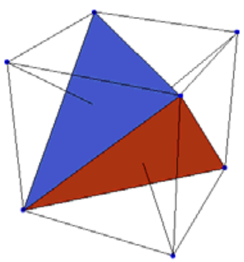
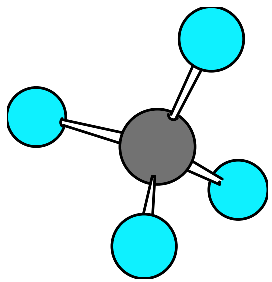
Chem 59-250 Identifying point groups

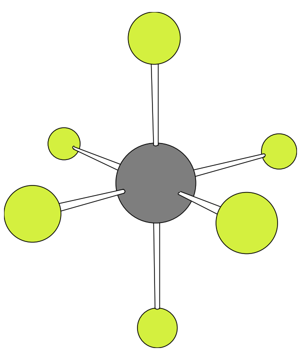
Special cases:

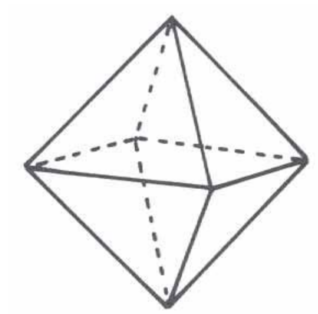
Perfect tetrahedral (T_d) e.g. P_4, CH_4



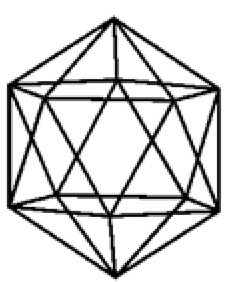


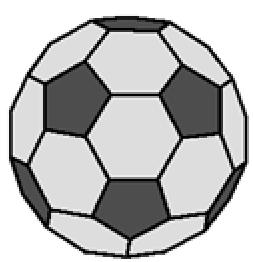
Perfect octahedral (O_h) e.g. SF_6, $[B_6H_6]^{-2}$

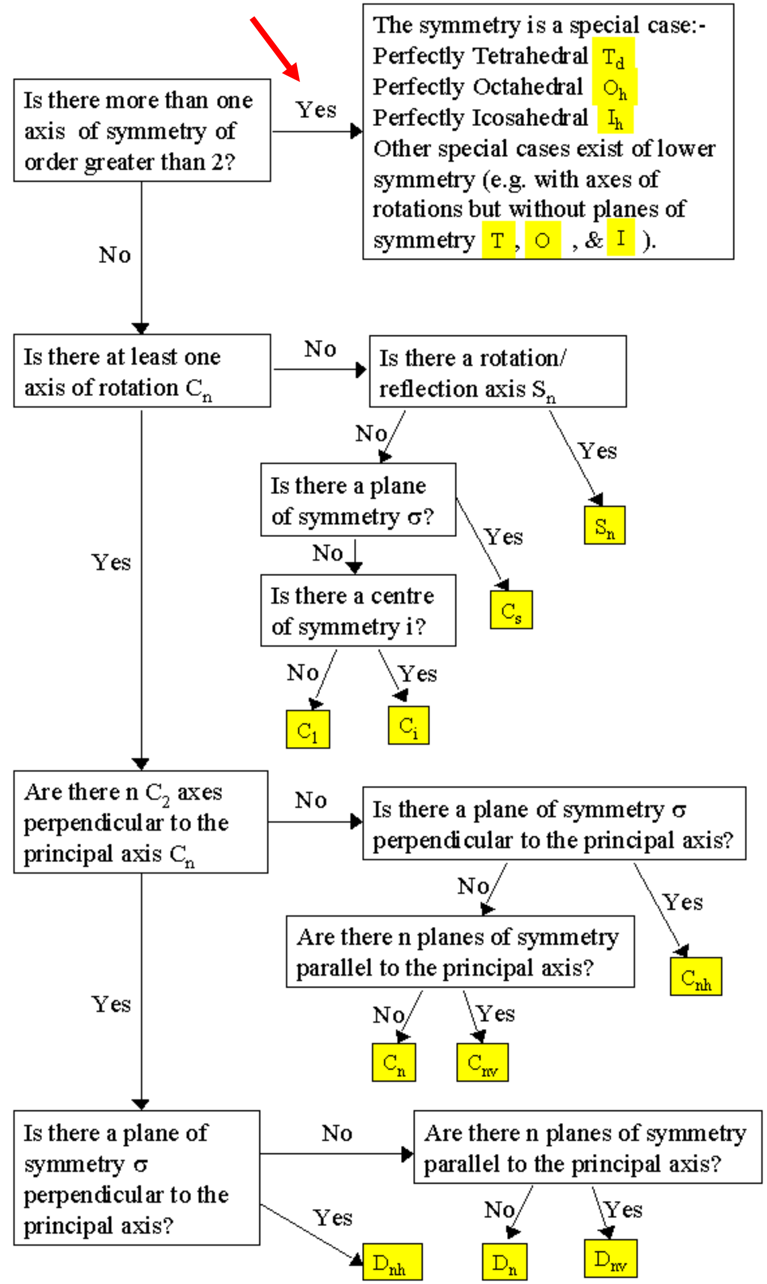




Perfect icosahedral (I_h) e.g. $[B_{12}H_{12}]^{-2}$, C_{60}





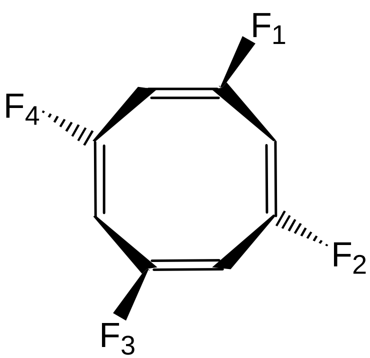


Chem 59-250 Identifying point groups

Low symmetry groups:

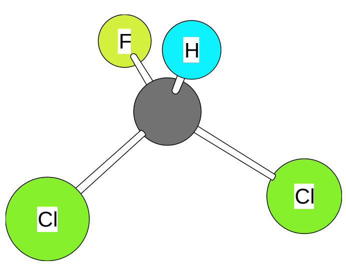
Only* an improper axis (S_n)

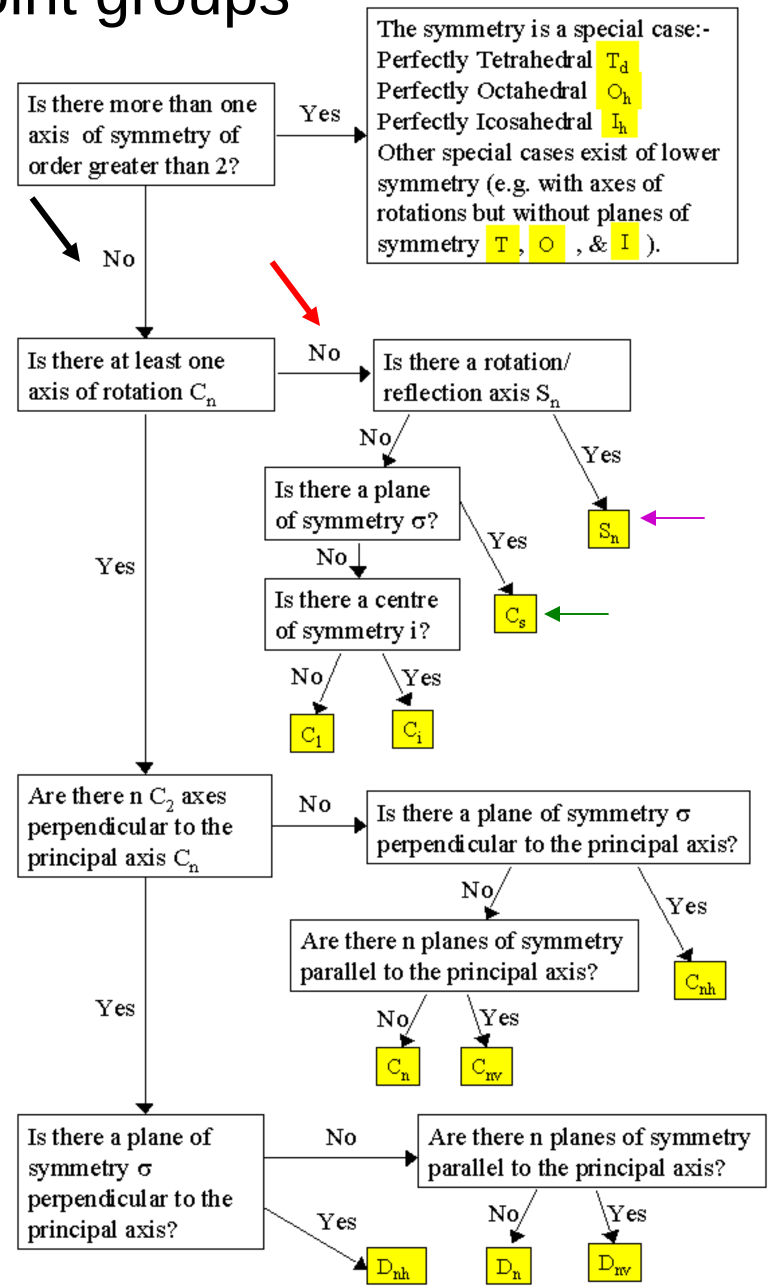
e.g. 1,3,5,7-tetrafluoroCOT, S_4



Only a mirror plane (C_s)

e.g. $CHFCl_2$



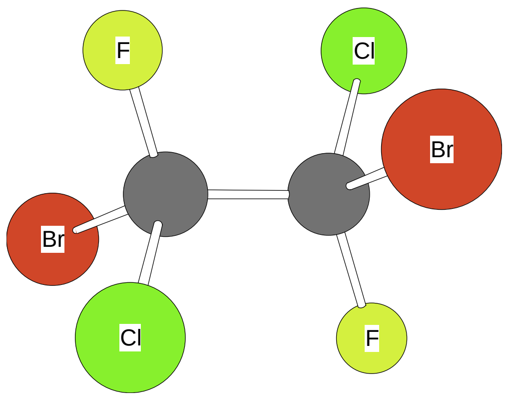


Chem 59-250 Identifying point groups

Low symmetry groups:

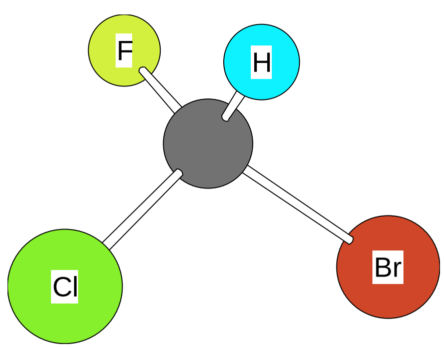
Only an inversion center (C_i)

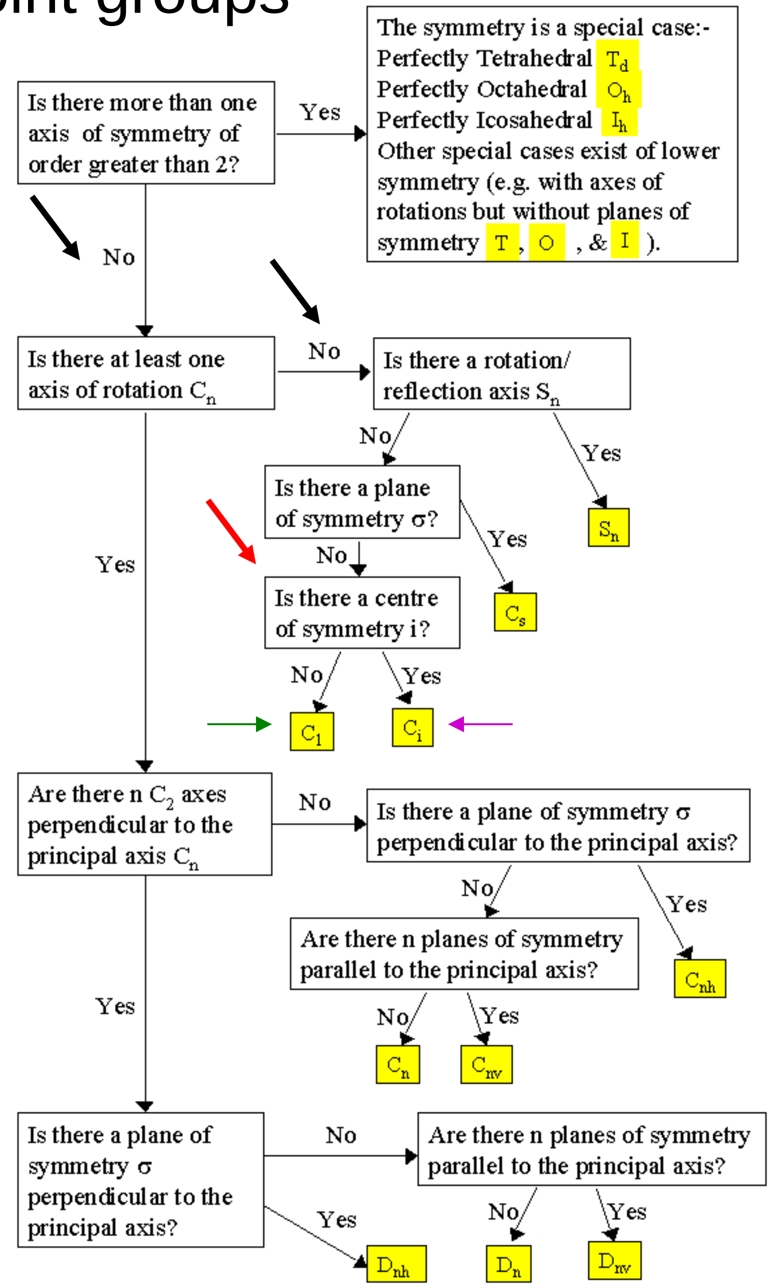
e.g. (conformation is important !)



No symmetry (C_1)

e.g. CHFClBr



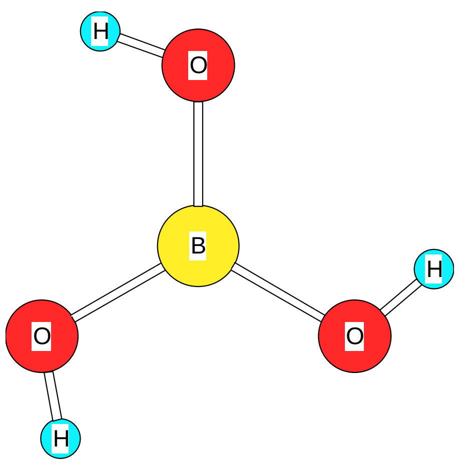


Identifying point groups

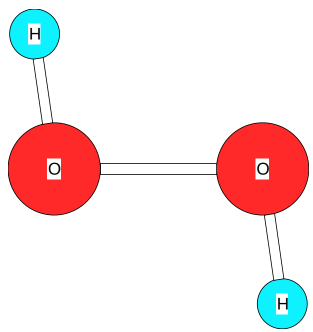
C_n type groups:

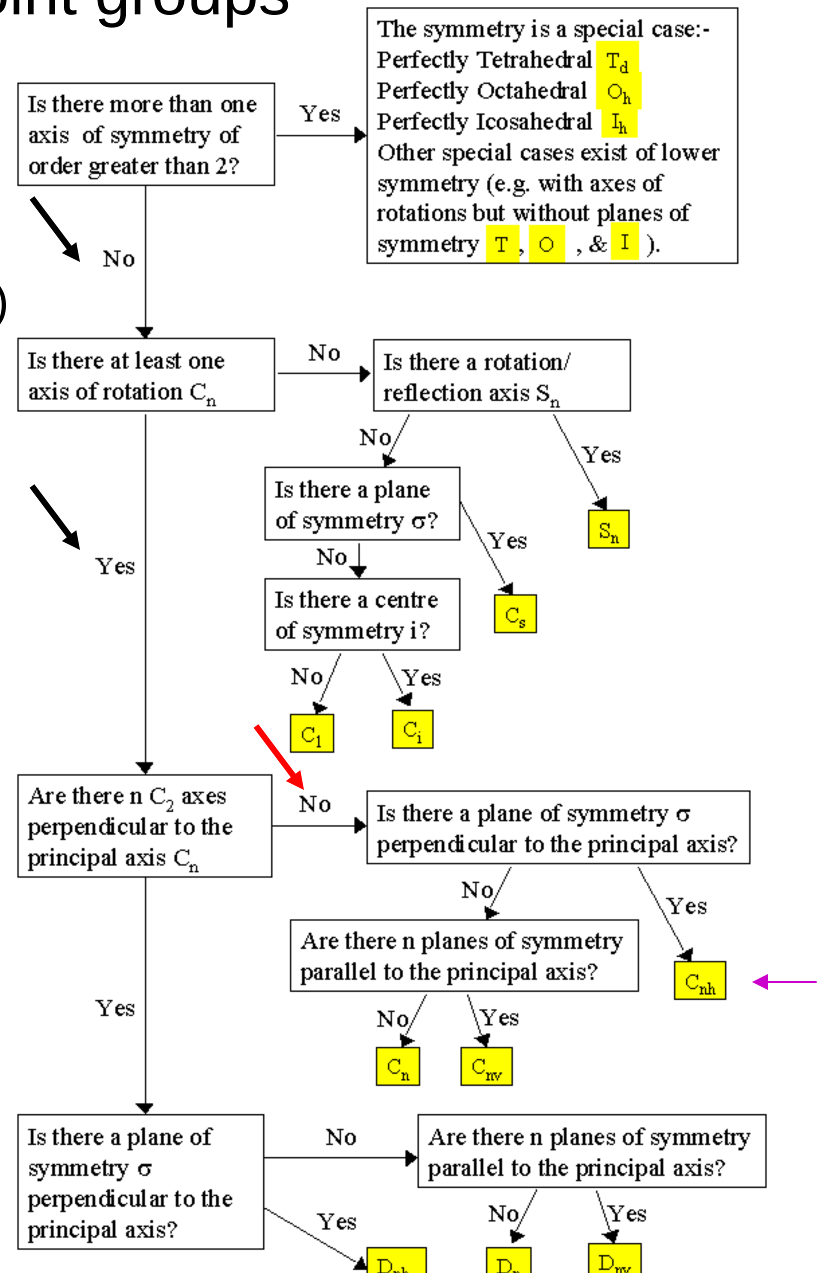
A C_n axis and a σ_h (C_{nh}) ←

e.g. $B(OH)_3$ (C_{3h}, conformation is important !)



e.g. H_2O_2 (C_{2h}, conformation is important !)





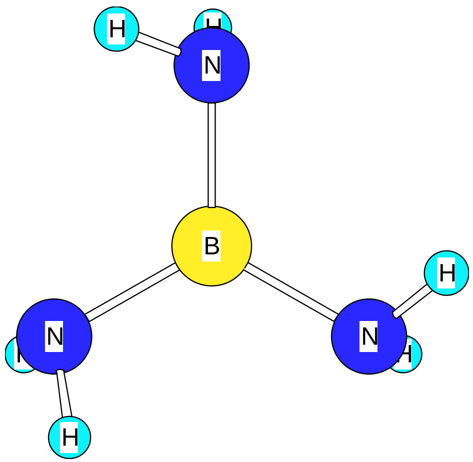
Note: molecule does not have to be planar e.g. $B(NH_2)_3$ (C_{3h}, conformation is important !)

Chem 59-250 Identifying point groups

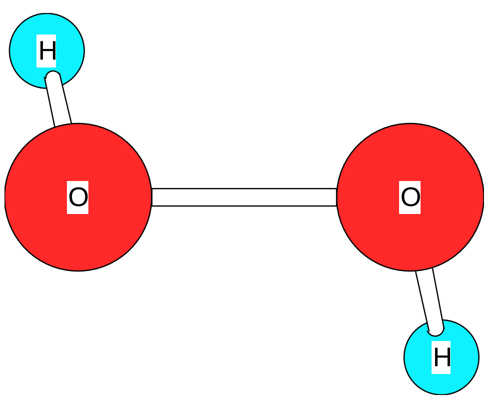
C_n type groups:

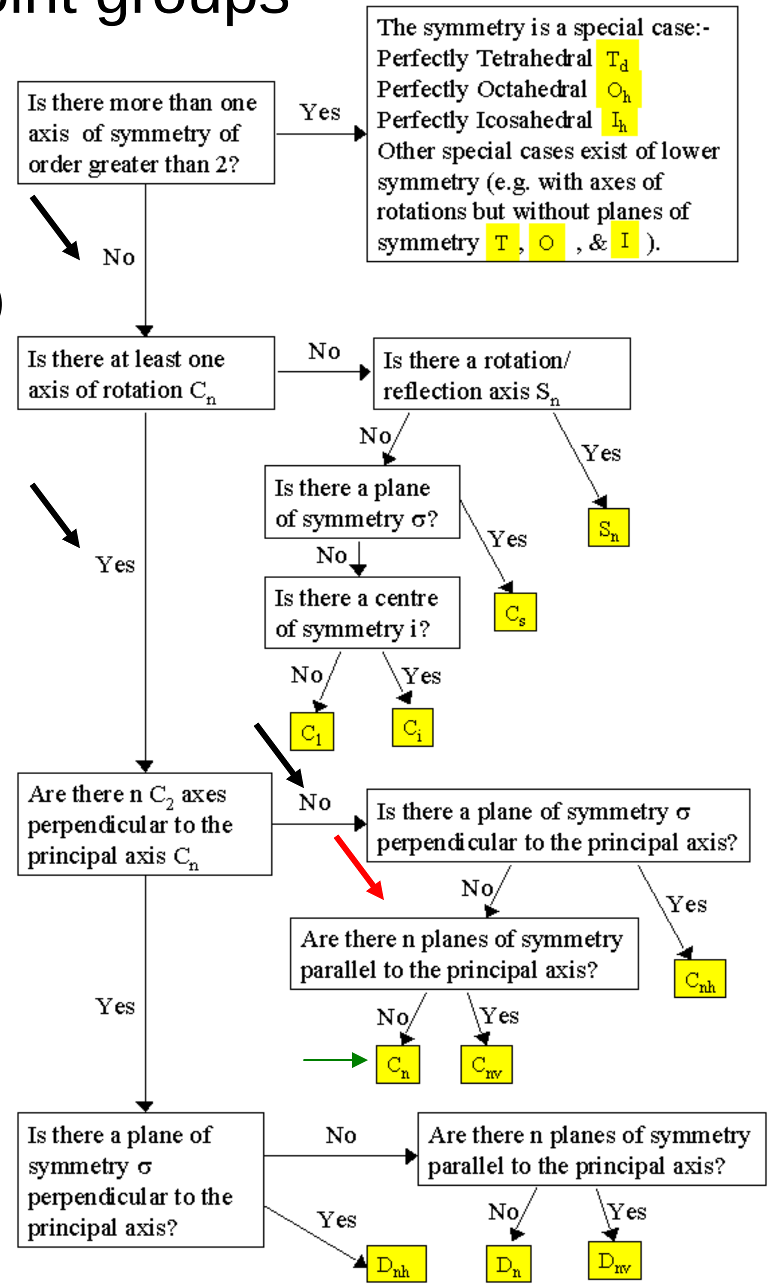
Only a C_n axis (C_n)

e.g. $B(NH_2)_3$ (C_3, conformation is important !)



e.g. H_2O_2 (C_2, conformation is important !)



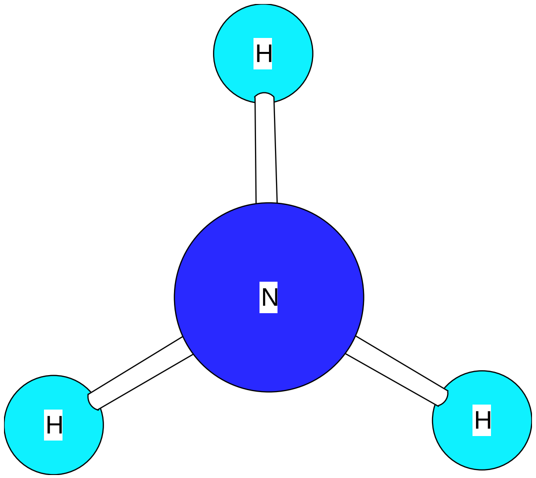


Chem 59-250 Identifying point groups

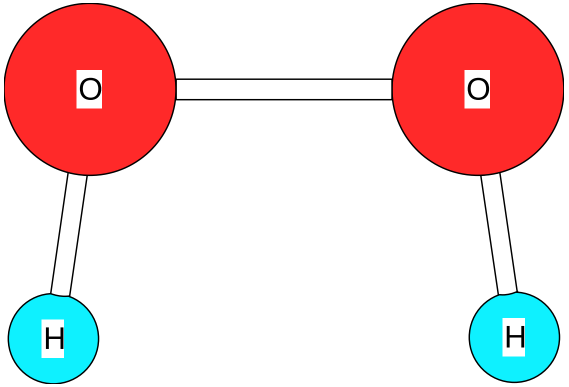
C_n *type groups:*

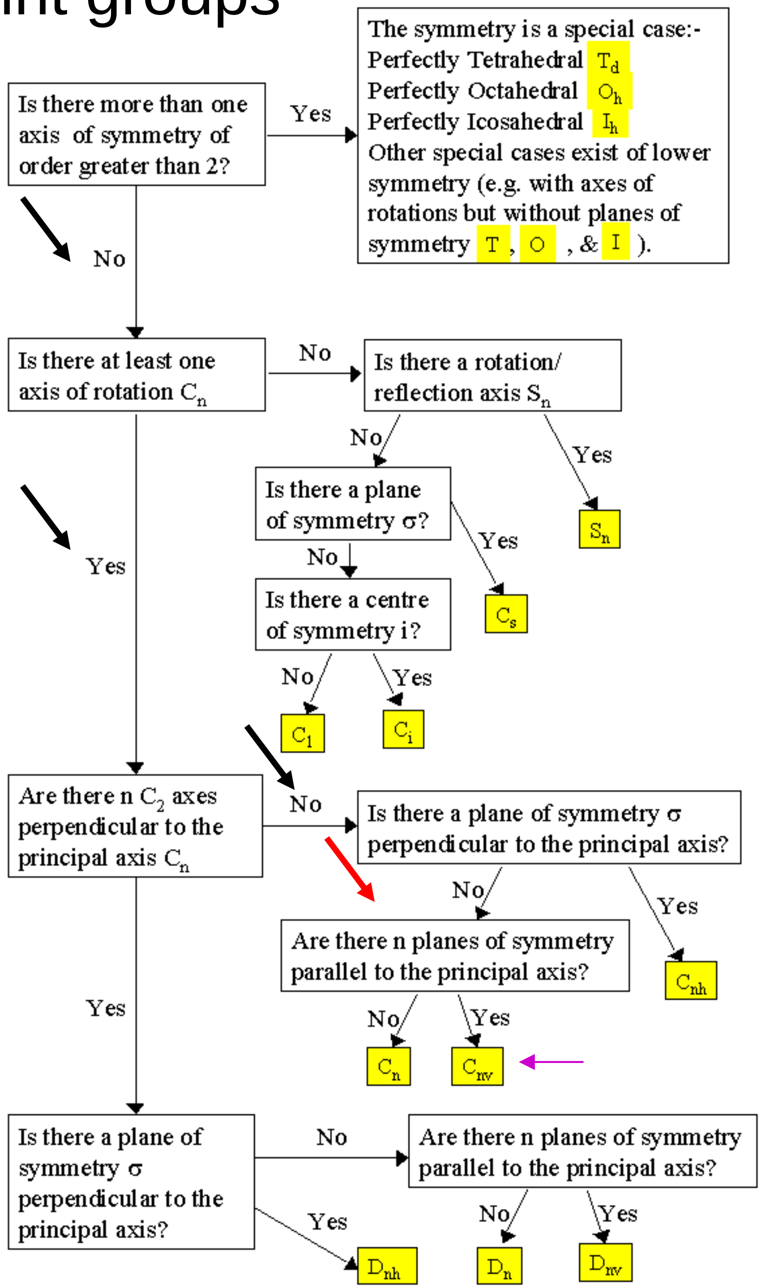
A C_n axis and a σ_v (C_{nv}) ←

e.g. NH_3 (C_{3v})



e.g. H_2O_2 (C_{2v}, conformation is important !)



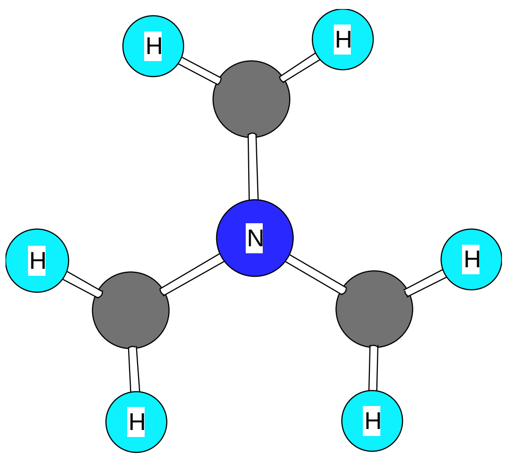


Identifying point groups

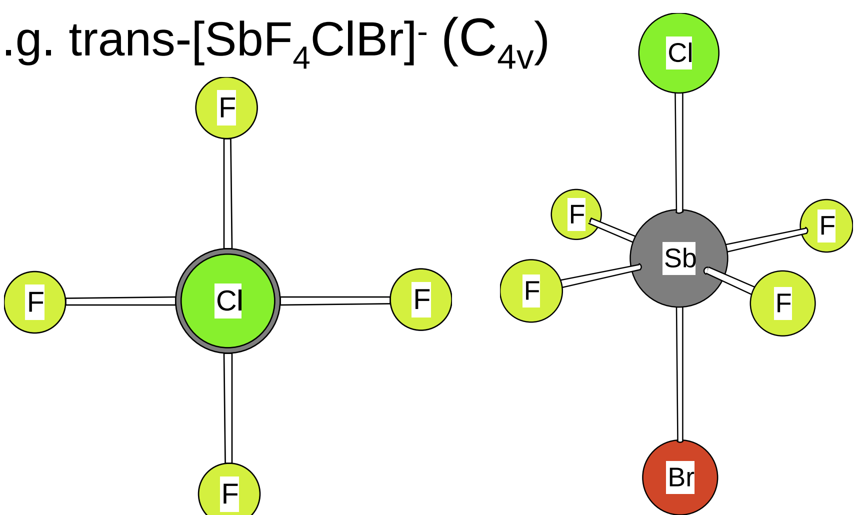
C_n type groups:

A C_n axis and a σ_v (C_{nv})

e.g. NH_3 (C_{3v}, conformation is important !)

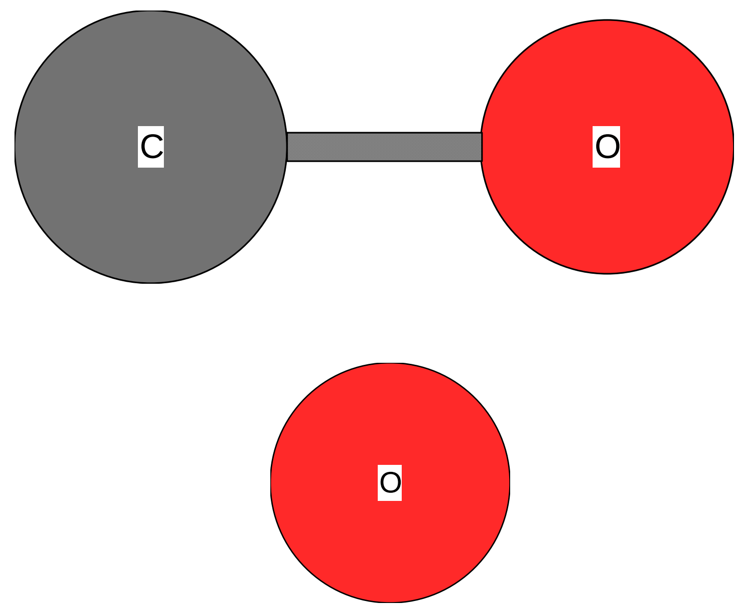


e.g. trans-$[SbF_4ClBr]^-$ (C_{4v})



e.g. carbon monoxide, CO ($C_{\infty v}$)

There are an infinite number of possible C_n axes and σ_v mirror planes.

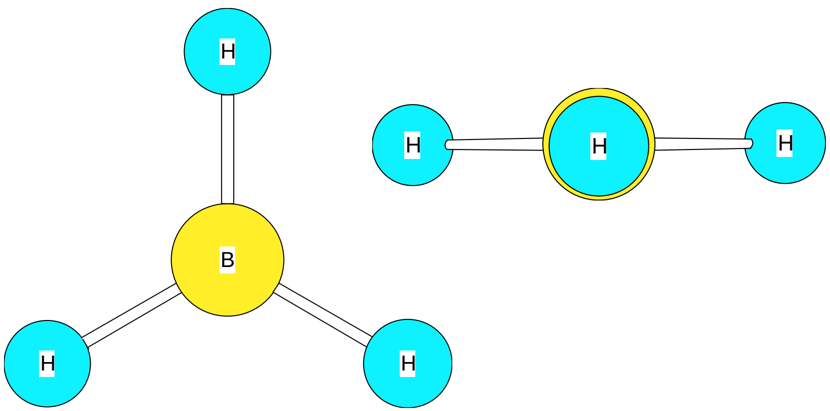


Chem 59-250 Identifying point groups

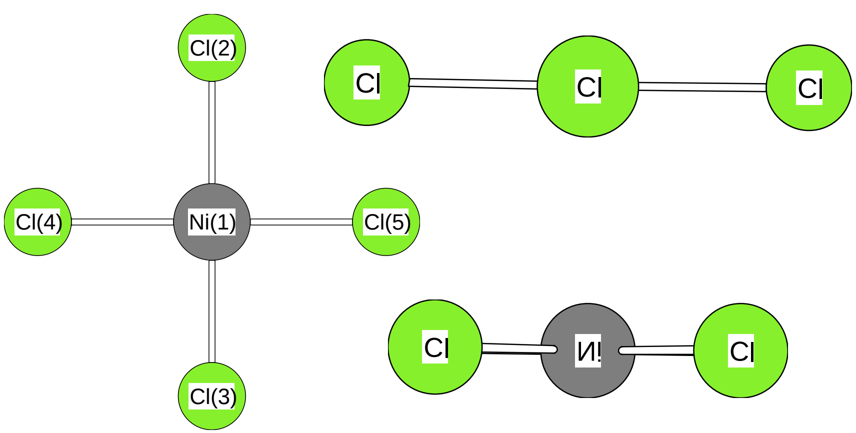
D_n *type groups:*

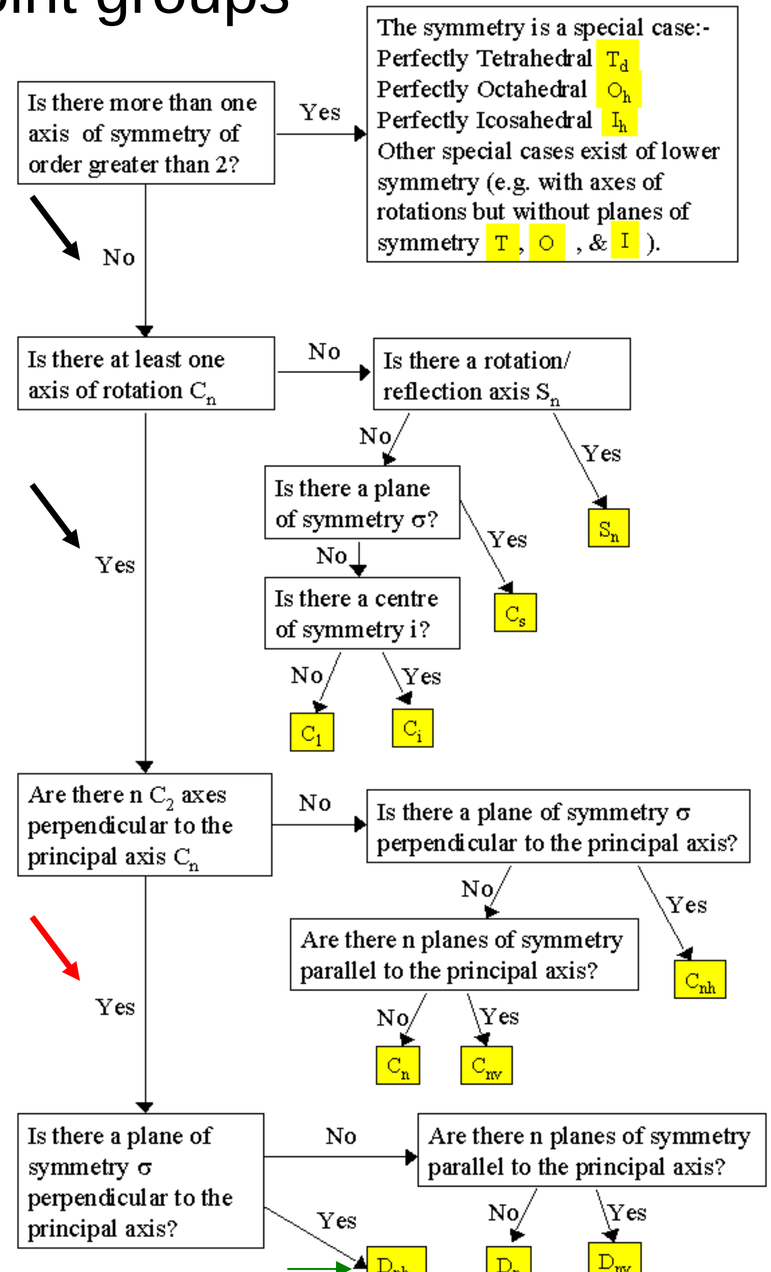
A C_n axis, n perpendicular C_2 axes and a σ_h (D_{nh}) ←

e.g. BH_3 (D_{3h})



e.g. $NiCl_4$ (D_{4h})



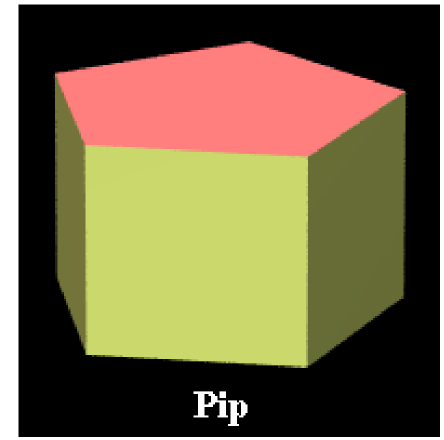


Identifying point groups

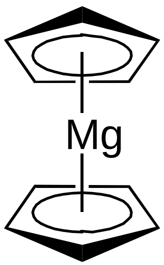
D_n type groups:

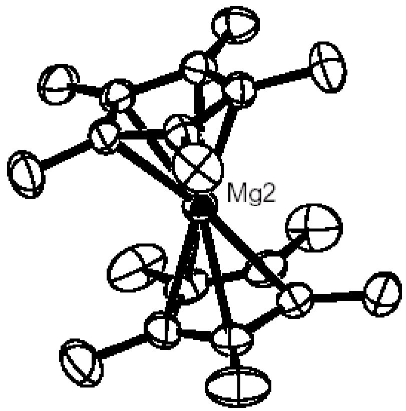
A C_n axis, n perpendicular C_2 axes and a σ_h (D_{nh})

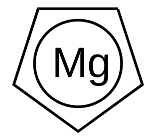
e.g. pentagonal prism (D_{5h})



e.g. $Mg(\eta^5\text{-}Cp)_2$ (D_{5h} in the *eclipsed* conformation)

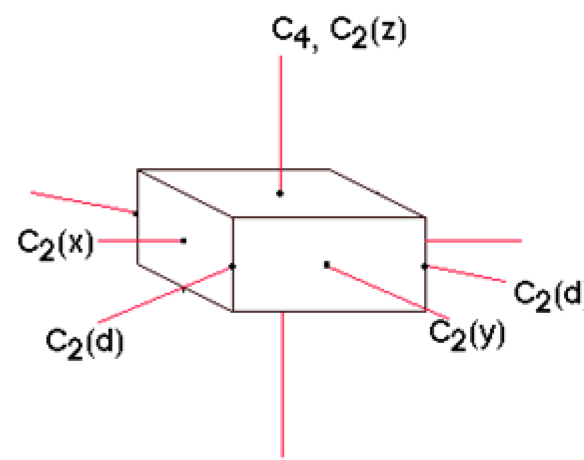






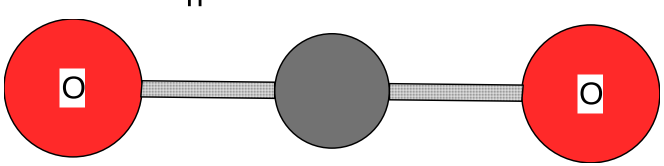
View down the C_5 axis

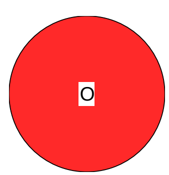
e.g. square prism (D_{4h})



e.g. carbon dioxide, CO_2 or N_2 ($D_{\infty h}$)

There are an infinite number of possible C_n axes and σ_v mirror planes in addition to the σ_h.





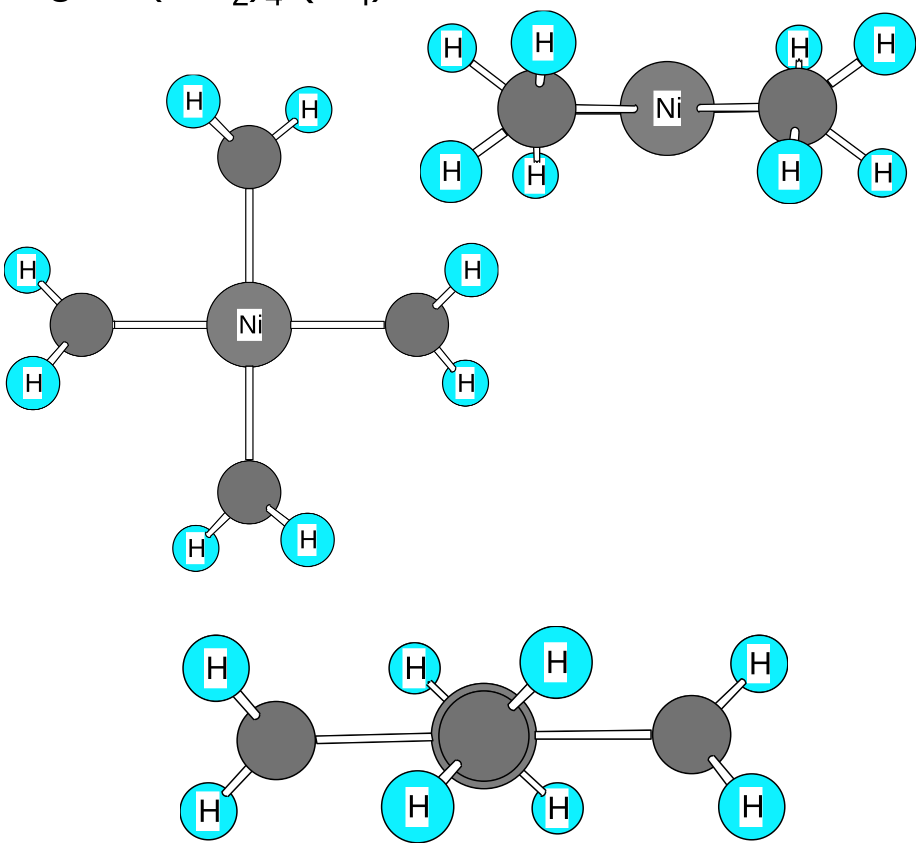
Chem 59-250 Identifying point groups

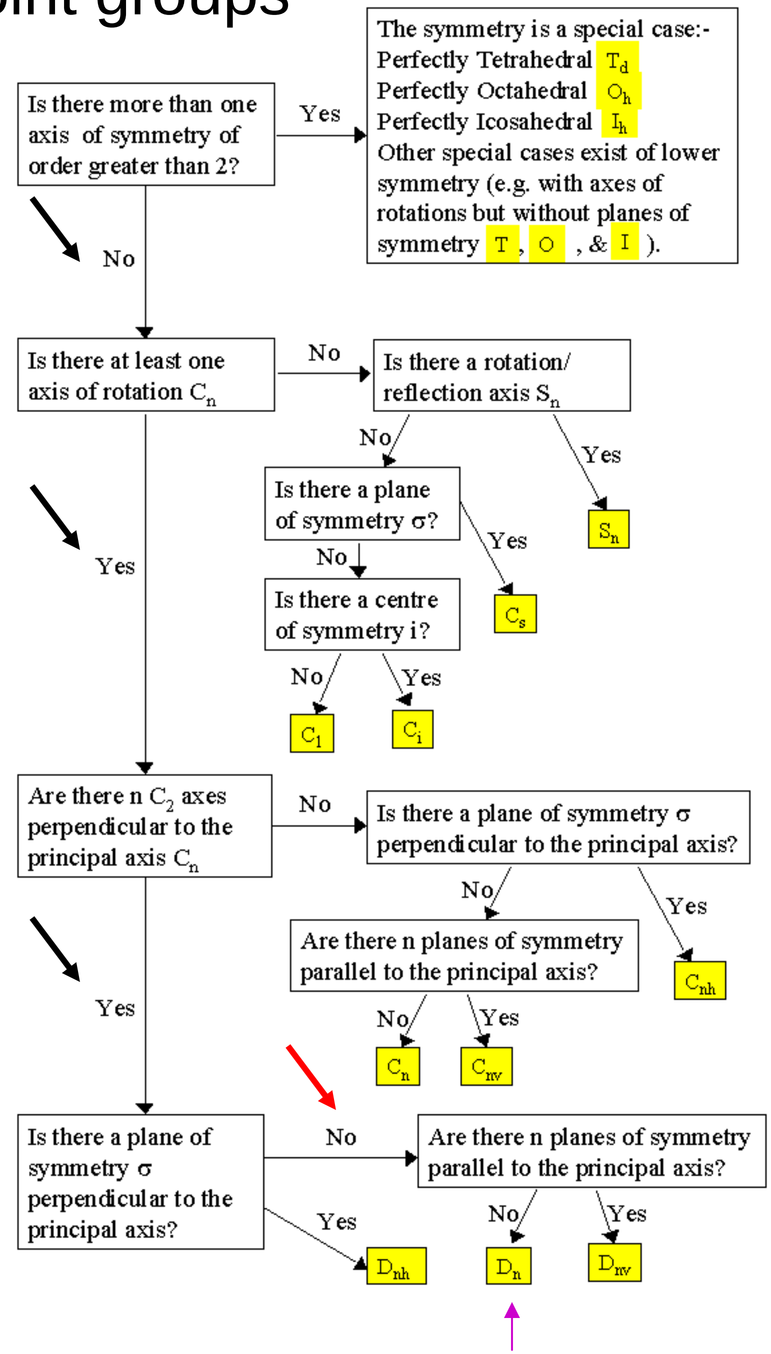
D_n *type groups:*

A C_n axis, n perpendicular C_2 axes and **no mirror planes** (D_n)

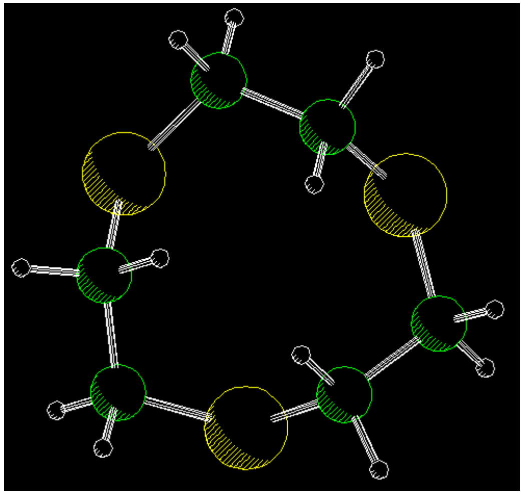
-propellor shapes

e.g. $Ni(CH_2)_4$ (D_4)



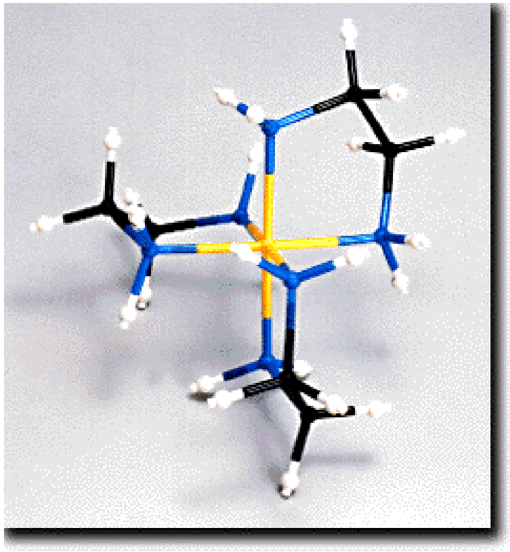


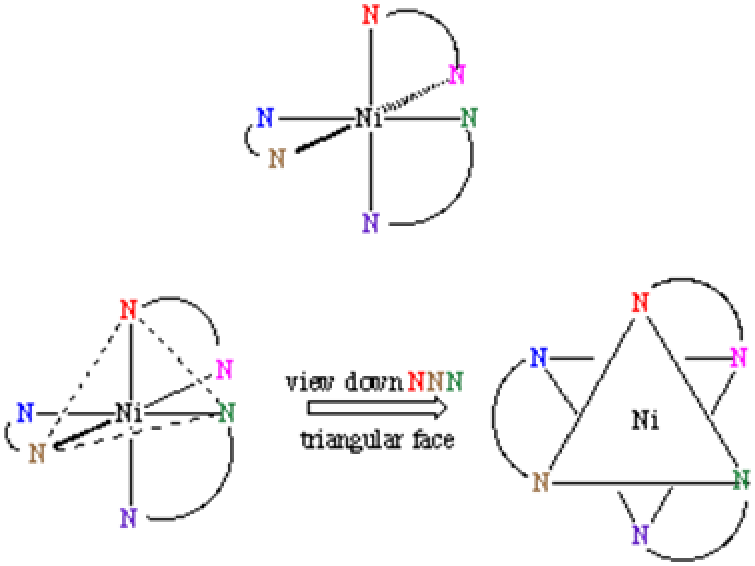
e.g. $(SCH_2CH_2)_3$ (D_3 conformation is important!)



e.g. propellor (D_3)

e.g. $Ni(en)_3$ (D_3 conformation is important!) en = $H_2NCH_2CH_2NH_2$



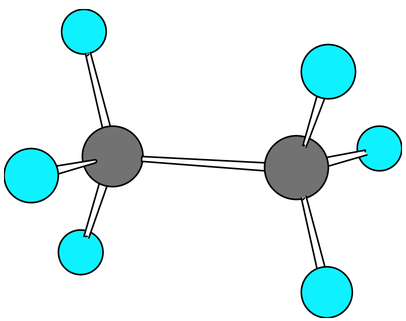


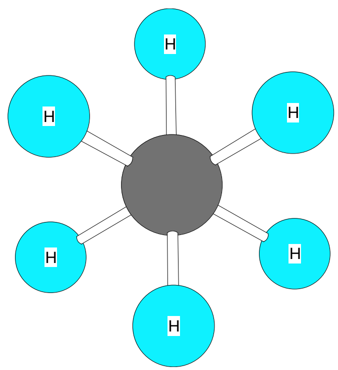
Chem 59-250 Identifying point groups

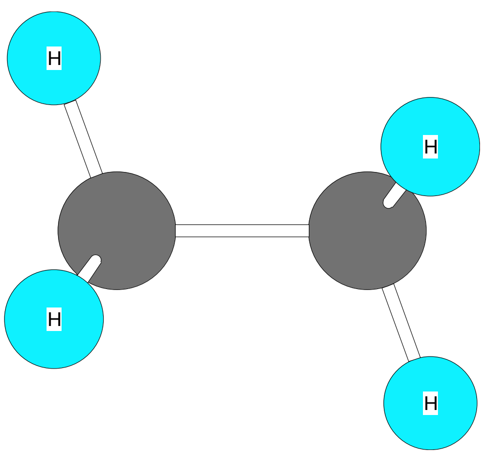
D_n type groups:

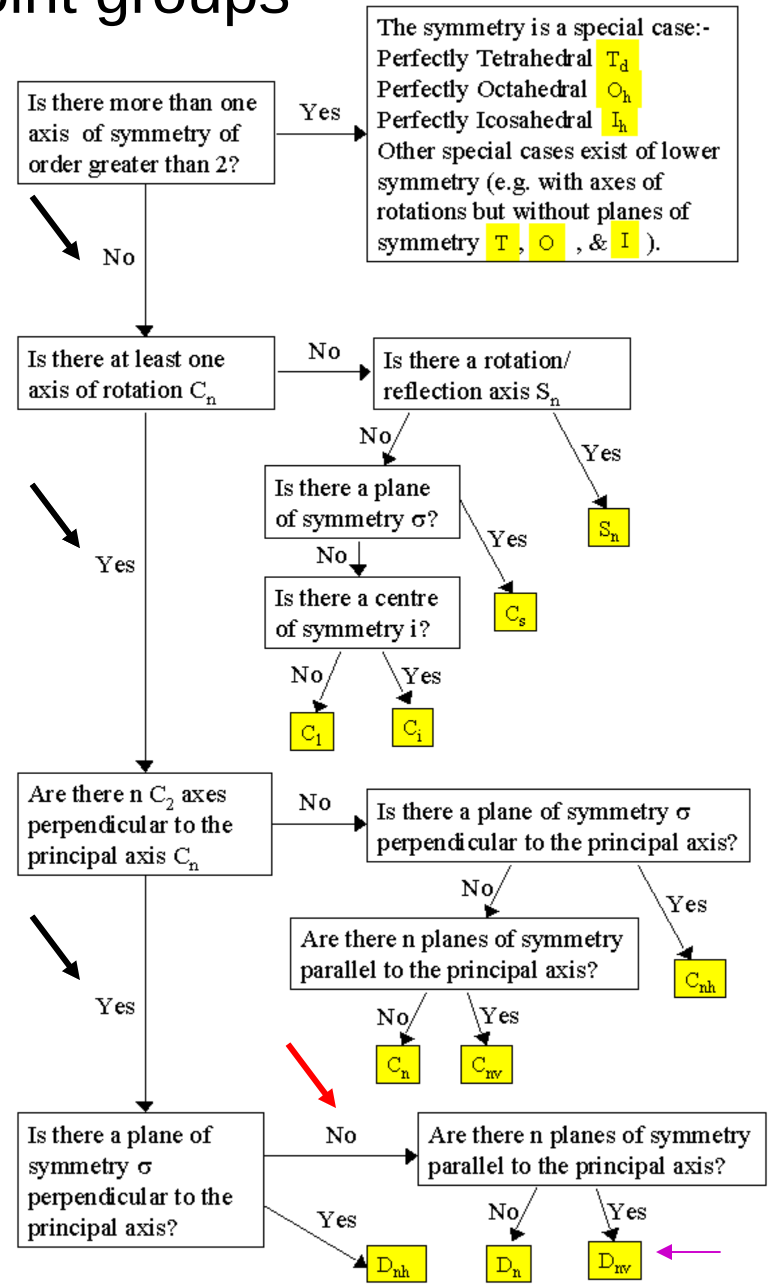
A C_n axis, n perpendicular C_2 axes and a σ_d (D_{nd})

e.g. ethane, $H_3C\text{-}CH_3$
(D_{3d} in the staggered conformation)

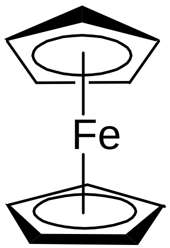


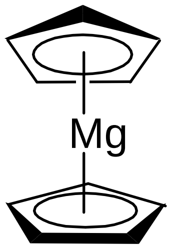


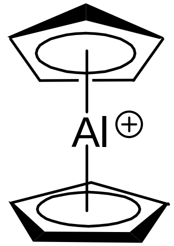


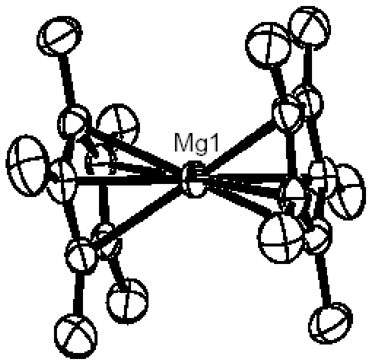


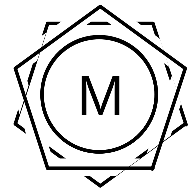
dihedral means between sides or planes – this is where you find the C_2 axes e.g. $Mg(\eta^5\text{-}Cp)_2$ and other metallocenes in the staggered conformation (D_{5d})



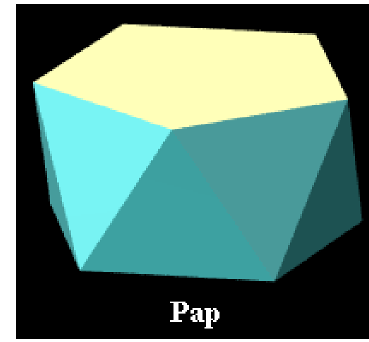






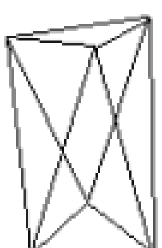


View down the C_5 axis

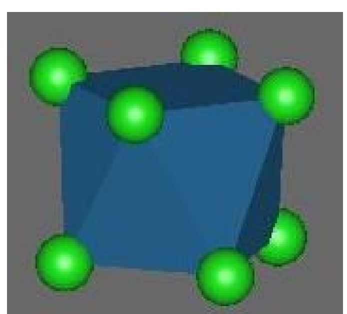


These are pentagonal antiprisms

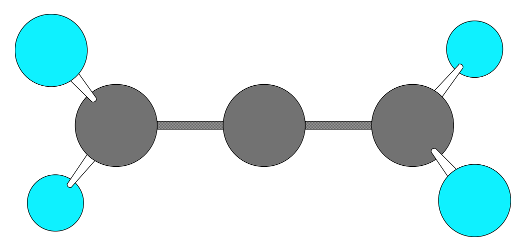
e.g. triagular antiprism (D_{3d})



e.g. square antiprism (D_{4d})



e.g. allene or a tennis ball (D_{2d})



Identifying point groups

We can use a flow chart such as this one to determine the point group of any object. The steps in this process are:

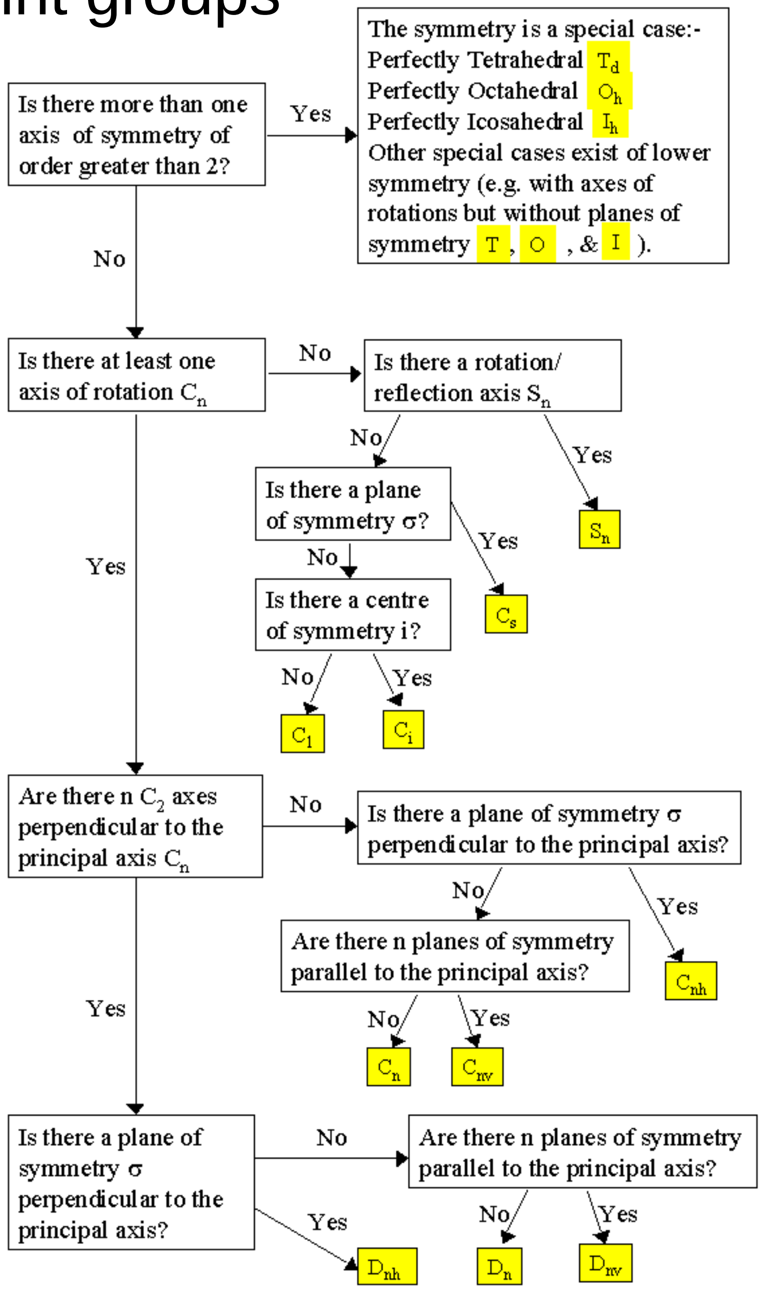
1. Determine the symmetry is special (e.g. tetrahedral).

2. Determine if there is a principal rotation axis.

3. Determine if there are rotation axes perpendicular to the principal axis.

4. Determine if there are mirror planes and where they are.

5. Assign point group.



NMR Spectroscopy and Symmetry

One type of spectroscopy that provides us structural information about molecules is Nuclear Magnetic Resonance (NMR) spectroscopy. An understanding of symmetry helps us to understand the number and intensity of signals we will observe.

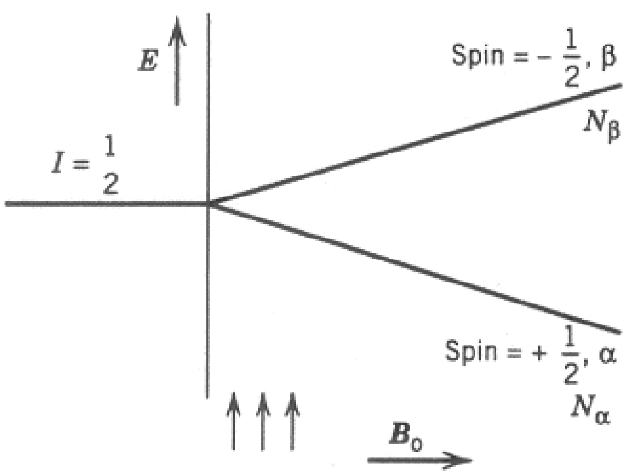
As with electrons, nuclei also have a spin quantum number, *I*. When *I* = 1/2, the possible values are +1/2 and -1/2. **In a magnetic field**, the nuclei have slightly different energies; we can measure this difference, ΔE, to produce a spectrum. The actual ΔE for a nucleus depends on the strength of the magnetic field and on its **exact molecular environment** so these are typically reported as a field-independent chemical shift, δ. Since the differences in the energies of signals that are observed are very small, the chemical shift is reported in parts per million (ppm) with respect to a reference compound selected for each nucleus: $\delta = [(\nu_{obs} - \nu_{ref})\times10^6] / \nu_{ref}$. In practice, *only atoms that are related by symmetry will have the same* ***chemical shift***.

$\Delta E = (h\nu/2\pi)B_o$

h = Plank's constant

B_o = strength of the magnetic field

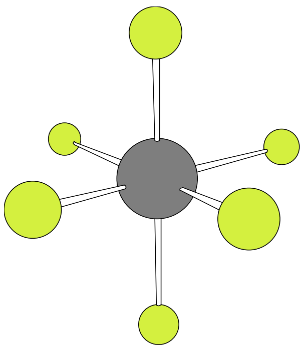
ν = frequency of signal (radio frequency)



This means that the number of signals in a spectrum tells provides the number of nuclei that are not related by symmetry and the relative intensity of each signal is proportional to the number of nuclei that are related to each other by symmetry.

Chem 59-250 NMR Spectroscopy and Symmetry

This means that we can determine the symmetry of a molecule based on the number of signals that we see in the appropriate NMR spectrum (or vice versa). As an example, here are the number of signals that we would predict for the ^{19}F NMR spectrum of a series of hexa-haloantimonate anions.

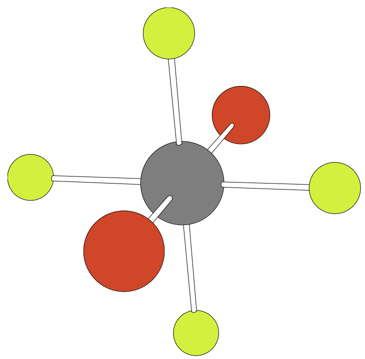


$[SbF_6]^-$

p.g.: O_h

All F's related

1 signal

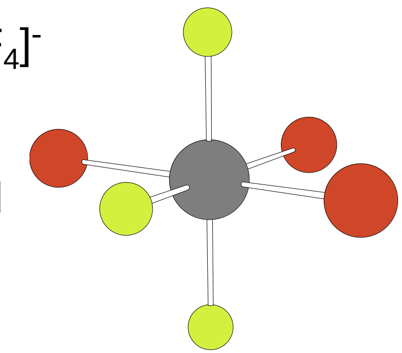


trans-$[SbBr_2F_4]^-$

p.g.: D_{4h}

All F's related

1 signal

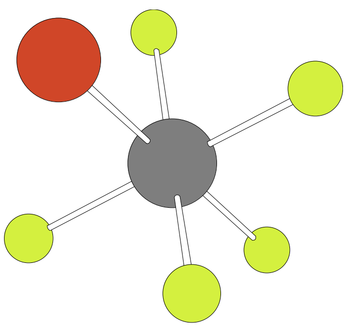


mer-$[SbBr_3F_3]^-$

p.g.: C_{2v}

2 signals

2:1 intensity

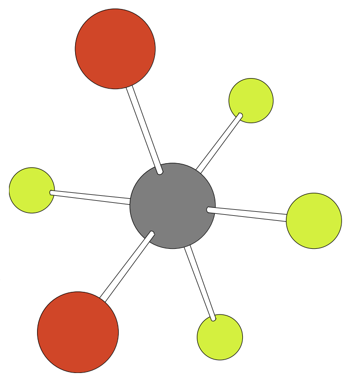


$[SbBrF_5]^-$

p.g.: C_{4v}

2 signals

4:1 intensity

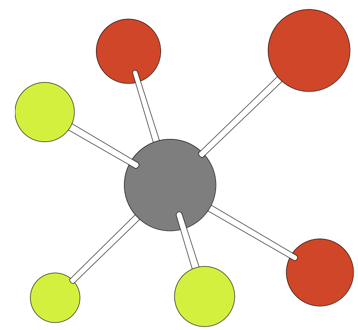


cis-$[SbBr_2F_4]^-$

p.g.: C_{2v}

2 signals

1:1 intensity



fac-$[SbBr_3F_3]^-$

p.g.: C_{3v}

All F's related

1 signal

This is a gross oversimplification! NMR is one of the most powerful spectroscopic techniques and you will get much more detailed treatments in other classes. Read H&S 3.11 to get an idea of what other information is provided by multinuclear NMR spectroscopy (e.g. homonuclear and heteronuclear coupling, dynamic processes, etc.) that we will ignore. For the purposes of this course, we will assume that the structures of the molecules are static and that there is no coupling.