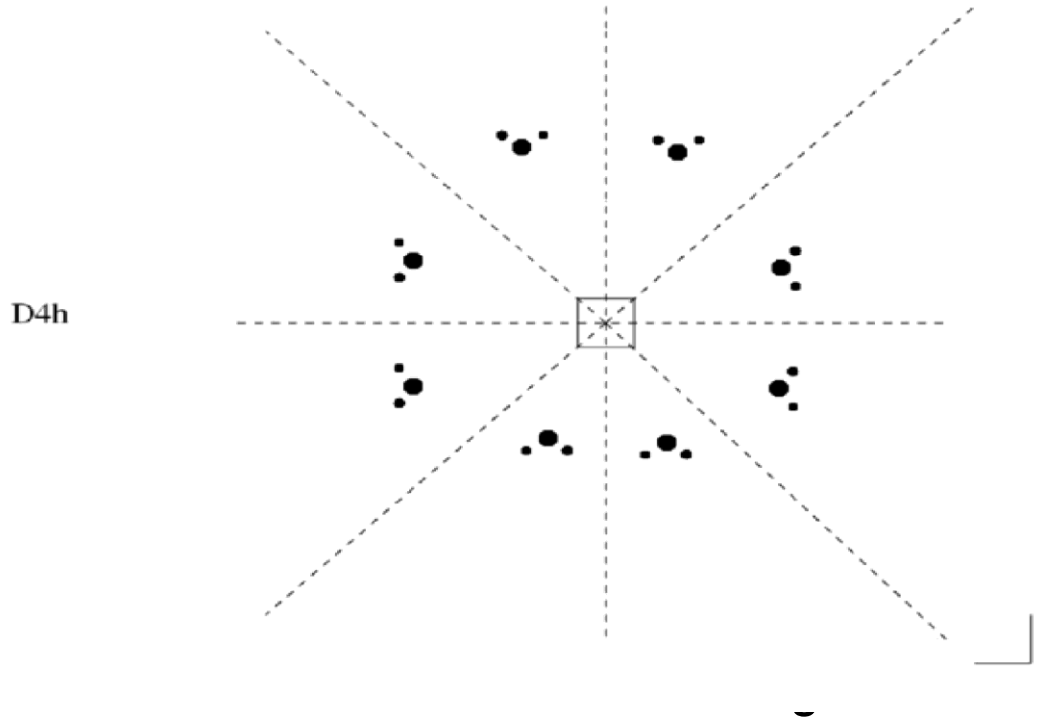
- Is it possible to place water into the D4h pattern?
- Water has C2v symmetry which is very much lower than D4h so at first the answer would appear to be NO.

4 Waters in 4/mmm



In this packing the 2 of the water aligns with the 2 of the 4/mmm and the two mirrors align with the horizontal and vertical mirrors! When the space group and molecule share one or more symmetry elements the molecule is sitting on a special position!

8 Waters in 4/mmm



The 2-fold and other mirror are not duplicated by the crystal symmetry.
In this case the two hydrogen atoms are not symmetry related
The water can be rotated by 90º in which case there would only be one unique hydrogen atom
The molecule still resides on a special position

In General

- It is possible to place items with any or no symmetry in 4/mmm.
- Place 8 above and 8 below the horizontal mirror plane.
- Therefore there are 16 objects in the pattern
- Note D4h has 16 symmetry operations
- When an object is placed so it shares no symmetry elements of the space group it it is said to be located on a general position.

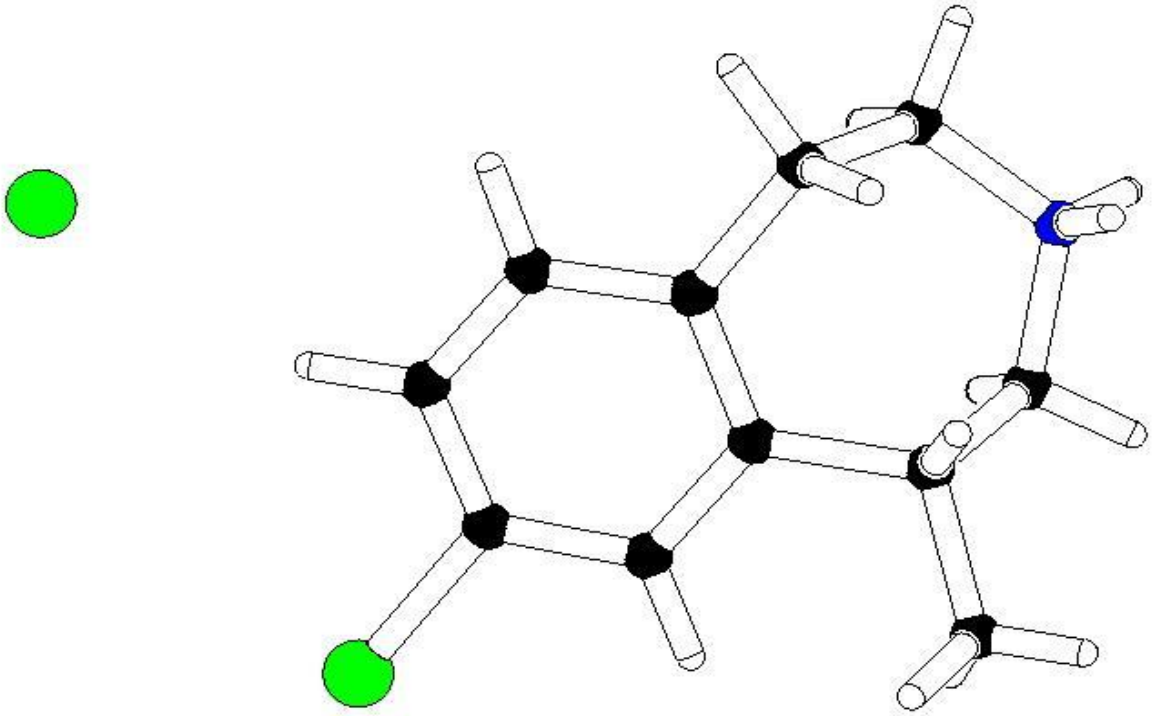
The Crystallographic Symmetry

- The crystallographic symmetry of fragment(that is a molecule, ion, etc.) is the symmetry of the site it occupies.
- A fragment located on a general position has no crystallographic symmetry in the crystal even if it appears to be quite symmetric.
- A fragment on a special position has whatever the symmetry of the position is.

Fragment vs Crystal Symmetry

- There is no correlation between the symmetry of a molecule and the cell it crystallizes in.
- Very symmetric molecules crystallize in low symmetry cells.
- Very asymmetric molecules can crystallize in surprisingly high symmetry cells

An Example



Crystallizes in a tetragonal space group!

Some Definitions

- Asymmetric Unit – A unique part of the unit cell. When the symmetry operations are applied to the asymmetric unit the entire unit cell is created. The volume of the asymmetric unit is the volume of the unit cell divided by the number of symmetry operations (NSO)
- Z—the number of formula units in the unit cell.
- Z'—the number of formula units in the asymmetric unit = Z/NSO

- Z must be an integer
- Z' can range from fractional to values > 1
- Whenever Z' is non-integral it means that a fragment is located on a special position.
- Whenever Z' is greater than 1 it means there is more than one independent fragment in the asymmetric unit.

Lets look at this.

- The International Tables for Crystallography can be found on-line as follows (note this only works from Purdue computers as the library pays for on-line access)
  - Log on to http://www.iucr.org/
  - At the right click on the International Tables
  - Click on Volume A which deals with symmetry
  - Go to space group P4/mmm (no. 123)
- Note space groups are like German Symphonies –they have a name and number/

Crystallographic Coordinates

- The coordinate system used to define the unit cell will always have the symmetry of the cell.
- This requires that under any symmetry operation in the cell the axes go into themselves or an equivalent axes.
- This is not true for Cartesian coordinates where there is a 3-fold or 6-fold rotation axis.

For a 3-fold Axes

- For this to work there must be 3 equivalent axes perpendicular to the 3-fold rotation.
- Obviously it does not take 4 axes to define 3 dimensional space so one must be defined by the other two.
- This is where the 4 indices hkil come from where i=-(h+k)

Hexangonal Axes

Part 6: The Hexagonal System

Now we will consider the only crystal system that has 4 crystallographic axes! You will find that the Miller indices should actually be termed Bravais indices, but most people, probably out of habit, still call them Miller indices. Because there are 4 axes, there are 4 letters or numbers in the notation.

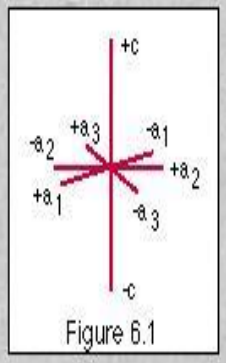


Figure 6.1

The forms of the **hexagonal system** are defined by the axial cross relationships. The hexagonal axes (fig. 6.1) consist of 4 axes, 3 of which are of equal length and in the same plane, as proposed by Bravais. These 3 axes, labeled a1, a2, and a3 have an angular relationship to each other of 120 degrees (between the + ends). At right angle (geometrical mathematicians say "normal") to the plane of the a axes is the c axis. Its length may vary from less than to greater than the length of any of the a axes. It will not equal the length of an a axis, however.

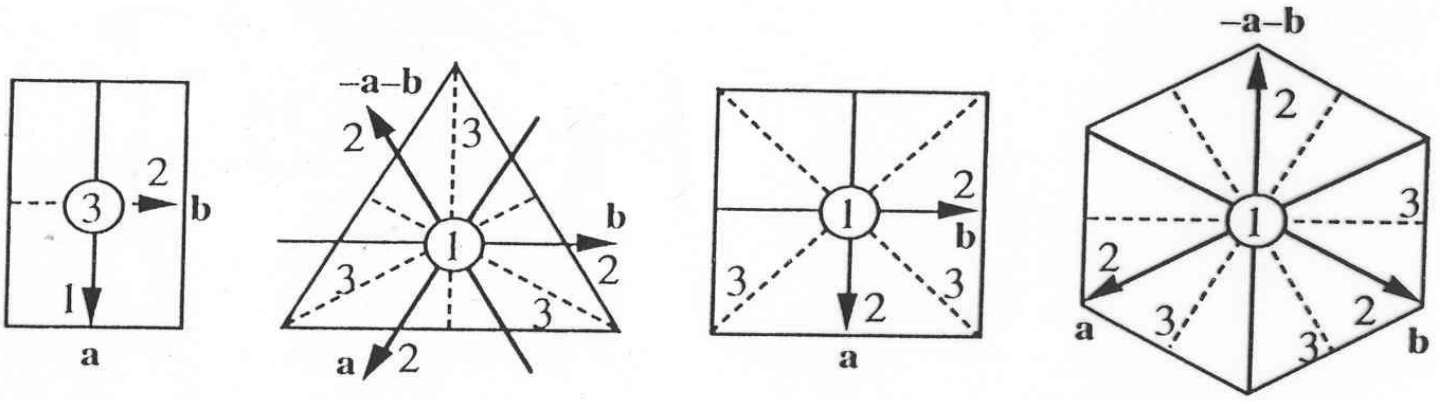
Note the orientation of the 4 axes and their + and - ends. If viewed vertically (down the c axis), the axes divide a circle into 6 equal parts and the axial notation reads (starting with a +) as +,-,+,-,+,-. The positive and negative ends alternating. In stating the indices of any face, four numbers (the Bravais symbol) must be given. In the Hermann-Mauguin symmetry notation, the first number refers to the principal axis of symmetry, which is coincident with c in this case. The second and third symbols, if present, refer to the symmetry elements parallel with and normal to the a1, a2, a3 crystallographic axes, respectively.

Now, surprise!! We find that the Hexagonal system has two divisions, based on symmetry. There are seven possible classes, all having 6-fold symmetry, in the **Hexagonal division** and five possible classes, all having 3-fold symmetry, in the **Trigonal division**. The general symbol for any form in the Hexagonal system is (hk-il). The angular relation of the three horizontal axes (a1, a2, a3) shows that the algebraic sum of the indices h, k, i, is equal to 0.

Note a3=-(a1+a2)

Table 2.10. Order of the symbols for the symmetry elements which make up the symbol of a point group

System	1st place	2nd place	3rd place
triclinic	1 or $\bar{1}$		
monoclinic	**a**	**b**	**c**
orthorhombic	**a**	**b**	**c**
tetragonal	**c**	**a, b**	**a + b, a − b**
trigonal	**c**	**a, b, a + b**	**2a + b, a + 2b, −a + b**
hexagonal	**c**	**a, b, a + b**	**2a + b, a + 2b, −a + b**
	unique axis	sides of an n-gon	diagonals between sides
cubic	**a, b, c**	**a ± b ± c**	**a ± b, b ± c, c ± a**
	edges of the cube	four body diagonals	six face diagonals



orthorhombic trigonal tetragonal hexagonal

Fig. 2.23. Order of the symbols for the symmetry elements (to be compared with Fig. 2.16)

Tetragonal Symmetry

- P4/mmm
- The 4/m involves the c axis from the chart on the last slide. That is there is a 4-fold axis with a horizontal mirror.
- The second m denotes that the xz and yz planes are mirrors
- The last m denotes mirrors at 45° to the axes

Homework

Look at the Space Group P21/c (#14). This is the most common space group for small molecules.

1. No protein has ever been found to crystallize in this space group. Why is that?

2. Someone reports a crystal in P21/c with Z=1. Is this possible? Why or why not.

3. What is the symmetry of the special positions in this space group?