

Lesson 9

- Point Group Symmetry
- Hermann-Mauguin Notation

Homework

- Using the monoclinic cell calculate:
 - The reciprocal cell constants—lengths and angles
 - The angle between \mathbf{a} and \mathbf{a}^*
 - The angle theta for the (2,5,2) reflection.

$a=15.168$ $b=10.348$ $c=15.847$ $\alpha=90.0$
 $\beta=100.035$ and $\gamma=90.0$

$$V=abc(1-\cos^2\beta)^{1/2}=2449.39$$

$$b^*=1/b=0.096637$$

$$a^*=bc\sin(\alpha)/V=bc/V=0.066949$$

$$c^*=ab\sin(\gamma)/V=ab/V=0.064081$$

$$\alpha^*=\gamma^*=90^\circ \quad \cos(\beta^*)=-\cos(\beta)=0.174249 \quad \beta^*=79.965$$

$$a \cdot a^*=1=|a||a^*|\cos(\text{ang})=0.066949 \cdot 15.168 \cdot \cos(\text{ang})$$

) $\text{ang}=10.02^\circ$

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|

$$|d^*| = [h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^* b^* \cos(\delta) + 2hla^* c^* \cos(\beta) + 2klb^* c^* \cos(\alpha)]^{1/2} = 0.511704$$

– $\sin(\theta) = d^* \lambda / 2$

– $\sin(\theta) = 0.511704 \lambda / 2$ For Cu(1.54178) is 23.24°

– For Mo(0.71069) = 10.48°

Why the concern with symmetry

- The object in forming a unit cell is to pack items as efficiently as possible.
- First idea is to put one item in the “box”.
- This does not lead to efficient packing







- From the previous pictures it should be obvious that adding symmetry between objects improves the packing.
- The most common symmetry item is the inversion center.

An Acknowledgment

- We will be looking at George Sheldrick's Power Points from his course at the University of Göttingen, Germany.
- Dr. Sheldrick was kind enough to let me use them.
- George Sheldrick is one of the finest crystallographers in the world and the author of the SHELX program series that we will use later.

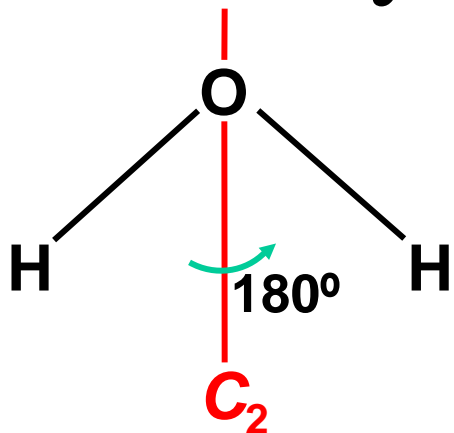
Symmetry and point groups

Although a couple of equations come in useful, the physical basics and mathematics of crystal structure determination are remarkably simple. The most difficult part is thinking in three dimensions and in particular symmetry.

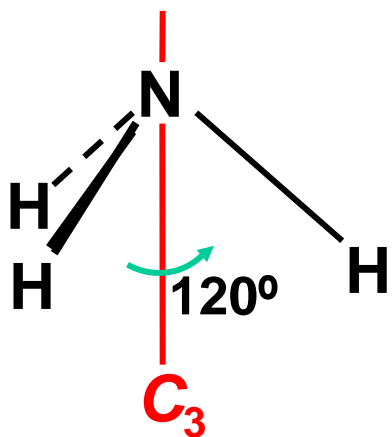
We will begin by looking at the symmetry of finite objects such as molecules and crystals. The symmetry of each finite object can be described by a self-consistent set of symmetry operations called a *point group*. These symmetry elements do indeed usually meet at a point in the middle of the object, but they can also meet in a line. Later in the course we will extend this to the symmetry of infinite periodic structures, which for our purposes means the 230 possible *space groups*.

Symmetry in its various manifestations pervades much of science. For example the biologically active unit of an enzyme complex or a virus shell often achieves efficiency with the help of surprisingly high symmetry.

Symmetry elements



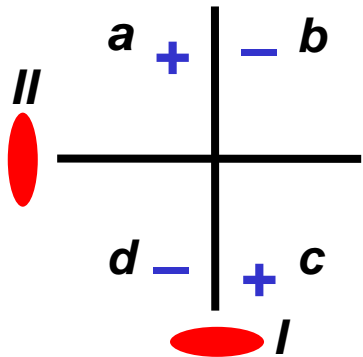
The molecule H₂O possesses a C₂ rotation axis along the angle bisector and two mirror planes that intersect each other along the rotation axis. The point group is called C_{2v} or 2mm. Each combination of two of these elements would generate the third.



The molecule NH₃ possesses a C₃ rotation axis and three mirror planes that intersect one another along the rotation axis. The point group is called C_{3v} or 3m.

Combination of symmetry elements

The combination of two symmetry elements always gives rise to a third, for example the combination of mirror plane and a twofold axis in the plane in C_{2v} creates another mirror plane perpendicular to the first (hence the alternative name $2mm$).



If there are two twofold axes I and II at right angles to one another, they create a third at right angles to both. The axis *I* transforms point *a* (the '+' means that it is above the plane of the drawing) to point *b*. The axis *II* transforms *b* to *c*, and it will be seen that *a* and *c* are related by a new twofold at right angles to both the other twofolds.

In a similar way, a twofold (or higher even symmetry axis, e.g. fourfold) at right angles to a mirror plane automatically generates a center of symmetry.

Schönflies and Hermann-Mauguin

The Schönflies system is mainly used by spectroscopists and the Hermann-Mauguin system mainly by crystallographers. Both systems have their idiosyncracies. An inversion center is called "i" (S) or $\bar{1}$ (H-M). When a vertical main rotation axis is present, vertical mirror planes are called "v" (S) or "m" (H-M); horizontal mirror planes are "h" (S) or "/m" (H-M). An N -fold rotation axis is referred to as C_N (S) or N (H-M).

There is always a 1:1 correspondence between the Schönflies and Hermann-Mauguin point groups. For example:

$$C_1=1; C_2=2; C_3=3; C_4=4; C_i=\bar{1}; C_s=m; C_{2v}=2mm; C_{2h}=2/m$$

[C_s can also be called C_{1v} and $2mm$ can be called $mm2$].

A comment

- One problem with the H-M notation is the bar on top of a number.
- This is read as n -bar where n is a number.
- This is very hard to produce with a word processor and frequently the bar is missing producing an incorrect symmetry label.
- Sometimes written as $-n$ to solve this problem
- On the following you need to look for the -

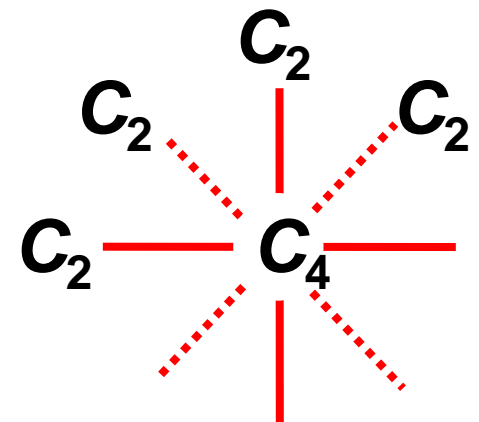
Schönflies and Hermann-Mauguin (cont.)

The Schönflies and Hermann-Mauguin systems are less similar when there is a twofold rotation axis at right angles to the main axis. It is denoted by D instead of C (S) or by a '2' after the symbol for the main axis (H-M).

e.g. $D_2=222$, $D_3=32$, $D_4=422$.

The H-M system is a little confusing here. The third '2' is always given in '222' and '422' although it is generated by the action of the other two symmetry elements, but in the case of '32' it is left out. The reason is that in '32', the (two) extra twofold axes

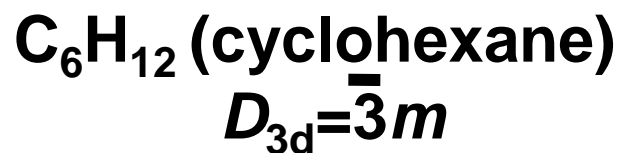
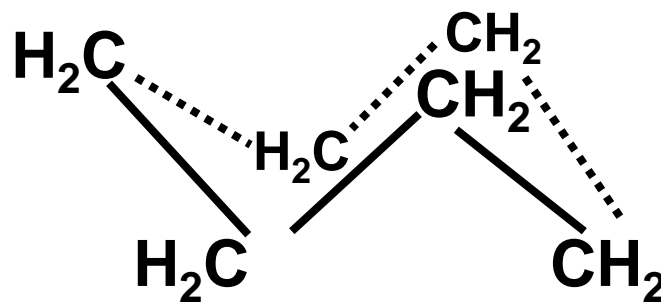
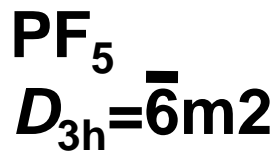
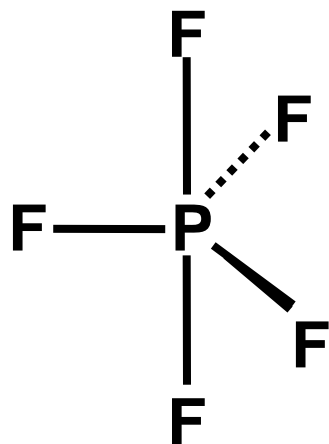
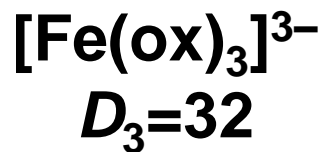
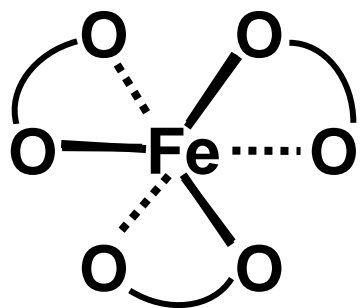
generated by the action of the threefold axis on the first twofold are *identical* to it by symmetry, whereas in 222 and 422 this is not the case (!).



Further D point groups (1)

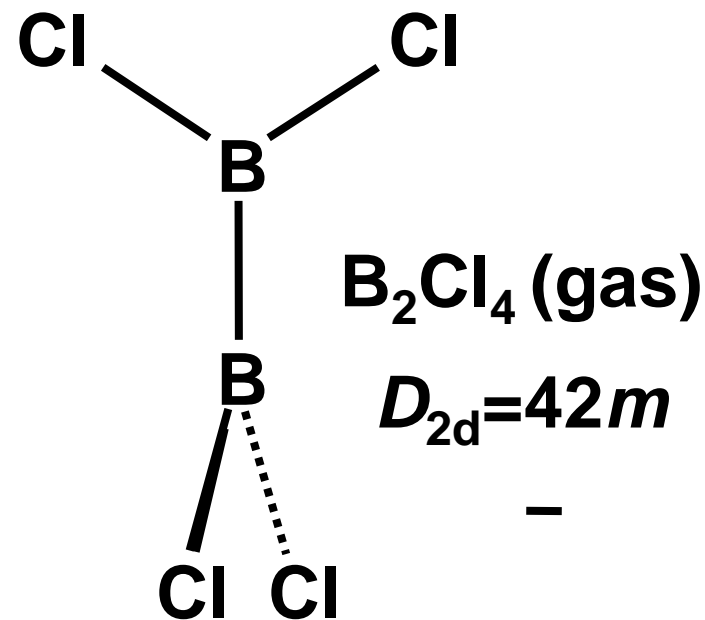
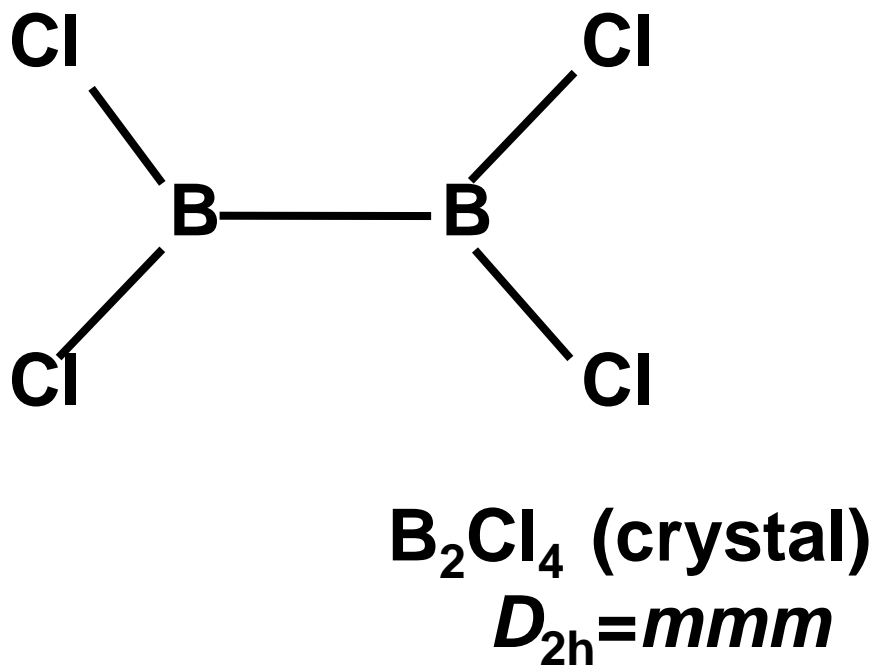
A point group D_N possesses both a C_N axis and twofold axes perpendicular to it. If vertical mirror planes are also present (between the twofold axes) but there are no horizontal mirror planes, the point group is called D_{Nd} . If both vertical and horizontal mirror planes are present, it is called D_{Nh} .

Examples:



Further D point groups (2)

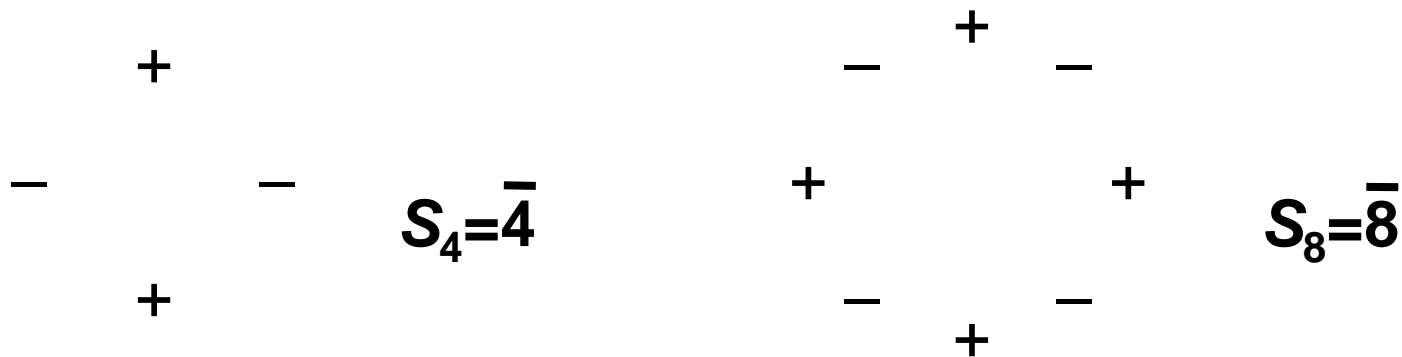
Whereas D_{2d} possesses a primary axis – the two mirror planes intersect along the ‘vertical’ axis - in $D_{2h}=mmm$ there are three twofold axes each perpendicular to a mirror plane, so that none of the three directions is special. B_2Cl_4 can adopt either of these point groups, depending on whether the structure is determined in the gas phase or in a crystal:



Inversion symmetry elements

In the Schönflies system there are *rotation-reflection axes* S_N that combine a $360^\circ/N$ rotation with a reflection in a plane at right angles to the axis. Since $S_1=C_s$ (mirror plane), $S_2=C_i$ (inversion center), $S_3=C_{3h}$ etc., only the axes S_4 , S_8 etc. are independent. The point group D_{2d} also includes a S_4 axis.

The Hermann-Mauguin system has *rotation-inversion axes* N that combine a $360^\circ/N$ rotation with an inversion. These axes with odd N are equivalent to both a rotation axis of order N and a center of inversion, z.B. $\bar{3}=3+\bar{1}$. For crystallographic purposes, $3/m$ is always written as 6 , because the diffraction pattern exhibits hexagonal symmetry, but m is never written as 2 .



Note

- -6 (6 bar) is the same as S_3
- -3(3 bar) is the same as S_6

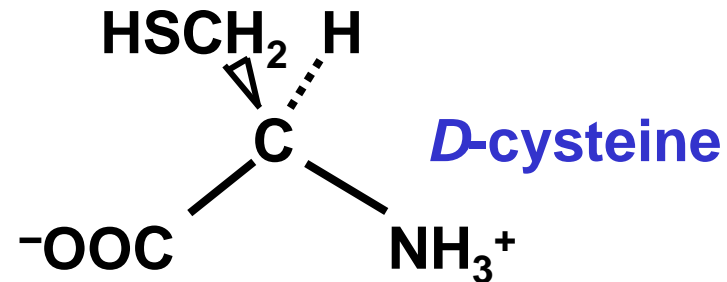
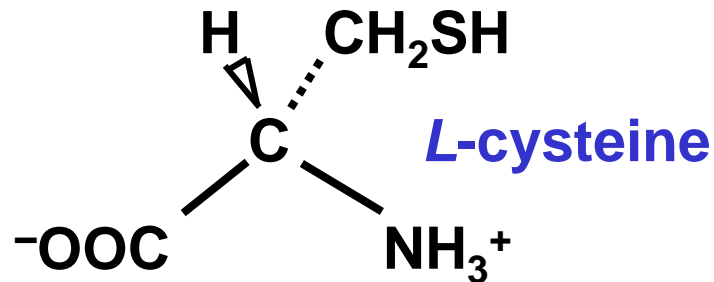
Symmetry elements - summary

In the Schönflies system, pure rotation axes are denoted by C_N , corresponding to a rotation of $360^\circ/N$. In the Hermann-Mauguin system they are given the symbol N . Twofold axes at right angles to the principal axis change C_N to D_N ; in the H-M system they are specified directly, e.g. 222 , 32 or 422 .

Mirror planes perpendicular to C - or D -axes are called h , e.g. C_{2h} . Vertical mirror planes, for which the principal axis lies in the plane, are called v for C point groups (e.g. C_{2v}) and d for D point groups (e.g. D_{3d}). Note that D_{Nh} point groups also contain vertical mirror planes, but D_{Nd} do not have horizontal mirror planes. In the H-M system mirror planes are called m ; a '/' is added before the first if it is perpendicular to a single principal axis, e.g. $2mm$, $2/m$ and mmm .

Chiral molecules (1)

Molecules that possess no symmetry or only pure rotation axes can exist as left- and right-handed forms which cannot be superimposed on each other, e.g. the amino-acid cysteine occurs naturally as the *L*-form:

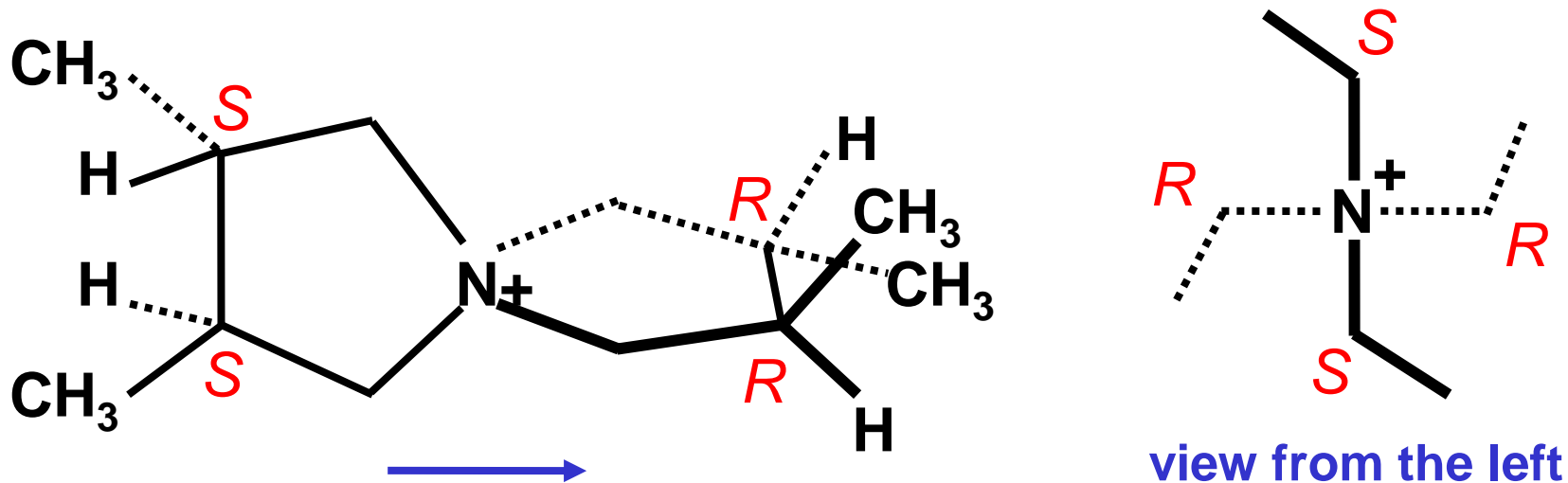


Reaction of cysteine with mild oxidizing agents (e.g. air) converts SH + HS to S—S and changes it to the amino-acid cystine. When racemic cysteine is oxidized, both the non-chiral *D,L*-cystine (identical to *L,D*-; point group $C_i=1$) and the chiral *L,L*- and *D,D*-cystines (point group $C_2=2$) are formed. The chiral forms have the same physical properties and so cannot be separated from each other directly, but differ from the *D,L*-form and can be separated from it by e.g. fractional crystallization.

Chiral molecules (2)

Molecules that possess S_N axes are identical to their mirror images and thus not chiral. Molecules that do not possess any S_N axes are chiral.

One should take into account that S_2 represents an inversion center and S_1 a mirror plane. However a molecule or ion with only S_4 symmetry is also not chiral, although it possesses neither an inversion center nor a mirror plane; an example – with four asymmetric carbon atoms (!) – is:



Special point groups

A tetrahedral molecule like CCl_4 has the point group $T_d=\bar{4}32$. When the mirror planes and S_4 axis are missing, for example for R_4Si when the ligand R is chiral, the symmetry is reduced to $T=23$.

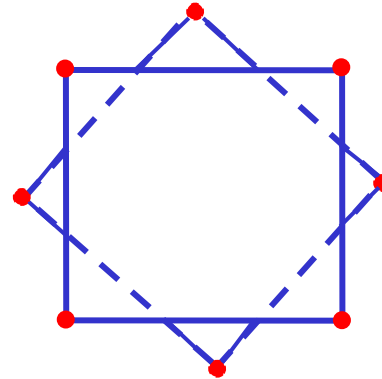
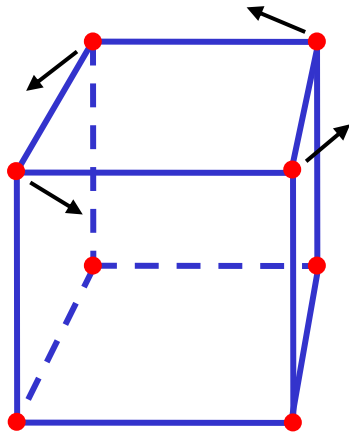
Octahedral coordination like SF_6 or a cubic molecule like cubane $[(\text{CH})_8]$ possess the point group $O_h=m\bar{3}m$.

When the S_4 axes are removed but the four C_3 axes retained, the results are $T_h=m\bar{3}$ ($\text{P}_{12}\text{N}_{14}\text{S}_{12}^{6-}$) or $O=432$ (no known molecular example, but adopted by the iron-storage protein ferritin!).

C_{60} and $[\text{B}_{12}\text{H}_{12}]^{2-}$ possess the non-crystallographic point group $I_h=53m$. Many virus shells have $I=532$ symmetry, which gives the maximum enclosed volume per independent (chiral) amino-acid used to make the shell.

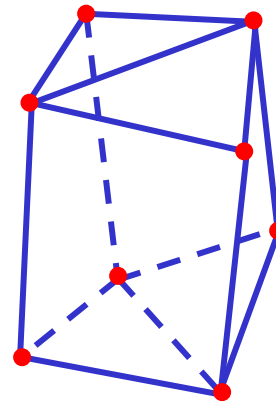
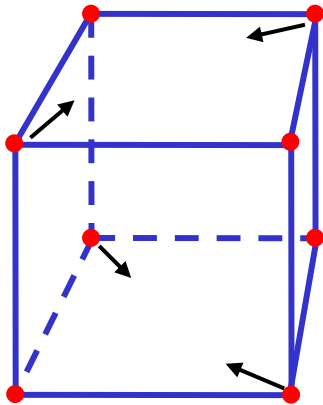
Eightfold coordination

According to the VSEPR model, eightfold coordination can either be quadratic antiprismatic or rhombic dodecahedral. In the case of $\text{Mo}(\text{CN})_8^{4-}$ both are known, with different cations. A cube would be unfavorable.



$$D_{4d} = \bar{8}2m$$

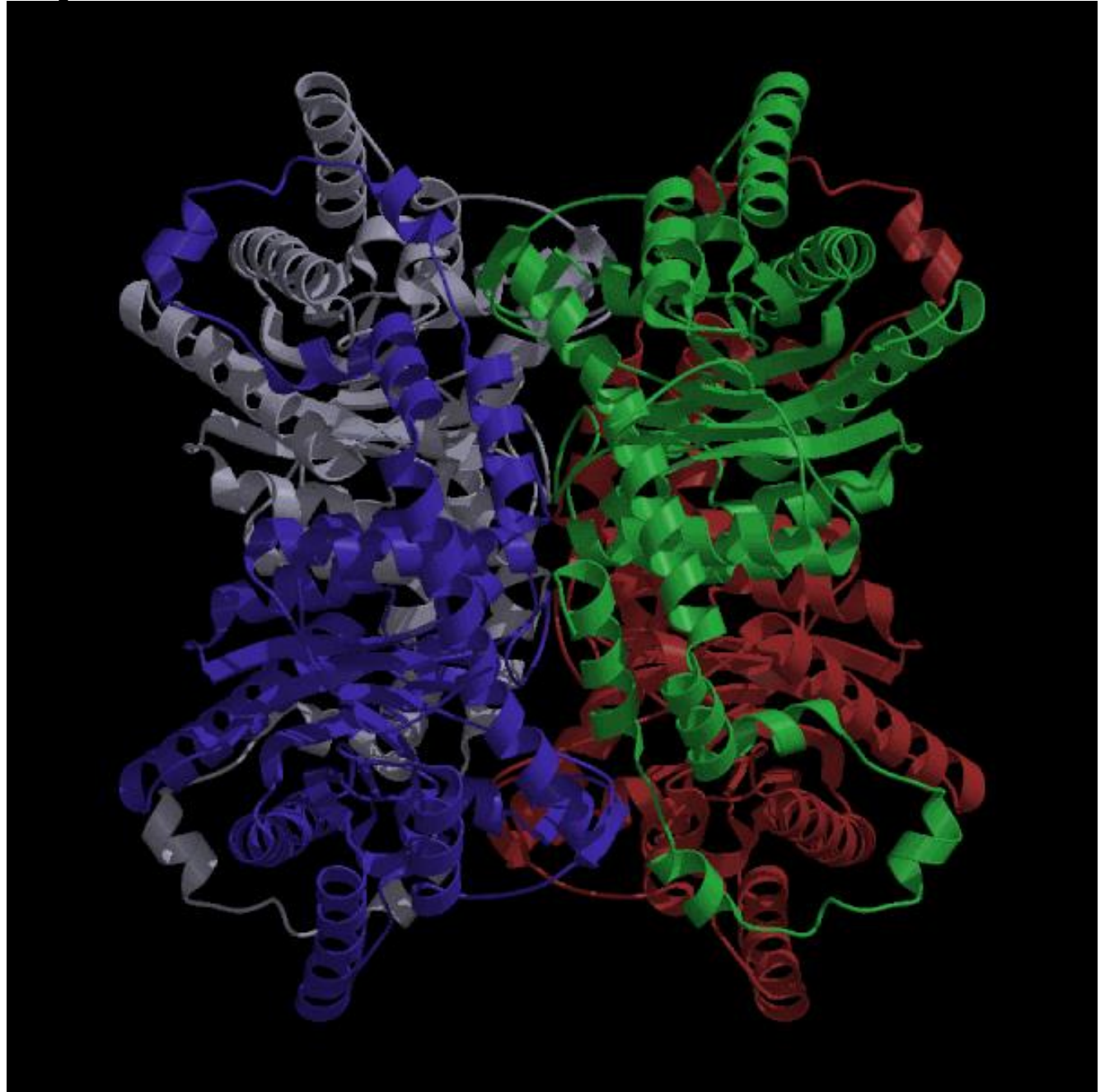
$$O_h = m\bar{3}m$$



$$D_{2d} = \bar{4}2m$$

Point groups of macromolecular

Biological macromolecules are of course chiral, and so cannot possess S_N operators, e.g. 1 , m and S_4 . This leaves C_N , D_N , T , O and I as possible point groups. An example is the D_2 tetramer unit of *glucose isomerase* in solution and in the crystal (but it is probable that the biologically active unit is a dimer).



Graphic by Burkhard Heisen

The 32 crystallographic point groups

Schönflies Hermann-
Mauguin

C_1	1
C_i	$\bar{1}$
C_2	2
$C_s = C_{1v}$	m
C_{2h}	$2/m$
C_{2v}	$mm2$ ($mm2$)
D_2	222
D_{2h}	mmm
C_4	$\underline{4}$
S_4	4
D_4	422
C_{4v}	$4mm$
C_{4h}	$4/m$
D_{2d}	$\bar{4}2m$
D_{4h}	$4/mmm$

C_3	3
$C_{3i} (S_6)$	$\bar{3}$
D_3	32
C_{3v}	$3m$
D_{3d}	$\bar{3}m$
C_6	6
C_{3h}	$\bar{6}$
D_6	622
D_{3h}	$\bar{6}m2$
C_{6h}	$\bar{6}/m$
C_{6v}	$6mm$
D_{6h}	$6/mmm$
T	23
T_h	$m\bar{3}$
T_d	$4\bar{3}m$
O	432
O_h	$m\bar{3}m$

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?