

**Methods in Chemistry III – Part 1**  
**Modul M.Che.1101 WS 2010/11 – 2**  
*Modern Methods of Inorganic Chemistry*

**Mi 10:15-12:00, Hörsaal II**

**George Sheldrick**

**[gsheldr@shelx.uni-ac.gwdg.de](mailto:gsheldr@shelx.uni-ac.gwdg.de)**

# Symmetry elements - summary

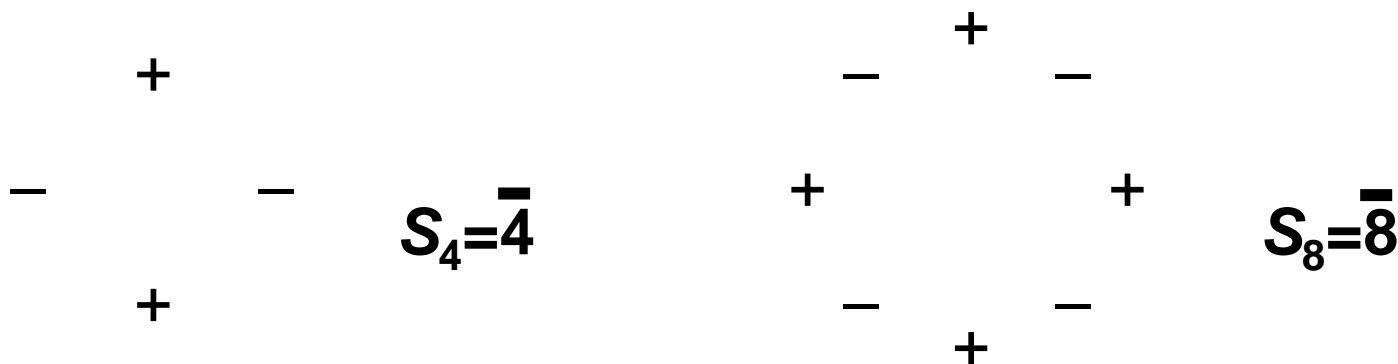
In the Schönflies system, pure rotation axes are denoted by  $C_N$ , corresponding to a rotation of  $360^\circ/N$ . In the Hermann-Mauguin system they are given the symbol  $N$ . Twofold axes at right angles to the principal axis change  $C_N$  to  $D_N$ ; in the H-M system they are specified directly, 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  $m$  if it is perpendicular to a single principal axis (i.e. the axis of highest symmetry), e.g.  $2mm$ ,  $2/m$  and  $mmm$ .

# Inversion symmetry elements

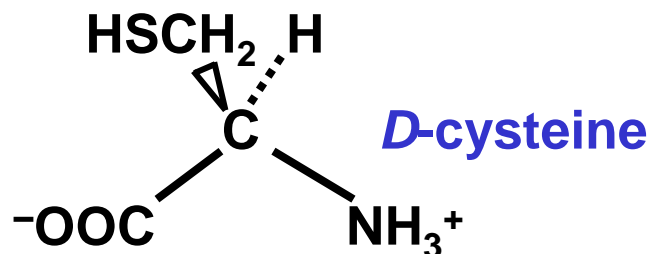
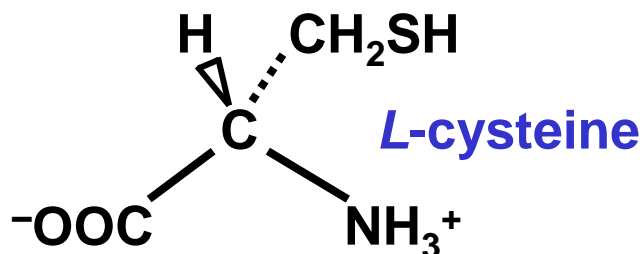
In the Schönflies system there are rotation-reflection axes  $S_N$  that combine a  $360^\circ/N$  rotation with a reflection in a plane at right angles to the axis. Since  $S_1=C_s$  (mirror plane),  $S_2=C_i$  (inversion center),  $S_3=C_{3h}$  etc., only the axes  $S_4, S_8$  etc. ( $N=4n$ ) are independent. The point group  $D_{2d}$  also includes a  $S_4$  axis.

The Hermann-Mauguin system has rotation-inversion operators  $\bar{N}$  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, e. g.  $\bar{3}=3+\bar{1}$ . For crystallographic purposes,  $3/m$  is always written as  $\bar{6}$ , because the diffraction pattern exhibits hexagonal symmetry, but  $m$  is never written as  $\bar{2}$ .



# 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:

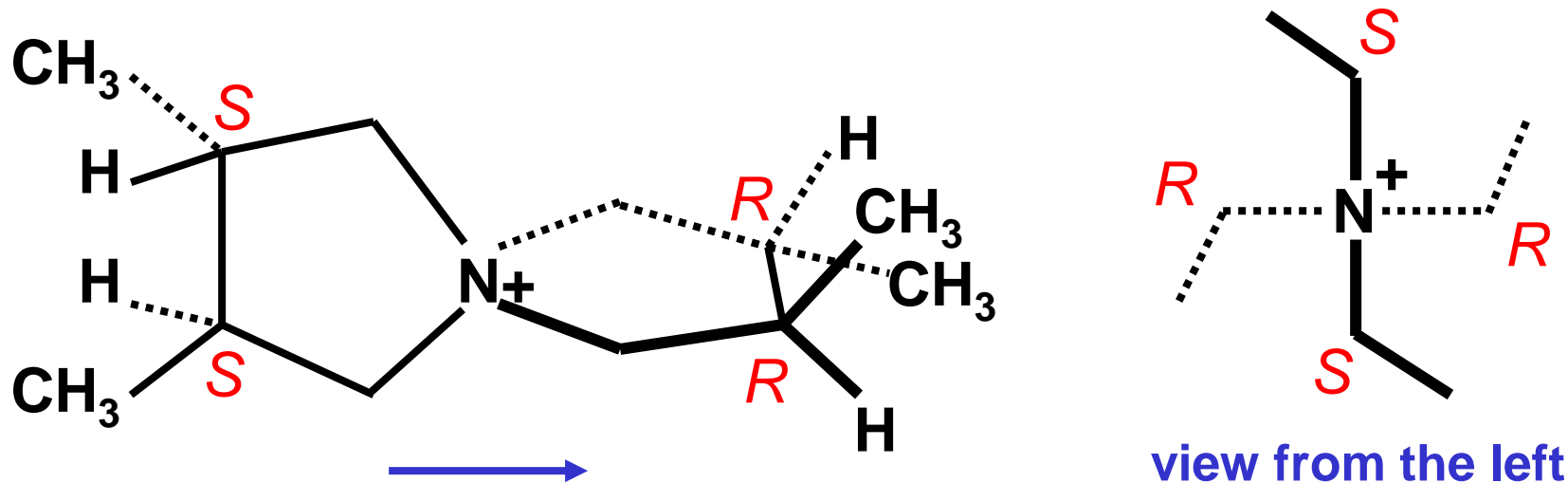


Reaction of cysteine with mild oxidizing agents (e.g. air) converts SH + HS to S—S and changes it to the amino-acid cystine. When racemic cysteine is oxidized, both the non-chiral *D,L*-cystine (identical to *L,D*-; point group  $C_i = \bar{1}$ ) and the chiral *L,L*- and *D,D*-cystines (point group  $C_2 = 2$ ) 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

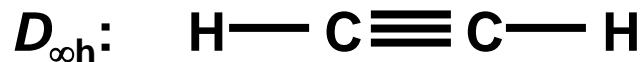
A tetrahedral molecule like  $\text{CCl}_4$  has the point group  $T_d = \bar{4}3m$ . When the mirror planes and  $S_4$  axis are missing, for example for  $\text{R}_4\text{Si}$  when the ligand R is chiral, the symmetry is reduced to  $T = 23$ .

Octahedral coordination like  $\text{SF}_6$  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 small molecule example, but adopted by the iron-storage protein ferritin!).

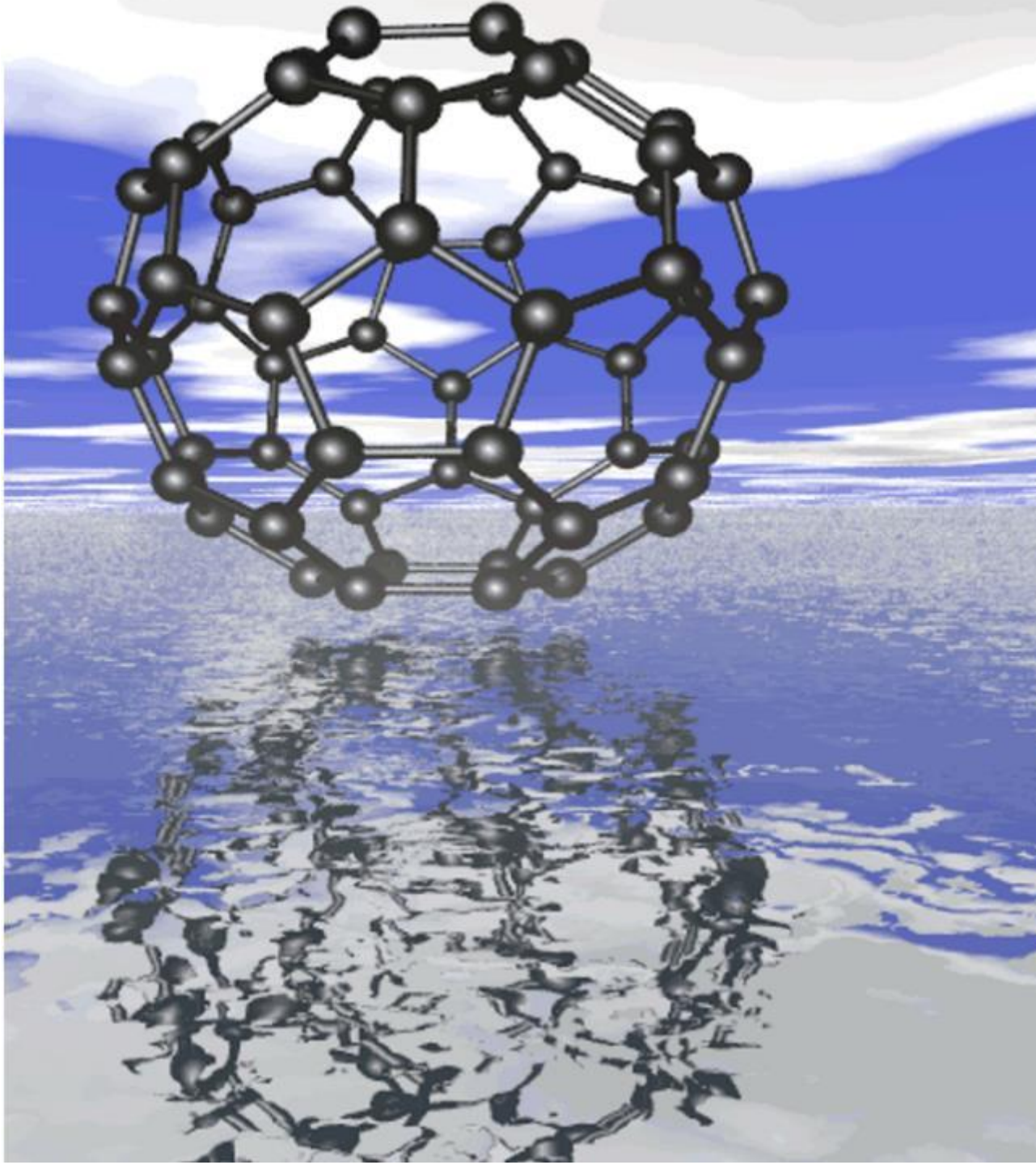
$\text{C}_{60}$  and  $[\text{B}_{12}\text{H}_{12}]^{2-}$  possess the non-crystallographic point group  $I_h = \bar{5}3m$ . Many virus shells have  $I = 532$  symmetry, which gives the maximum enclosed volume per independent nucleotide used to encode the shell proteins.

Linear molecules belong either to the point group  $C_{\infty v}$  (no further symmetry) or  $D_{\infty h}$  (an infinite number of twofold axes at right angles to the main axis). Examples:



# An example of point group $I_h$

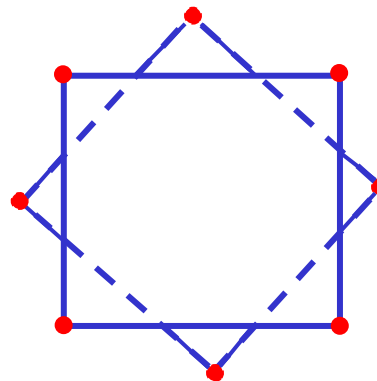
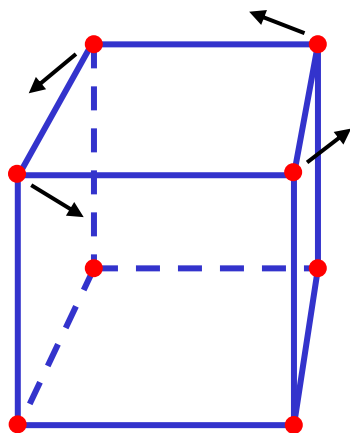
The  $C_{60}$  molecule illustrates the point group  $I_h = \overline{5}3m$ . There are  $\overline{5}$  axes (fivefold + inversion) through the five-membered rings and  $\overline{3}$  axes through the six-membered rings. The twofold axes bisect three of the C-C bonds in the six-membered rings.



Graphic by Voita Jancik

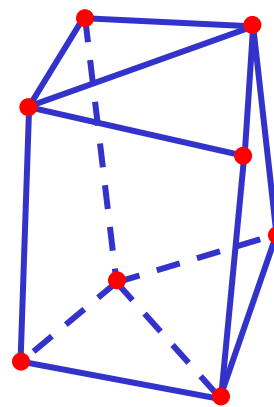
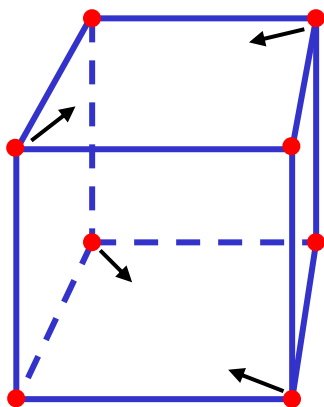
# Eightfold coordination

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.



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

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

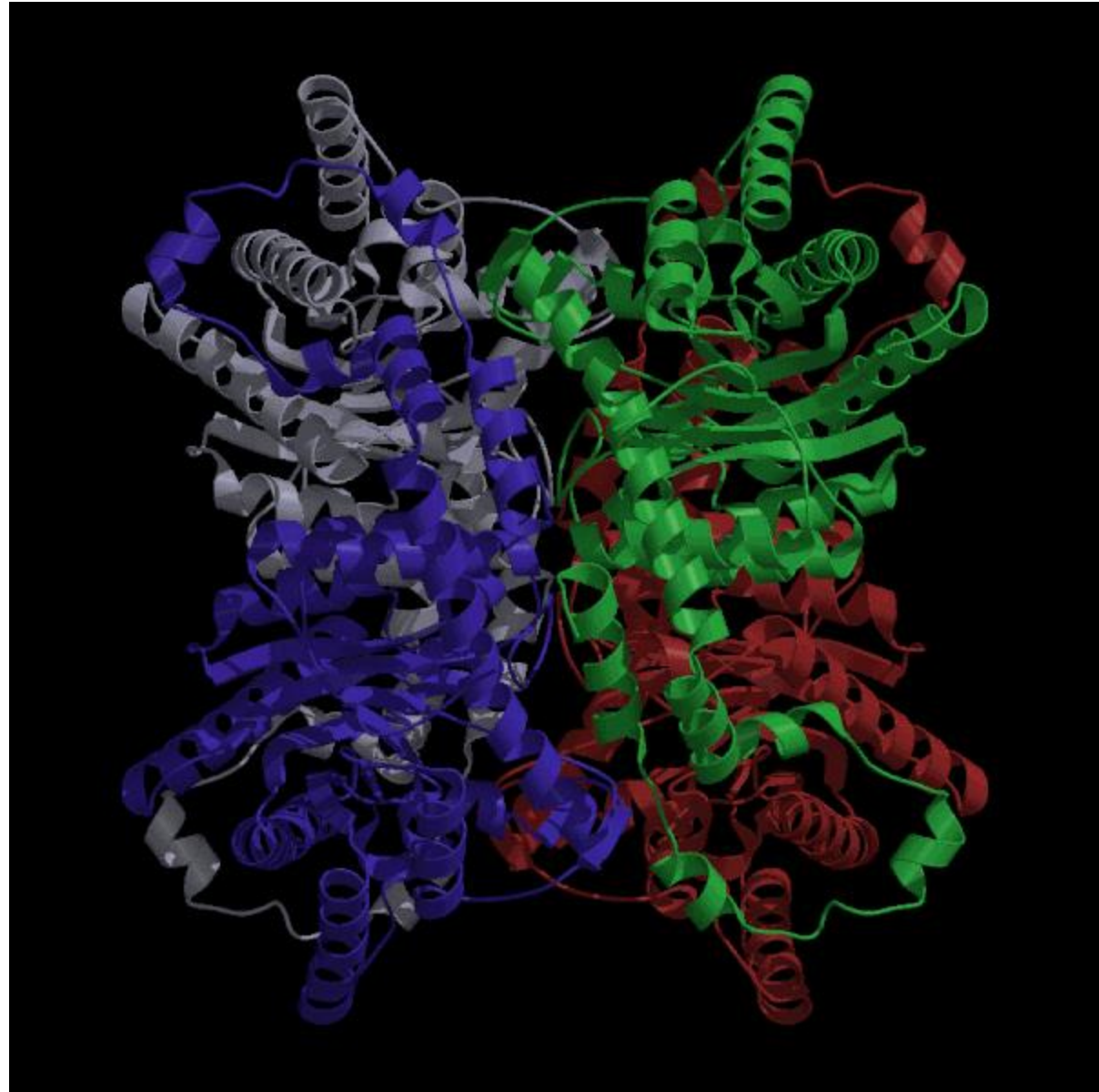


$$D_{2d} = \bar{4}2m$$



# Point groups of macromolecular complexes

Biological molecules are of course chiral, and so cannot possess  $S_N$  operators, e.g.  $\bar{1} = S_2$ ,  $m = S_1$  and  $\bar{4} = S_4$ . 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 (however it is probable that the biologically active unit is a dimer).



Graphic by Burkhard Heisen

# Point group determination

No rotation axes:  $C_1$ ,  $C_i$  or  $C_s$

Linear:  $C_{\infty v}$  or  $C_{\infty h}$

Multiple threefold axes:  $T$ ,  $T_d$ ,  $T_h$ ,  $O$ ,  $O_h$ ,  $I$ ,  $I_h$

N-fold but no perpendicular twofolds:  $C_N$ ,  $C_{Nv}$ ,  $C_{Nh}$  or  $S_{2N}$

N-fold with perpendicular twofolds:  $D_N$ ,  $D_{Nd}$  or  $D_{Nh}$

---

$h$  = mirror plane perpendicular to principal axis

$v$ ,  $d$  = mirror planes parallel to principal axis

$D_{Nh}$  has mirror planes perpendicular and parallel to principal axis

$C_i$ ,  $C_{\infty h}$ ,  $T_h$ ,  $O_h$  and  $I_h$  possess inversion centers

$O$  and  $O_h$  possess fourfold axes

$I$  and  $I_h$  possess fivefold axes

# 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
$D_{2h}$	$mmm$
$C_4$	4
$S_4$	$\bar{4}$
$D_4$	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
$D_{3h}$	$\bar{6}m2$
$C_{6h}$	$6/m$
$C_{6v}$	$6mm$
$D_{6h}$	$6/mmm$
$T$	23
$T_h$	$m\bar{3}$
$T_d$	$\bar{4}3m$
$O$	432
$O_h$	$m\bar{3}m$

# Exercises

1. Why do virus shells usually possess a high symmetry, and why do biological macromolecules often crystallize in space groups of higher symmetry than small molecules?
2. Which 10 crystallographic point groups would be suitable for oligomers of chiral monomers (e.g. proteins) and how many monomers would make up the oligomers in each case?
3. Attempt to assign the point group of a tennis ball, taking the stripe into account but ignoring any text.