

INDIAN INSTITUTE OF TECHNOLOGY PATNA

DEPARTMENT OF CHEMISTRY

CH 103

Instructor: Dr. Neeladri Das
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PhD: University of Utah, Salt Lake City, USA
Postdoc: University of California, Irvine, USA
Technical University, Dortmund, Germany

CH 103

- Lectures:
 - Tuesday — 10:00 – 10:55 am
 - Wednesday — 11:00 – 11:55 am
 - Thursday — 12:00 – 12:55 am
- Tutorial:
 - Monday — 9:00 – 9:55 am

Syllabus

- Inorganic

- Coordination chemistry:

- ligand, nomenclature, isomerism, stereochemistry, valence bond, crystal field and molecular orbital theories.

- Bioinorganic chemistry:

- Trace elements in biology, heme and non-heme oxygen carriers, haemoglobin and myoglobin;

- Organometallic chemistry.

- Organic

- Stereo and regio-chemistry of organic compounds, conformers.

- Bioorganic chemistry: amino acids, peptides, proteins, enzymes, carbohydrates, nucleic acids and lipids.

- Modern techniques in structural elucidation of compounds (UV – Vis, IR, NMR).

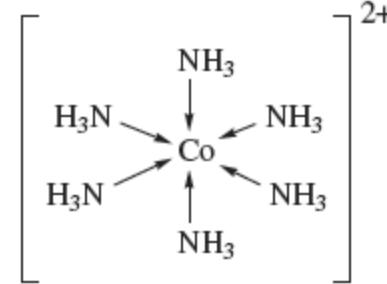
- Solid phase synthesis and combinatorial chemistry.

- Green chemical processes.

Inorganic portion

- Coordination chemistry
 - Ligands
 - nomenclature
 - isomerism
 - stereochemistry
 - valence bond
 - crystal field
 - molecular orbital theories

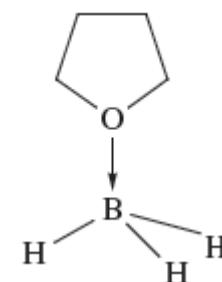
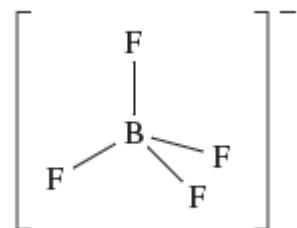
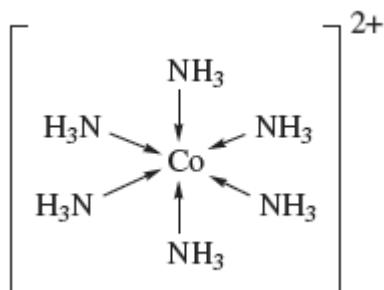
Ligands

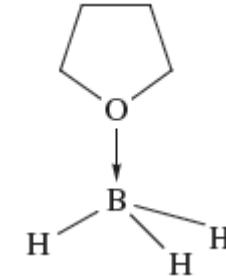
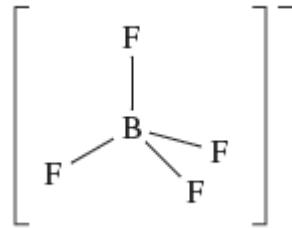
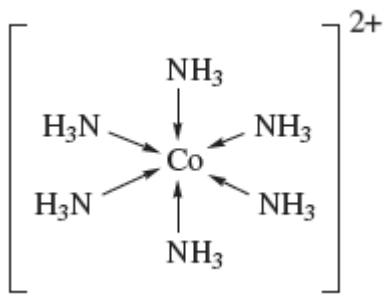


- The word ligand is derived from the Latin verb ‘ligare’ meaning ‘to bind’.
- In a coordination complex, a central atom or ion is coordinated by one or more molecules or ions (**ligands**)
- Ligands act as **Lewis bases**, forming coordinate bonds with the central atom or ion; the latter acts as a **Lewis acid**.
- Atoms in the ligands that are directly bonded to the central atom or ion are donor atoms.

Ligands

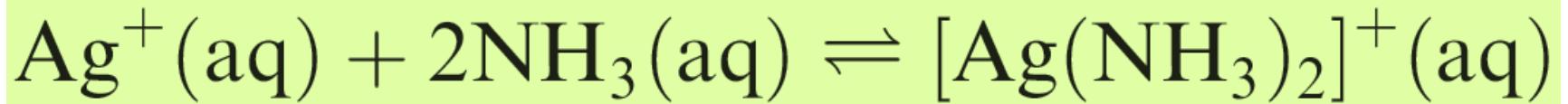
- Examples of coordination complexes include those involving d-block metal ions - $[\text{Co}(\text{NH}_3)_6]^{2+}$
- species with a central p-block element (e.g. $[\text{BF}_4]^-$, and $\text{H}_3\text{B}\cdot\text{THF}$)
- THF = tetrahydrofuran.



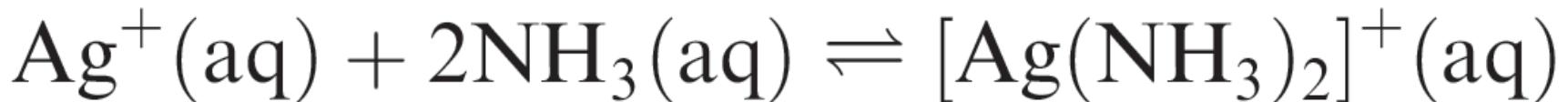


- When a Lewis base donates a pair of electrons to a Lewis acid, a **coordinate bond** is formed and the resulting species is an **adduct**.
- The centred dot in, for example, $\text{H}_3\text{B}\cdot\text{THF}$ indicates the formation of an adduct.
- The coordinate bond between the central atom or ion and a **neutral ligand** is denoted by an **arrow**, but if the **ligand is anionic**, the coordinate bond is indicated by a **line**.

Investigating coordination complex formation



- One method is to test the modifications of chemical properties
- What happens on adding a chloride-containing solution?
- no AgCl precipitate is observed
- What happens when iodide-containing solution is added?
- results in the precipitation of silver iodide



HOW TO RATIONALIZE THESE OBSERVATIONS:

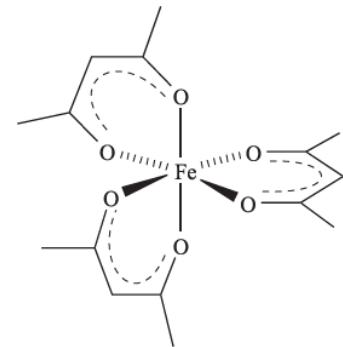
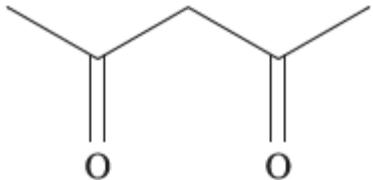
- AgI ($K_{sp} = 8.51 * 10^{-17}$) is much less soluble in aqueous solution than AgCl ($K_{sp} = 1.77 * 10^{-10}$).
- Why no AgCl is precipitated?
- the equilibrium constant for reaction is sufficiently large that the AgCl formed is soluble in the solution (i.e. very little uncomplexed Ag^+ is available for combination with Cl).
- The solubility of AgI is so low that even the formation of a small amount produces a precipitate.

Other methods to confirm complex formation

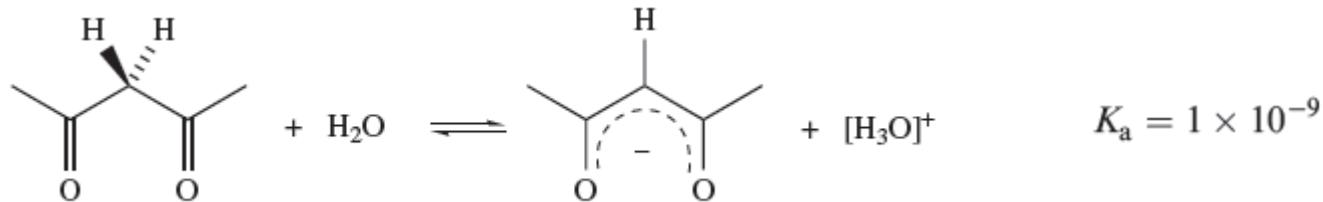
- Physical methods provide more reliable information
 1. spectroscopic,
 2. solubility or
 3. conductivity measurements
- Electronic spectroscopic method: UV-Visible spectroscopy
- Vibrational spectroscopic method: Infrared spectroscopy

List of common ligands

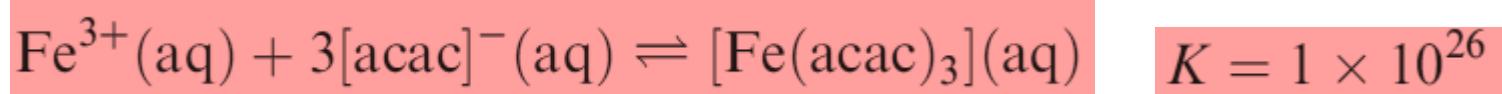
Anionic Ligands	Names	Neutral Ligands	Names
Br^-	bromo	NH_3	ammine
F^-	fluoro	H_2O	aqua
O^{2-}	oxo	NO	Nitrosyl
OH^-	Hydroxo	CO	Carbonyl
CN^-	cyano	O_2	dioxygen
$\text{C}_2\text{O}_4^{2-}$	oxalato	N_2	dinitrogen
CO_3^{2-}	carbonato	$\text{C}_5\text{H}_5\text{N}$	pyridine
CH_3COO^-	acetato	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethylenediamine



- Ligand is Hacac = the abbreviation for acetylacetone, the systematic name for which is pentane-2,4-dione
- Deprotonated ligand is anionic – forms neutral complex with M^{3+} such as $[Fe(acac)_3]$
- Neutral complexes are usually only sparingly soluble in water, but are often readily soluble in organic solvents.
- the red complex $[Fe(acac)_3]$ can be extracted from aqueous solution into benzene or chloroform
- the formation of $[Fe(acac)_3]$ is used as a means of extracting Fe(III) from aqueous solution.



- The formation of $[\text{Fe}(\text{acac})_3]$ in aqueous solution involves an equilibria



- The amount of complex formed depends on the pH of the solution.
- If the pH is too low**
 - H^+ ions compete with Fe^{3+} ions for the ligand.
- If the pH is too high**
 - $\text{Fe}(\text{III})$ is precipitated as $\text{Fe}(\text{OH})_3$ for which $K_{\text{sp}} = 2.64 * 10^{-39}$.



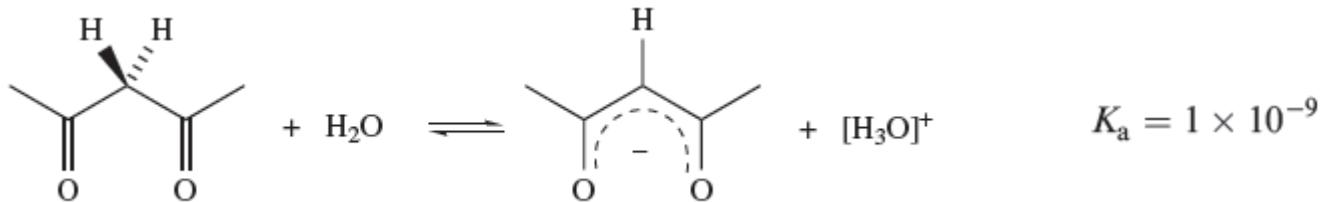
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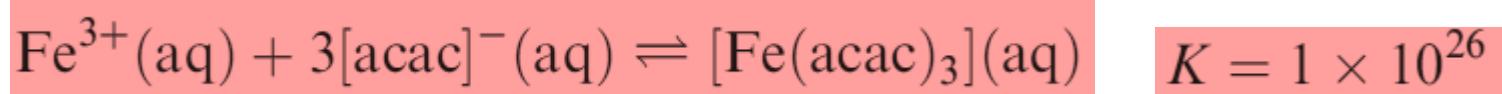
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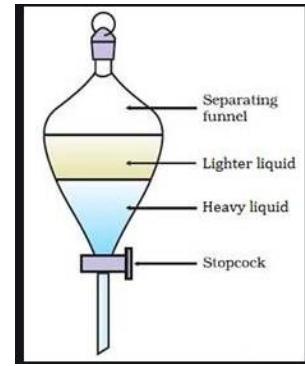
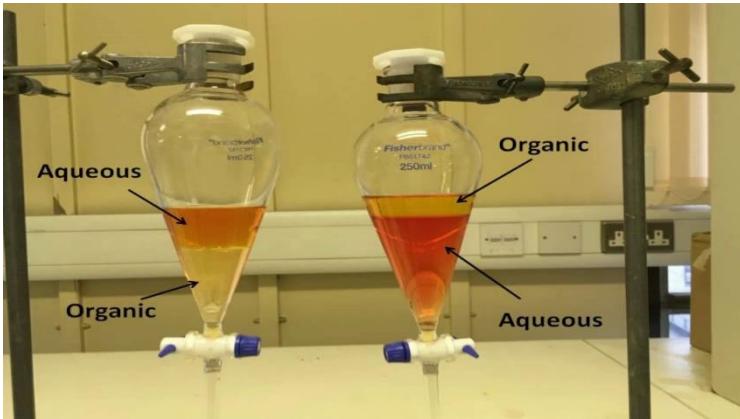
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Solvent extraction

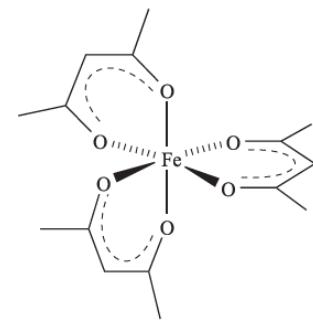
- Thus, there is an optimum pH for the extraction of Fe(III) from aqueous media using Hacac and a given organic solvent (e.g. CHCl_3).
- Accurate pH control is of great importance in studies of complex formation using certain ligands.
- Solvent extraction is important in the analytical and industrial separation of many metals.
- Apparatus used: separating funnel



- Solvent extraction involves the extraction of a substance using a suitable solvent;
- in a two-phase solvent system, the solute is extracted from one solvent into another,
- the extracting solvent being chosen so that impurities remain in the original solvent.
- **Benzene** : 0.876 g/cc ; **chloroform** : 1.49 g/cc

denticity of a ligand

- The number of donor atoms through which a ligand coordinates to a metal ion
- a **monodentate** ligand possesses one donor atom (e.g. NH_3),
- a **bidentate** ligand two (e.g. $[\text{acac}]$) and so on.
- In general, a ligand with more than one donor atom is termed **polydentate**.
- Coordination of a polydentate ligand to an ion leads to the formation of a **chelate ring**

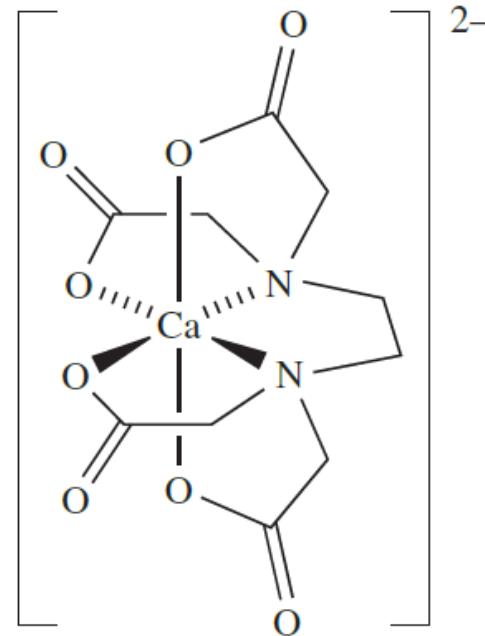
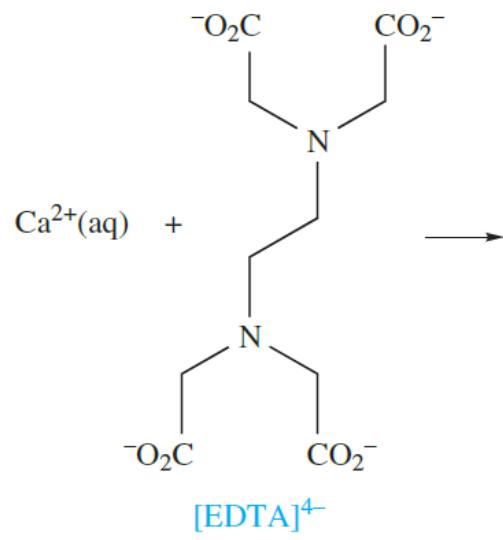


Chelate

- The word chelate is derived from the Greek for a crab's claw.
- some common chelating ligands
 - 1,2-Ethanediamine = (en)
 - Oxalate = $[ox]^{2-}$
 - 2,2'-Bipyridine = bpy or bipy
- These form 5-membered chelate rings on coordination to a metal ion
- coordination of $[acac]^-$ gives a 6-membered ring.
- **Both 5- and 6-membered chelate rings are common in metal complexes.**

Chelating ligands

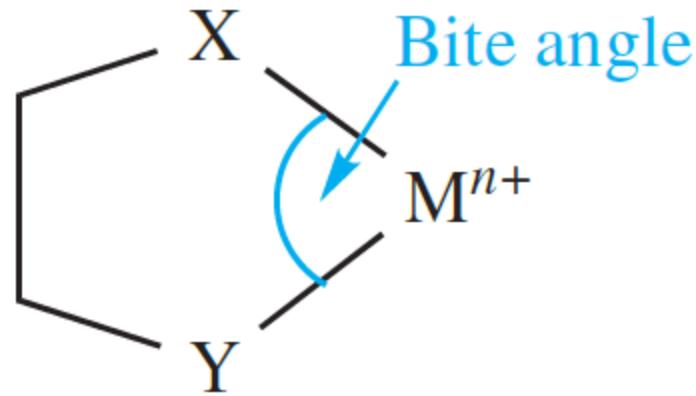
- EDTA = N,N,N',N'-Ethylenediaminetetraacetate ion (Hexadentate)
- How many chelate rings can be seen in $[\text{Ca}(\text{EDTA})]^{2-}$?
- Five
- Applications of edta?



Practical Applications of EDTA complexometric titrations

- determination of total hardness in water.
- analysis of calcium in dietary supplements
- evaluation of a water filtration system for its ability to remove calcium ions and decrease water hardness
- determination of calcium ion concentration in seawater,
- Analysis of calcium ions in human urine.
- zinc ion determination in cold lozenges,
- aluminum and magnesium ion determination in commercially available antacids,
- the evaluation of the aluminum content of antiperspirant.
- analysis of sulfate ions in water,

Bite angle



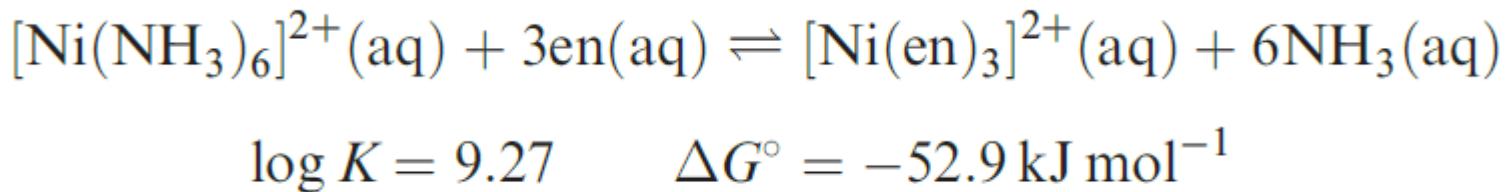
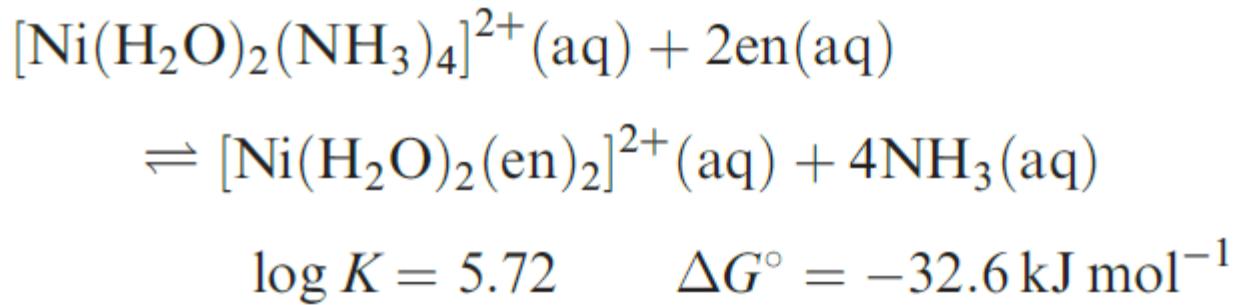
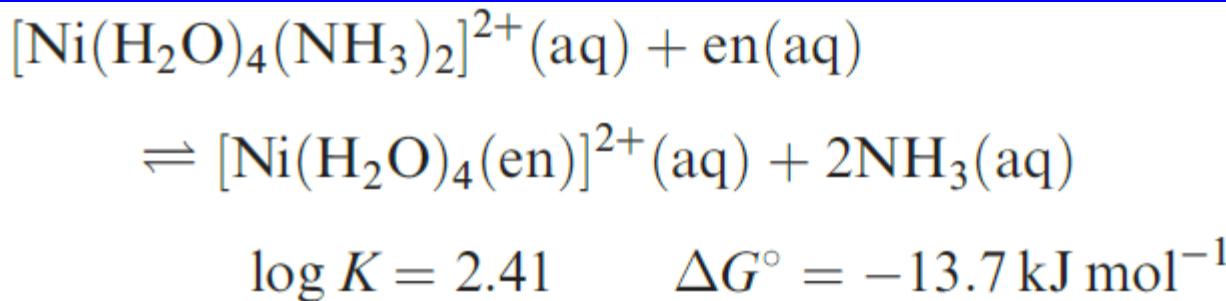
- Each chelate ring is characterized by a bite angle
 - the XMY angle where X and Y are the two donor atoms of the chelating ligand
- Ring-strain causes the formation of **3- and 4-membered** rings to be relatively **unfavourable**.

- experimental data reveal
 - small metal ions favour ligands that form **6-membered** chelate rings,
 - whereas **larger metal ions** favour ligands that give **5-membered** chelate rings.
- When diamines coordinate to larger metal ions (e.g. Pb^{2+} , Fe^{2+} , Co^{2+}), the most stable complexes tend to be those involving ligands that form **5-membered** chelate rings.

chelate effect

- For a given metal ion, the **thermodynamic stability of a chelated complex** (involving didentate or polydentate ligands) is **greater** than that of a complex containing a corresponding number of comparable monodentate ligands.

- For each monodentate ligand displacement, ΔG is **negative** and these data (or the values of $\log K$) illustrate that **the formation of each chelated complex is thermodynamically more favourable** than the formation of the corresponding ammine complex

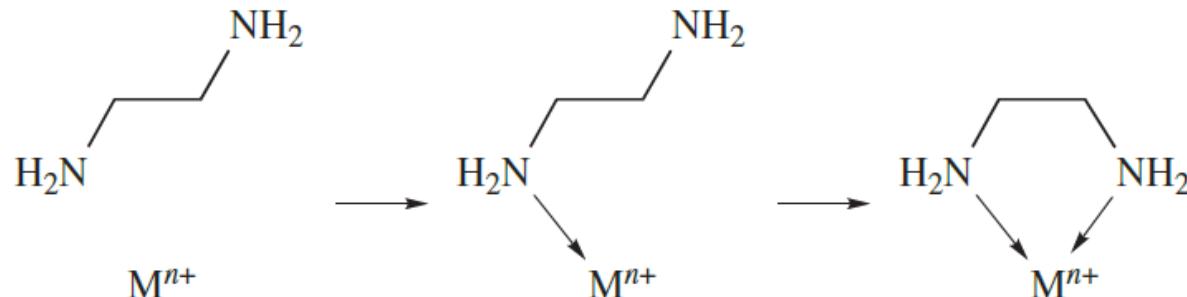


$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- For spontaneous reaction
 - negative ΔG
 - negative ΔH and
 - positive $T\Delta S$ terms
-
- Both enthalpy and entropy contribute to chelate effect

the enthalpy contribution to the chelate effect

- Compare NH_3 vs en
- a reduction in the electrostatic repulsion between the donor atoms (or negatively charged donor atoms in the case of some ligands) on going from two monodentate ligands (say NH_3) to one bidentate ligand (say en)
- an **inductive effect** of the CH_2CH_2 bridges in bidentate or polydentate ligands which **increases the donor strength of the ligand** with respect to a corresponding monodentate ligand, e.g. en versus NH_3 .





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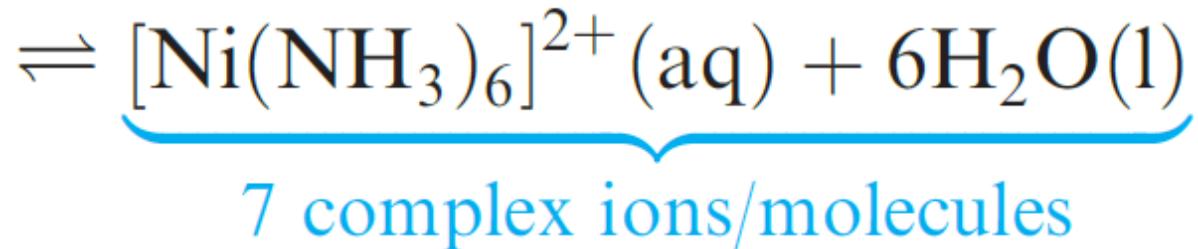
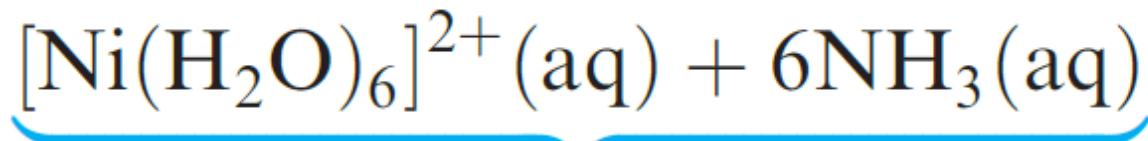
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entropy contribution to the chelate effect

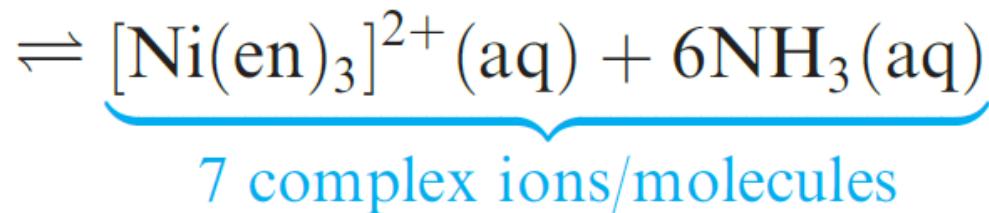
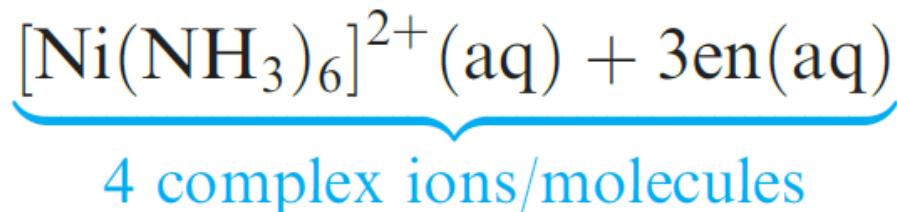


- In reaction involving monodentate ligands on both sides of the equation, there is no change in the number of molecules or complex ions on going from reactants to products.

entropy contribution

(interpreted as the degree of disorder or randomness in the system)

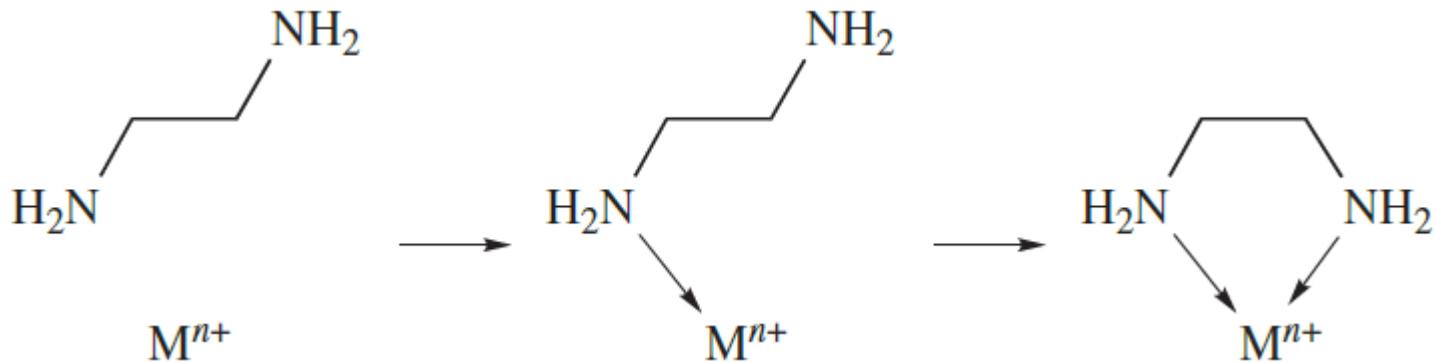
- reaction involving bidentate ligands replacing monodentate ligands



- the number of species in solution increases on going from reactants to products and there is a corresponding increase in entropy (**S is positive**).

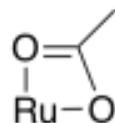
Chelate effect

- In forming a chelate ring, the probability of the metal ion attaching to the second donor atom is high because the ligand is already anchored to the metal centre.
- In contrast, the probability of the metal ion associating with a second monodentate ligand is much lower.

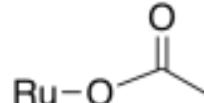


ligand with two donor centers

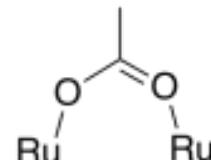
- Will a ligand with two donor centers always act as a bidentate chelating ligand?
- acetate ligand
- As a chelate :
- the four-membered ring through binding of both oxygens is a strained.
- Other binding modes
- binding through only one.
- Any other binding mode?
- one oxygen to bind to one metal atom and the other oxygen to bind to a second metal atom
- Bridging mode



bidentate mode
 κ^2 -acetate



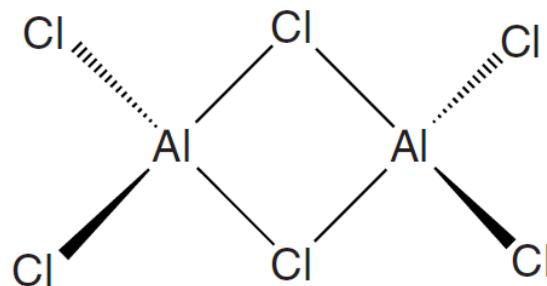
monodentate mode
 κ^1 -acetate



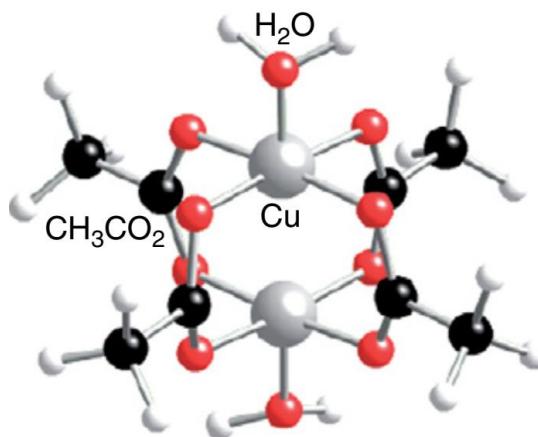
bridging mode
 μ -acetate

Bridging Ligands

- Form polynuclear species
 - **mu (μ)** as a prefix to the ligand formula or name



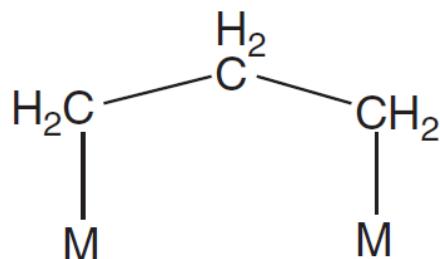
$[\text{Al}_2\text{Cl}_4(\mu\text{-Cl})_2]$ or $[\text{Cl}_2\text{Al}(\mu\text{-Cl})_2\text{AlCl}_2]$



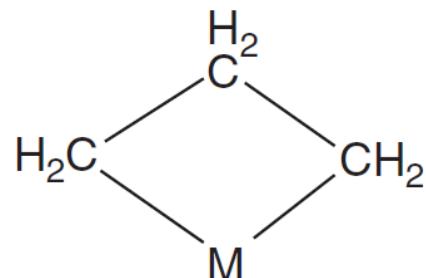
$$[(\text{H}_2\text{O})\text{Cu}(\mu\text{-CH}_3\text{CO}_2)_4\text{Cu}(\text{OH}_2)]$$

Bridging/Chelating Ligand

- mu (μ) convention



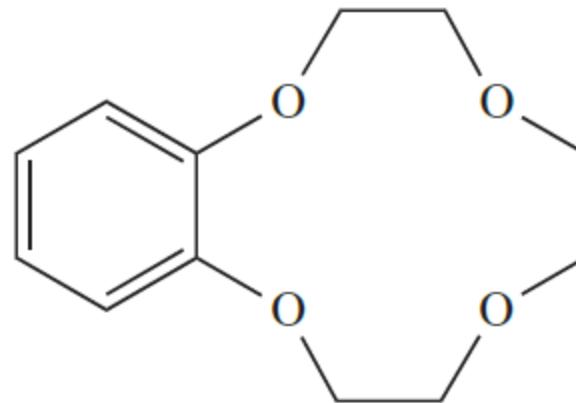
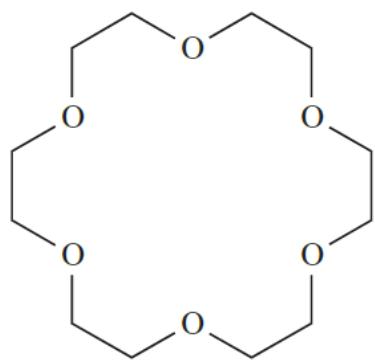
μ -propane-1,3-diyl
(bridging)



propane-1,3-diyl
(chelating)

macrocyclic ligands

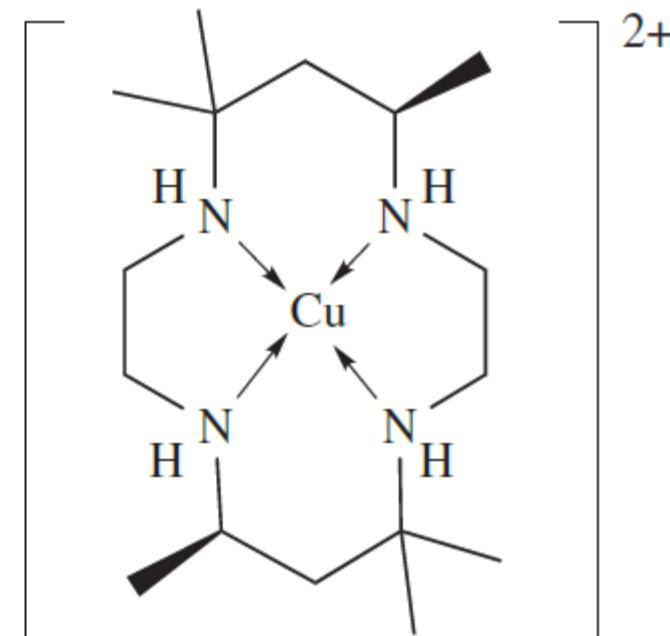
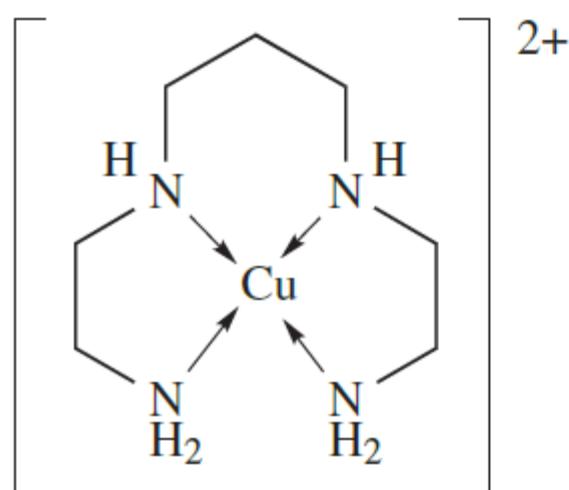
- includes the family of crown ethers
- (for example, 18-crown-6 and benzo-12-crown-4)



- Complex stability is enhanced when a macrocyclic ligand replaces a comparable acyclic (open-chain) ligand.

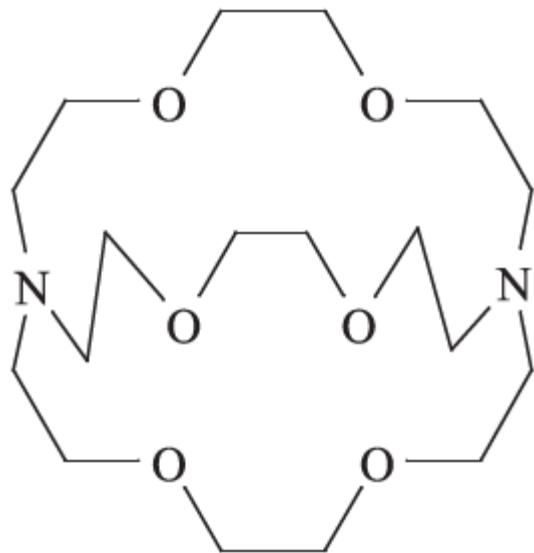
Macrocyclic effect

- A macrocyclic complex has far **greater thermodynamic stability** than a chelate complex.

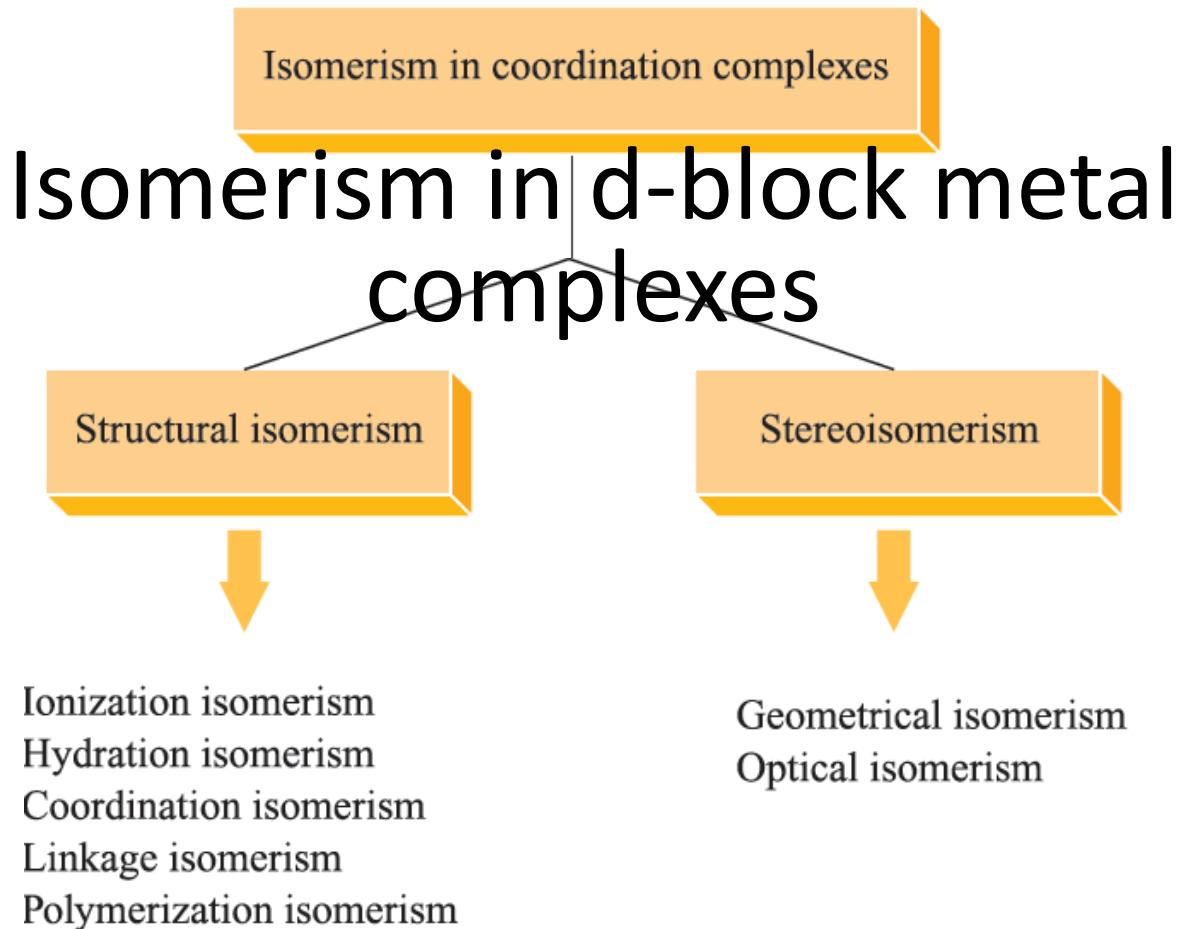


Cryptand ligand and Cryptate

- A cryptand is a polycyclic ligand containing a cavity
- When the ligand coordinates to a metal ion, the complex ion is called a cryptate.



Classification of types of isomerism in metal complexes



Structural isomerism: ionization isomers

- result from the interchange of an anionic ligand within the first coordination sphere with an anion outside the coordination sphere.
- **violet $[\text{Co}(\text{NH}_3)_5\text{Br}][\text{SO}_4]$** and
- **red $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$**
- These isomers can be readily distinguished by appropriate qualitative tests for ionic sulfate or bromide, respectively.

Structural isomerism: hydration isomers

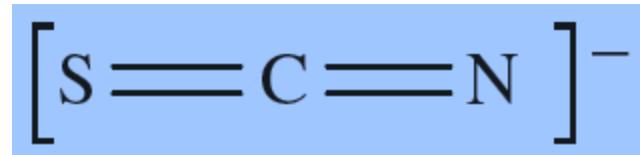
- result from the **interchange of H₂O and another ligand** between the first coordination sphere and the ligands outside it.
- The classic example of hydrate isomerism: compound with formula CrCl₃·6H₂O.
- **[Cr(H₂O)₄Cl₂]Cl·2H₂O**
- Green crystals of chromium(III) chloride formed from a hot solution obtained by reducing chromium(VI) oxide with concentrated HCl.
- When this is dissolved in water, the chloride ions in the complex are slowly replaced by water to give blue-green **[Cr(H₂O)₅Cl]Cl₂·H₂O** and finally violet **[Cr(H₂O)₆]Cl₃**.
- The complexes can be distinguished by precipitation of the free chloride ion using aqueous silver nitrate.

Structural isomerism: coordination isomerism

- Coordination isomers are **possible only for salts in which both cation and anion are complex ions**;
- the isomers arise from interchange of ligands between the two metal centres.
- Examples of coordination isomers are:
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$;
- $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ and
 $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$;
- $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{IV}}\text{Cl}_6]$ and $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2][\text{Pt}^{\text{II}}\text{Cl}_4]$.

Structural isomerism: linkage isomerism

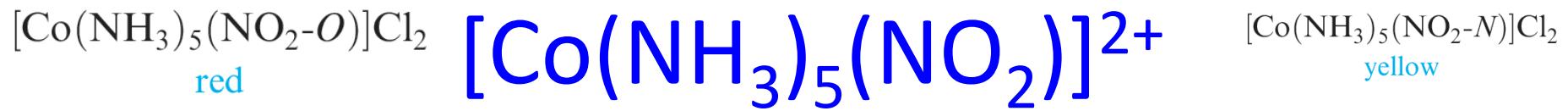
- Linkage isomers may arise when one or more of the ligands can coordinate to the metal ion in more than one way
- e.g. in $[\text{SCN}]^-$, both the N and S atoms are potential donor sites.



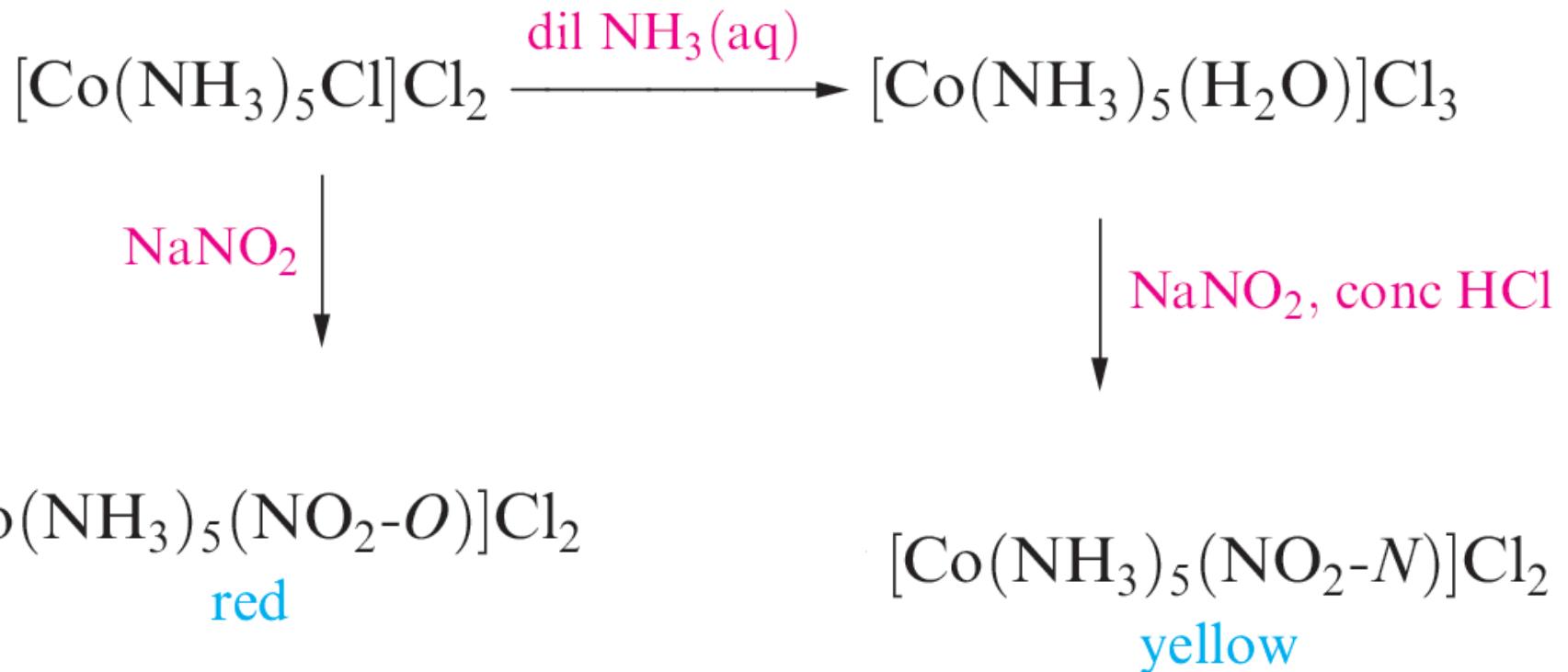
- thiocyanate can act as a nucleophile at either sulfur or nitrogen — it is an ambidentate ligand.

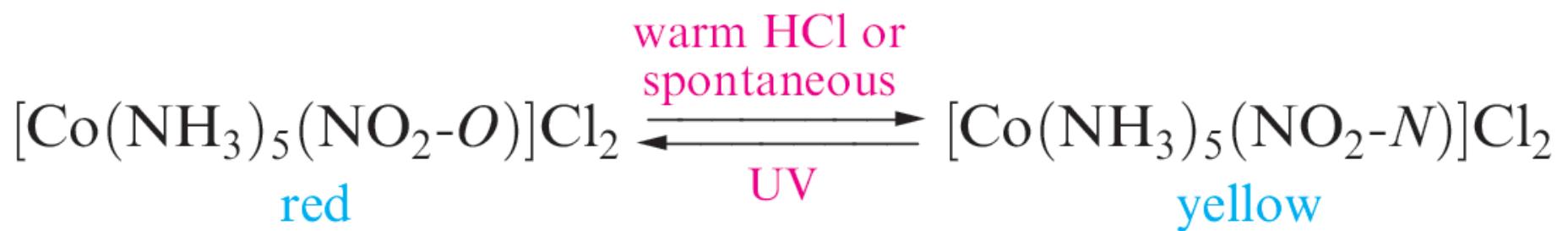
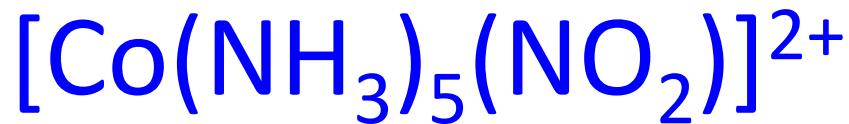
Structural isomerism: linkage isomerism

- Thus, the complex $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ has two isomers
- These are distinguished by using the following nomenclature:
- in $[\text{Co}(\text{NH}_3)_5(\text{NCS-N})]^{2+}$,
 - the thiocyanate ligand coordinates through the nitrogen donor atom;
- in $[\text{Co}(\text{NH}_3)_5(\text{NCS-S})]^{2+}$,
 - the thiocyanate ion is bonded to the metal centre through the sulfur atom.



- Another example of linkage isomers
- Synthesis





Structural isomerism: polymerization isomerism

- Polymerization isomers denote complexes which have the **same empirical formulae but different molecular masses**
- Examples of polymerization isomers are:
- $[\text{PtCl}_2(\text{NH}_3)_2]$ and $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$
- $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ and $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$.



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DEPARTMENT OF CHEMISTRY

CH 103

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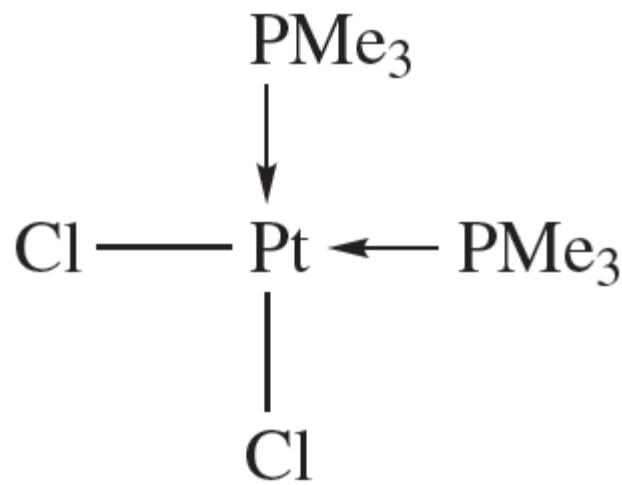
Associate Professor, Chemistry Dept., IIT Patna
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Chemistry department
IIT Patna

geometrical isomerism

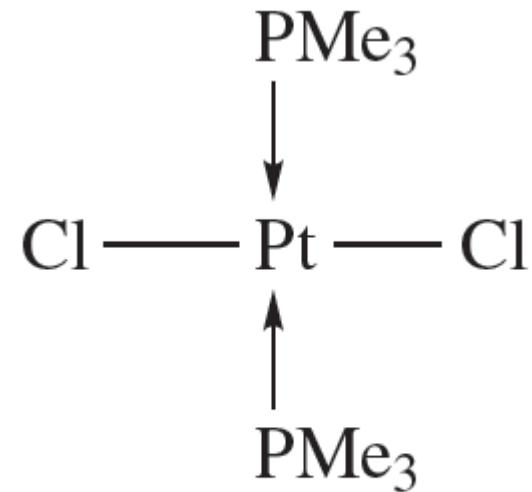
- Two species have the
 - same molecular formulae and
 - **same structural framework,**
 - but differ in the spatial arrangement of different atoms or groups about a **central atom** or a **double bond**, then the compounds are geometrical isomers.
- Where do we find such examples?
- Square planar species
- Octahedral species
- Trigonal bipyramidal species

Square planar species

- Square planar species of the general form EX_2Y_2 or EX_2YZ may possess cis- and trans-isomers.



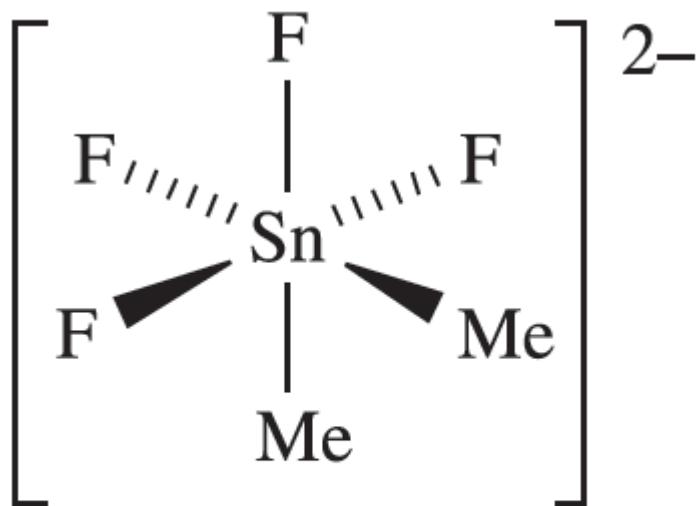
cis-isomer



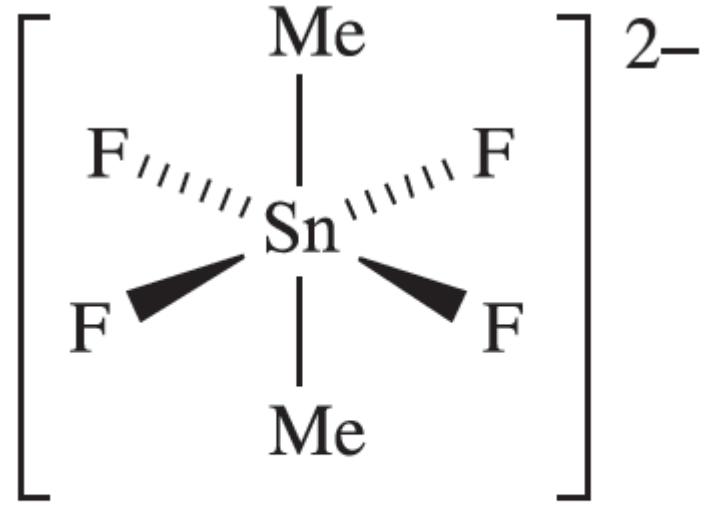
trans-isomer

Octahedral species: EX_2Y_4

- two types of geometrical isomerism associated with octahedral species.
- In EX_2Y_4 , the X groups may be mutually cis or trans



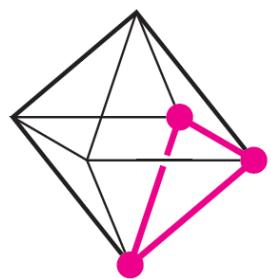
cis-isomer



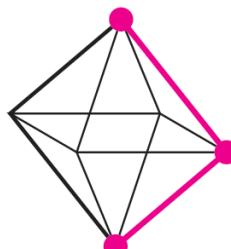
trans-isomer

Octahedral species : EX_3Y_3

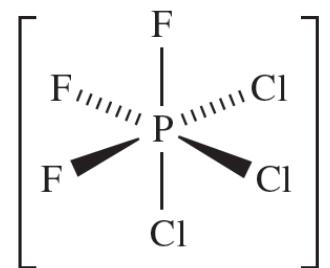
- If an octahedral species has the general formula EX_3Y_3 , then the X groups (and also the Y groups) may be arranged so as to define one face of the octahedron or may lie in a plane that also contains the central atom E.
- These geometrical isomers are labelled fac (facial) and mer (meridional) respectively.



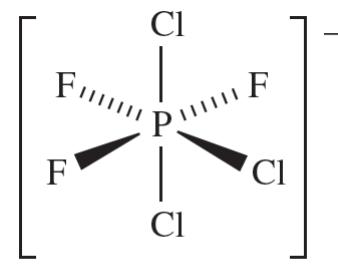
Facial
arrangement
fac-isomer



Meridional
arrangement
mer-isomer



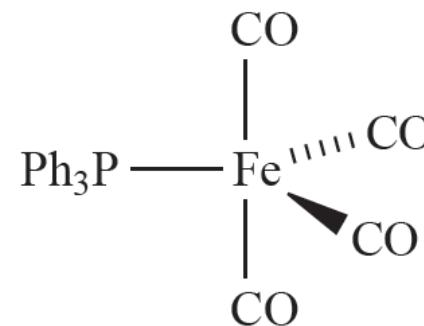
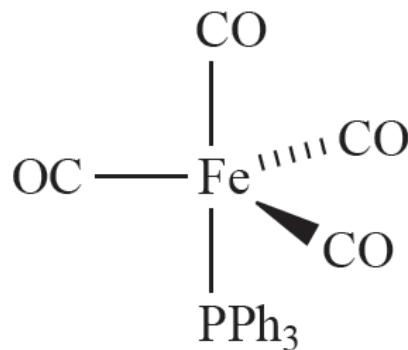
fac-isomer



mer-isomer

Trigonal bipyramidal species: EXY₄ type

- In trigonal bipyramidal EX₅, there are two types of X atom: axial and equatorial.
- This leads to the possibility of geometrical isomerism **when more than one type of substituent** is attached to the central atom.

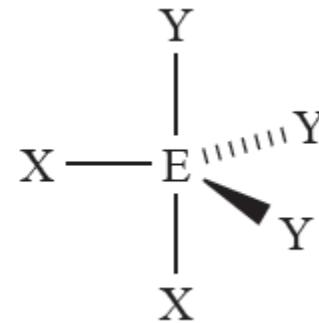
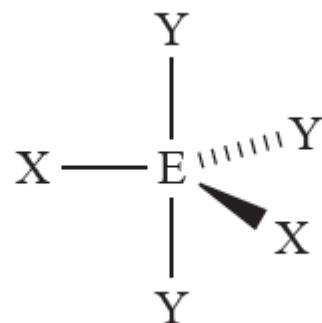
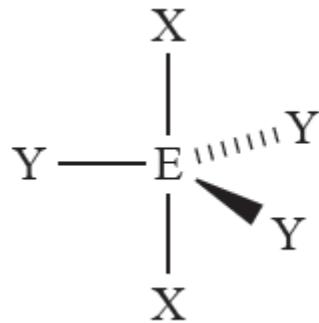


- two geometrical isomers are possible depending on **whether the PPh₃ ligand is axial or equatorial**.

Trigonal bipyramidal species:

EX_2Y_3 type

- **How many geometrical isomers are possible ?**
- depending on the relative positions of the X atoms, **three** geometrical isomers are possible.

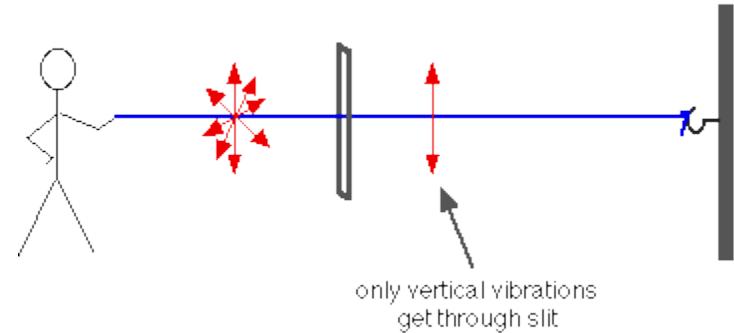
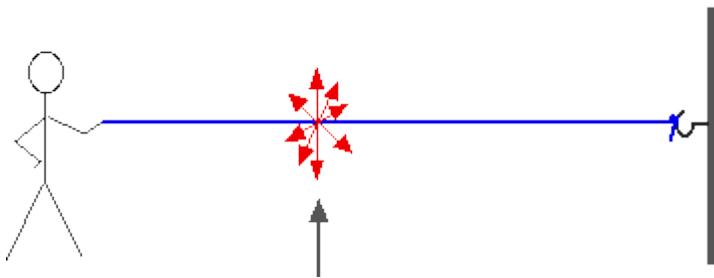


- **Which isomer is preferred given a set of ligands?**
- Steric factors may dictate which isomer is preferred for a given species

Other forms of geometrical isomers

- The existence of ions or molecules in different structures is just a special case of geometrical isomerism.
- e.g. $[\text{Ni}(\text{CN})_5]^{3-}$.
- trigonal bipyramidal and square-based pyramidal
- $[\text{NiBr}_2(\text{PBzPh}_2)_2]$ (Bz = benzyl)
- tetrahedral and square planar forms
- These can be distinguished by the fact that they exhibit different magnetic properties
- To complicate matters, square planar $[\text{NiBr}_2(\text{PBzPh}_2)_2]$ may exist as either trans- or cis-isomers.

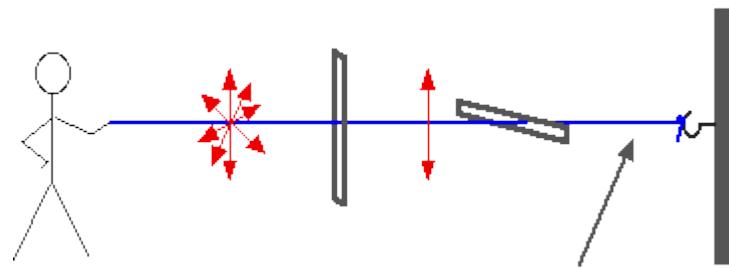
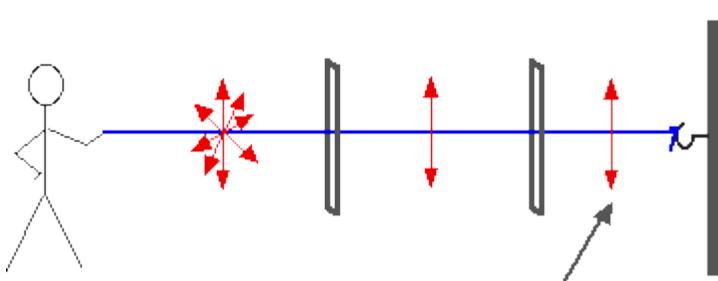
Plane polarized light



The string will be vibrating in all possible directions - up-and-down, side-to-side, and all the directions in-between - giving it a really complex overall motion

suppose you passed the string through a vertical slit. The only vibrations still happening the other side of the slit will be vertical ones. All the others will be prevented by the slit.

Plane polarized light

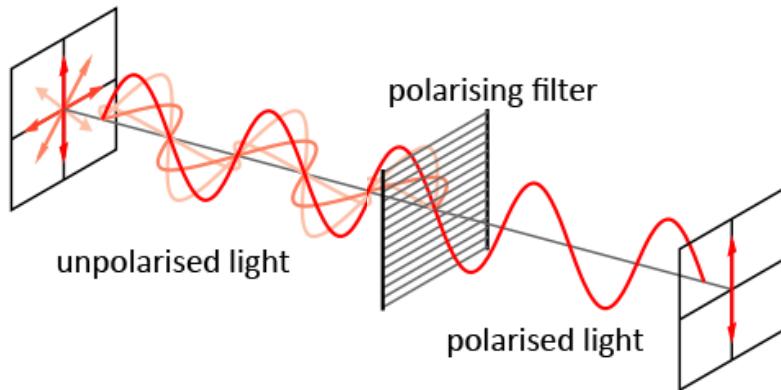


put a second slit on the string.
If it is aligned the same way as
the first one, the vibrations will
still get through.

if the second slit is at 90° to
the first one, the string will
stop vibrating entirely to the
right of the second slit.
The second slit will only let
through horizontal vibrations -
and there aren't any

Plane polarized light

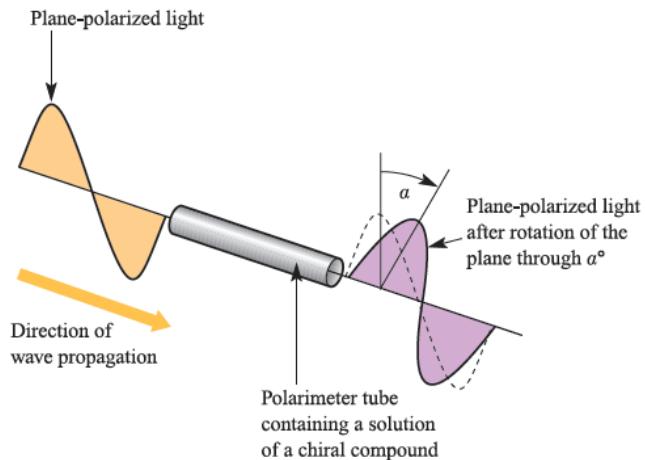
- Light is also made up of vibrations - this time, electromagnetic ones.
- Some materials have the ability to screen out all the vibrations apart from those in one plane and so produce **plane polarised light**.



- It is important not to take the string analogy too far. **The polaroid material doesn't consist of "slits"** in any sense of the word. The way it actually polarises the light is quite different.

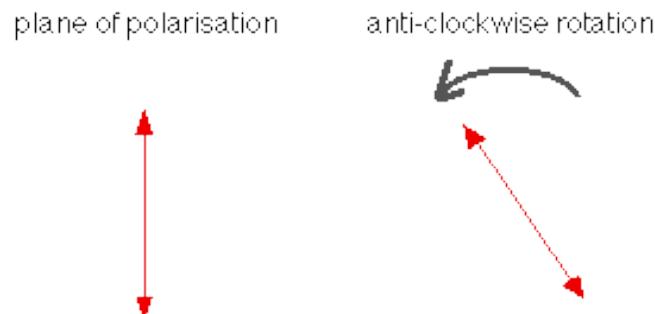
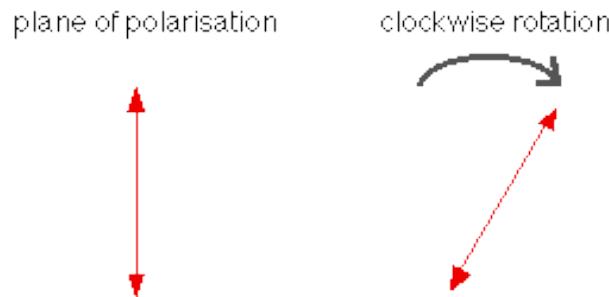
Optically active substances

- An optically active substance is one which can **rotate the plane of polarisation** of **plane polarised light**.
- if you shine a beam of polarised monochromatic light through a solution of an optically active substance, when the light emerges, its plane of polarisation is found to have rotated.

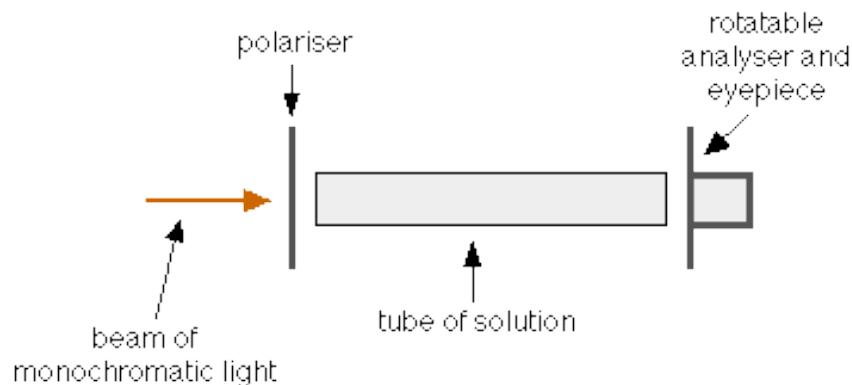


Optically active substances

- The rotation may be either clockwise or anti-clockwise.
- Assuming the original plane of polarisation was vertical, you might get either of these results.



- How can you tell that the plane of polarisation has been rotated?
- Use a polarimeter

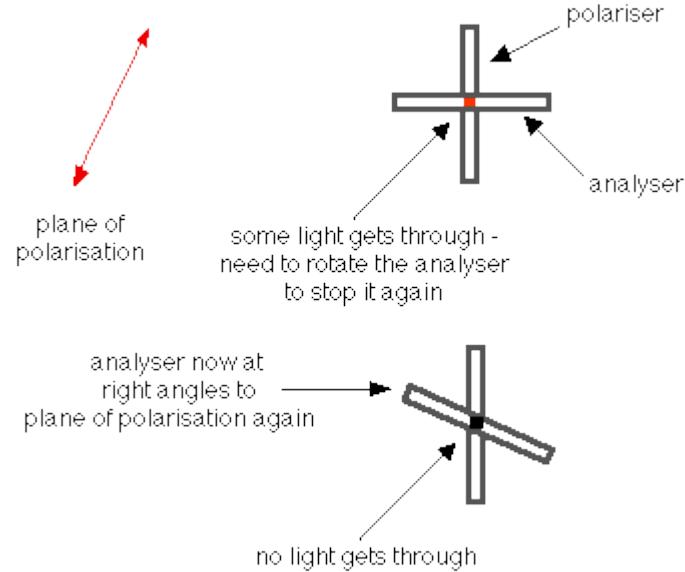
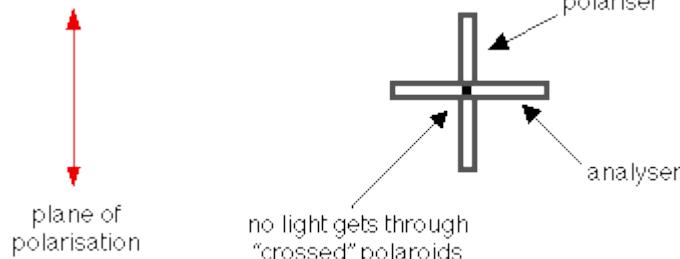


- The polariser and analyser are both made of polaroid material.

polarimeter

The polarimeter is originally set up with water in the tube. Water isn't optically active - it has no effect on the plane of polarisation.

The analyser is rotated until you can't see any light coming through the instrument. **The polaroids are then "crossed".**



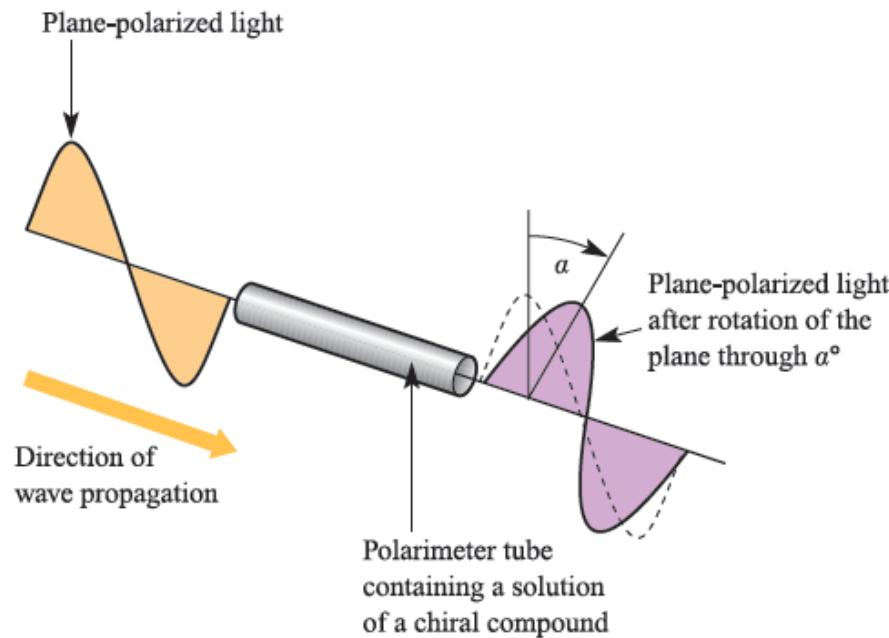
Now you put a solution of an optically active substance into the tube.

It rotates the plane of polarisation of the light, and so the analyser won't be at right-angles to it any longer and some light will get through.

You would have to rotate the analyser in order to cut the light off again.

Stereoisomerism: optical isomers

- Optical isomerism is concerned with chirality
- Chiral molecules can rotate the plane of plane-polarized light.
- This property is known as optical activity and the two mirror images are known as optical isomers or enantiomers.
- Enantiomers rotate the light to equal extents, but in opposite directions,
- the dextrorotatory (d) enantiomer to the right and the laevorotatory (l) to the left





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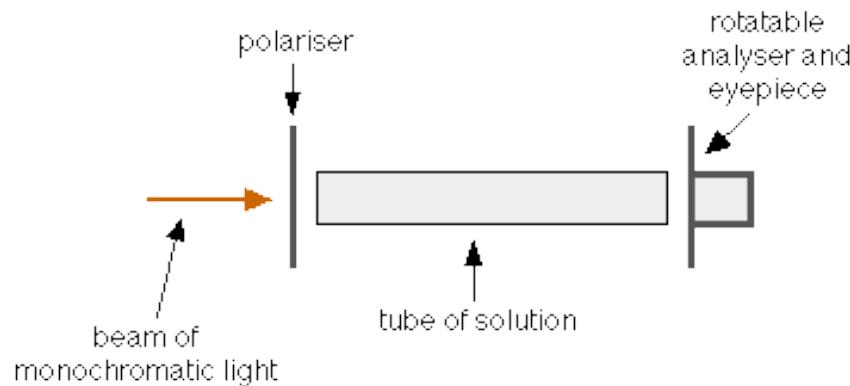
DEPARTMENT OF CHEMISTRY

CH 103

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- How can you tell that the plane of polarisation has been rotated?
- Use a polarimeter

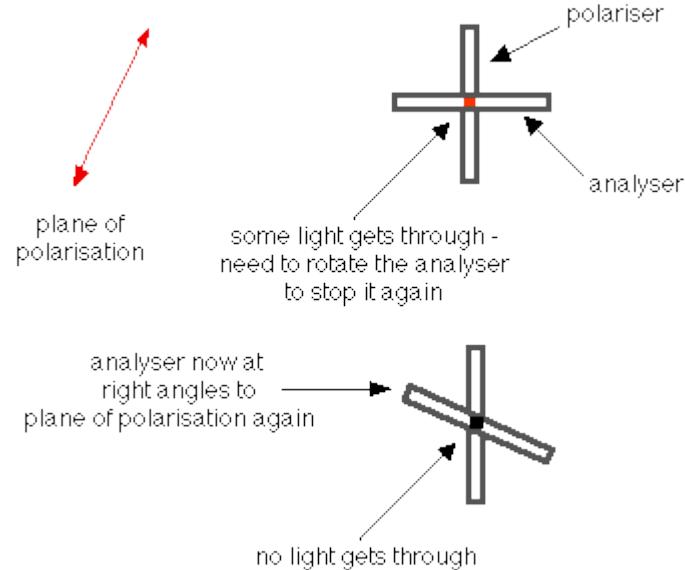
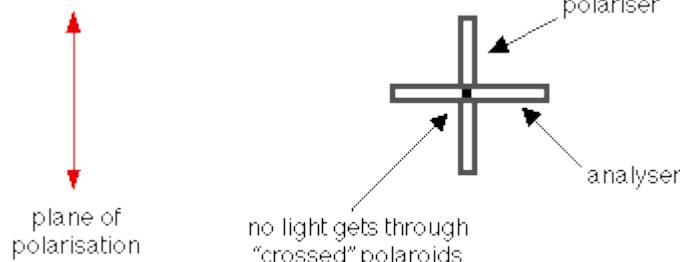


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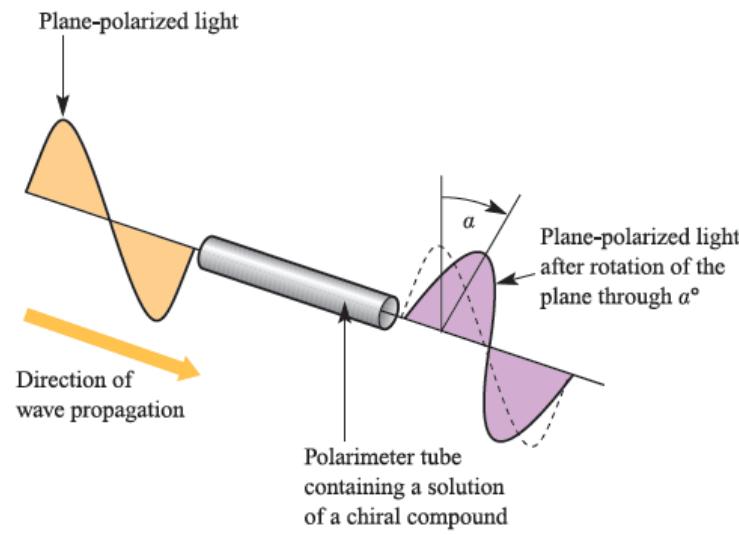
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You would have to rotate the analyser in order to cut the light off again.

Stereoisomerism: optical isomers

- Optical isomerism is concerned with chirality
- Chiral molecules can rotate the plane of plane-polarized light.
- **What is a chiral (from the Greek word for ‘hand’) molecule?**
- **A chiral molecule is a molecule that cannot be superimposed on its own mirror image**
- two mirror images : known as **optical isomers or enantiomers**.
- Enantiomers rotate the light to equal extents, but in opposite directions,
- the dextrorotatory (d) enantiomer to the right and the laevorotatory (l) to the left.



[Cr(acac)₃]



Λ -enantiomer



Δ -enantiomer

Mirror plane
through
which molecule
is reflected

The specific rotation $[\alpha]_D$

- The specific rotation, $[\alpha]$, for a chiral compound in solution is given by the following equation

$$[\alpha] = \frac{\alpha}{c \times l}$$

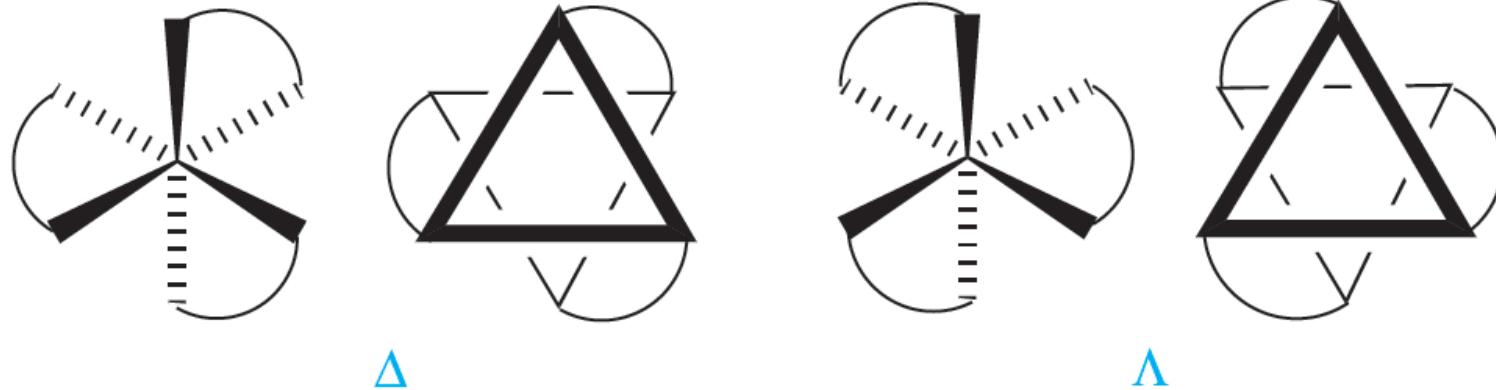
- α = observed rotation, l = path length of solution in the polarimeter (in dm) and c = concentration (in g/cm³).
- Light of a single frequency is used** for specific rotation measurements and a common choice is the sodium D-line in the emission spectrum of atomic sodium;
- the specific rotation at this wavelength is denoted as $[\alpha]_D$.

Stereoisomerism: optical isomers

- **Enantiomers**
 - pair of stereoisomers that are nonsuperposable mirror images.
- **Diastereomers**
 - stereoisomers that are not enantiomers.
- **(+)** and **(-)** prefixes: the specific rotation of enantiomers is equal and opposite,
- the sign of $[\alpha]_D$: a useful means of distinguishing between enantiomers.
- Thus, if two enantiomers of a compound A have $[\alpha]_D$ values of $+12^\circ$ and -12° , they are labelled **(+)-A** and **(-)-A**.
- (+)-A : rotates the plane of polarisation in a clockwise direction
- (-)-A : rotates the plane of polarisation in a anticlockwise direction

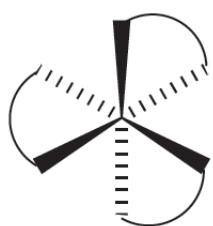
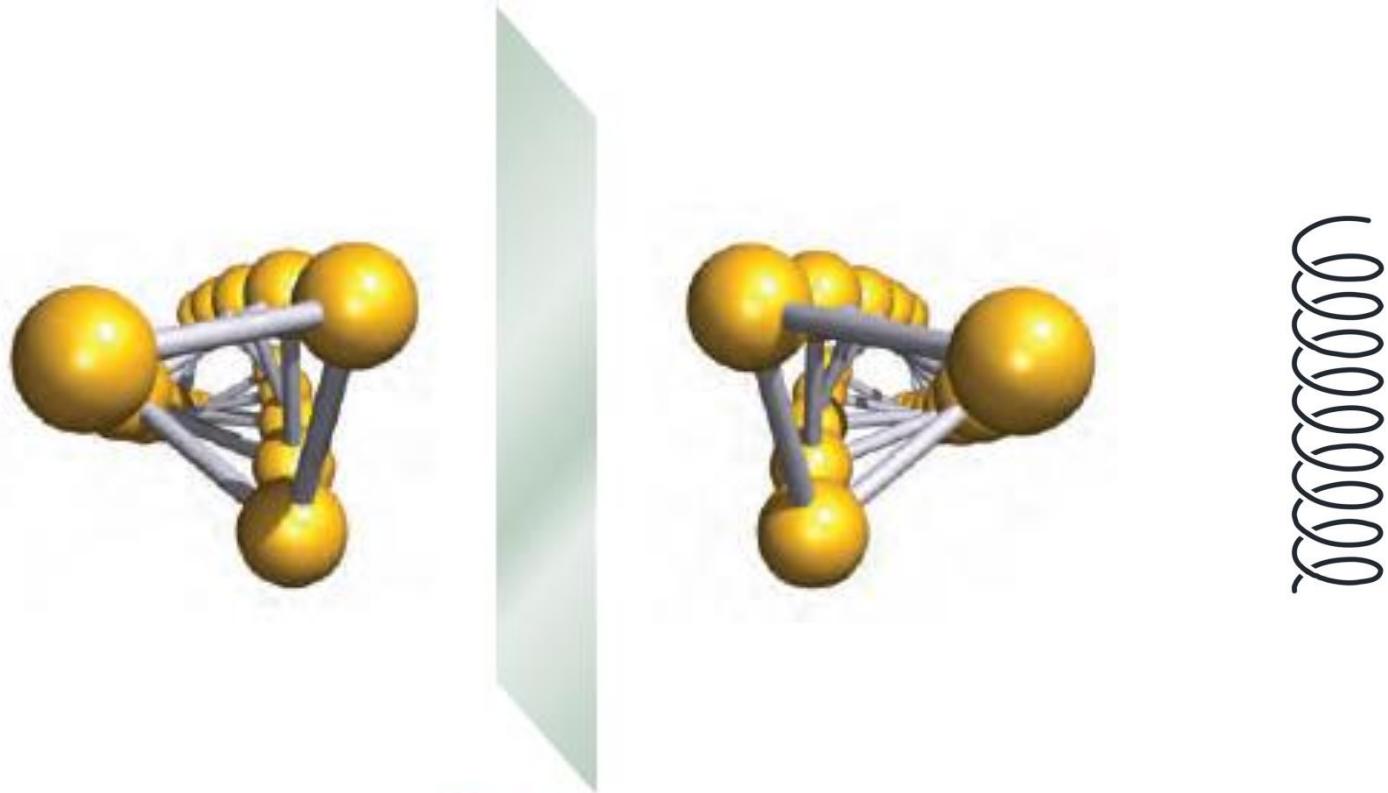
Δ and Λ notation for coordination complexes

- Δ and Λ prefixes: *enantiomers of octahedral complexes containing three equivalent didentate ligands (tris-chelate complexes)* are among those which are distinguished using (delta) and (lambda) prefixes.



- The octahedron is viewed down a three-fold axis, and the chelates then define either a right- or left-handed helix.
- The enantiomer with right-handedness is labelled Δ , and that with left-handedness is Λ .

right- or left-handedness of a helix



optical isomers tris-chelate complexes.

- The simplest case of optical isomerism among d-block complexes involves a metal ion surrounded by three didentate ligands
- $[\text{Cr}(\text{acac})_3]$ or $[\text{Co}(\text{en})_3]^{3+}$.
- Pairs of enantiomers such as Δ and Λ $[\text{Cr}(\text{acac})_3]$ differ only in their action on polarized light.

Separation of enantiomers

- So if a mixture of enantiomers is obtained, how can they be separated?
- **Conversion to diastereomers**

Separation of enantiomers

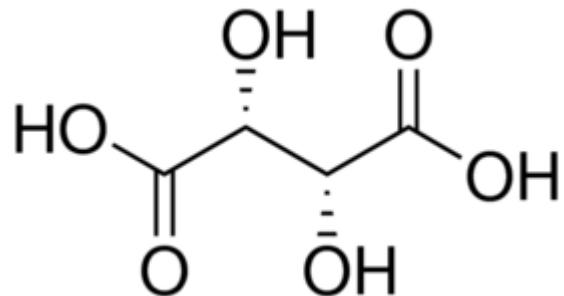
- for ionic complexes such as $[\text{Co}(\text{en})_3]^{3+}$, there is the opportunity to form salts with a chiral counter-ion A^- .
- These salts now contain two different types of chirality: the Δ – or Λ - chirality at the metal centre and the (+) or (–) chirality of the anion.

Separation of enantiomers

- Four combinations are possible of which the pair $\{\Delta\cdot(+)\}$ and $\{\Lambda\cdot(-)\}$ is enantiomeric as is the pair $\{\Delta\cdot(-)\}$ and $\{\Lambda\cdot(+)\}$.
- However, with a given anion chirality, the pair of salts $\{\Delta\cdot(-)\}$ and $\{\Lambda\cdot(-)\}$ are diastereomers
- These diastereomers may differ in the packing of the ions in the solid state, and separation by fractional crystallization is often possible.

Chiral anion

- Derived from Tartaric acid





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CH 103

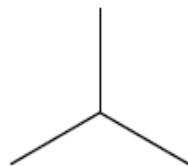
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IIT Patna

Coordination number and geometry

Three-coordination

trigonal plane



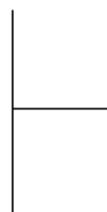
TP-3

trigonal pyramid



TPY-3

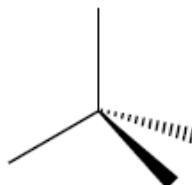
T-shape



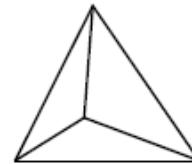
TS-3

Four-coordination

tetrahedron



T-4



square plane



SP-4

square pyramid



SPY-4

see-saw



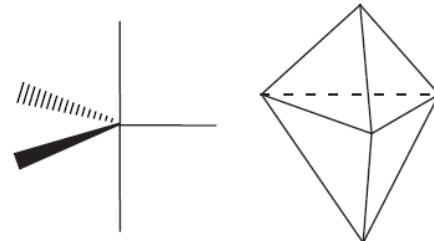
SS-4



Coordination number and geometry

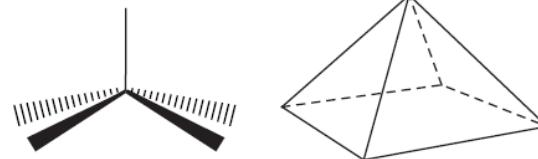
Five-coordination

trigonal bipyramid



TBPY-5

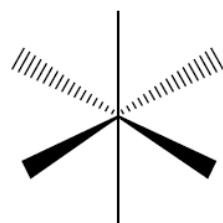
square pyramid



SPY-5

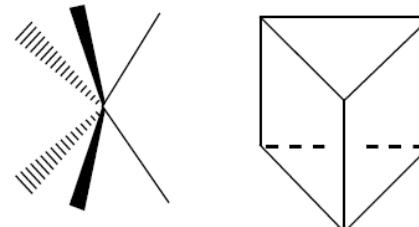
Six-coordination

octahedron



OC-6

trigonal prism

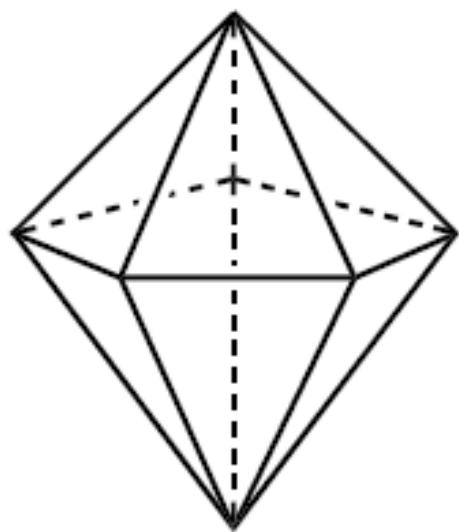


TPR-6

Coordination number and geometry

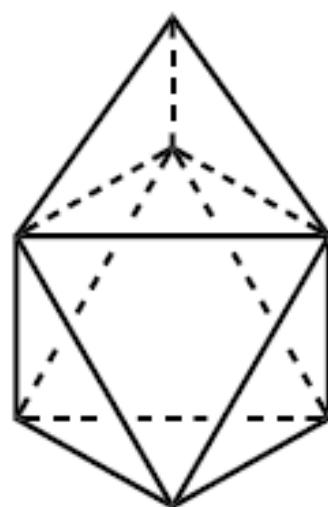
Seven-coordination

pentagonal
bipyramid



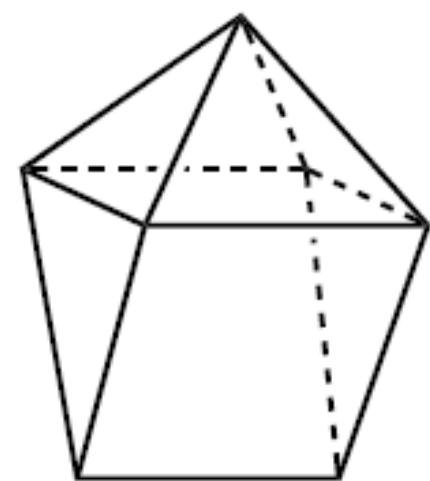
PBPY-7

octahedron, face
monocapped



OCF-7

trigonal prism,
square-face monocapped

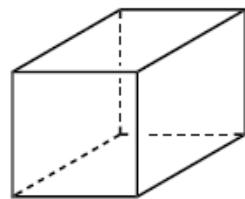


TPRS-7

Coordination number and geometry

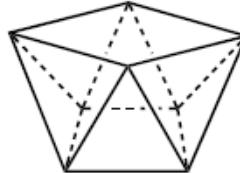
Eight-coordination

cube



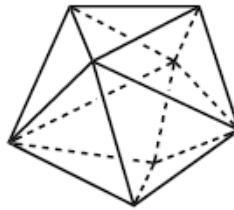
CU-8

square
antiprism



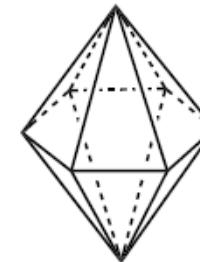
SAPR-8

dodecahedron



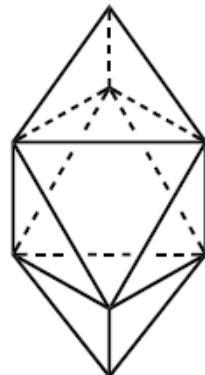
DD-8

hexagonal
bipyramid



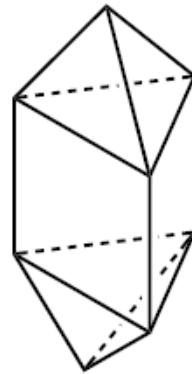
HBPY-8

octahedron,
trans-bicapped



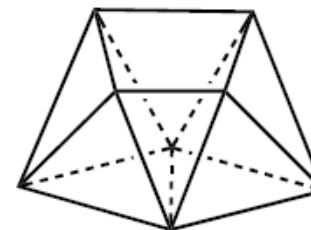
OCT-8

trigonal prism,
triangular-face bicapped



TPRT-8

trigonal prism,
square-face bicapped

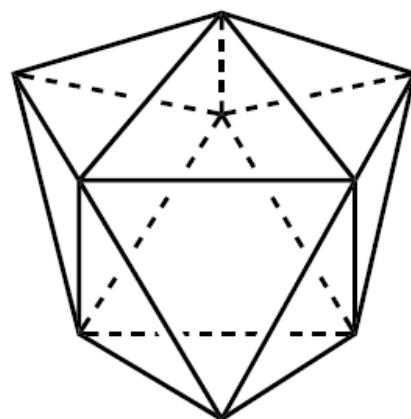


TPRS-8

Coordination number and geometry

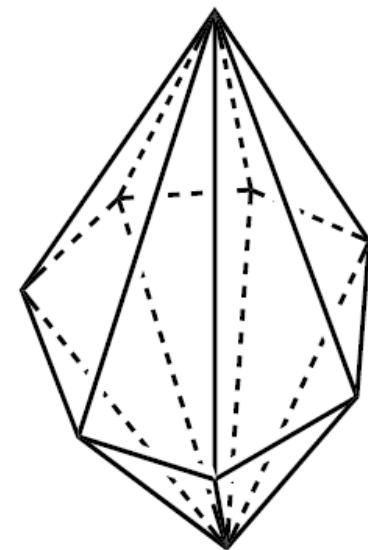
Nine-coordination

trigonal prism,
square-face tricapped



TPRS-9

heptagonal
bipyramid



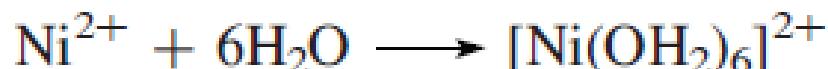
HBPY-9

Coordination nomenclature

- an additive nomenclature
- To name a coordination compound, no matter whether the complex ion is the cation or the anion, **always name the cation before the anion**

Example:

1. Addition of ligands to a central atom:



Addition of ligand names to a central atom name:

hexaaquanickel(II)

Naming Coordination Compounds

- ligand names are listed **before** the name(s) of the **central atom**
- **no spaces** are left between parts of the name that refer to the same coordination entity,
- **ligand names** are listed in **alphabetical order** (multiplicative prefixes indicating the number of ligands are not considered in determining that order),
- Names of anionic coordination entities are furthermore given the ending '**ate**'.

1. $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$
pentaamminechloridocobalt(2+) chloride
2. $[\text{AuXe}_4]^{2+}$
tetraxenonidogold(2+)

$\text{K}_4[\text{Fe}(\text{CN})_6]$
potassium hexacyanidoferrate(II)

Number of ligands

- Greek prefixes used to designate the number of each type of ligand in the complex ion.

Number	Prefix	Number	Prefix	Number	Prefix
1	mono	5	penta (pentakis)	9	nona (ennea)
2	di (bis)	6	hexa (hexakis)	10	deca
3	tri (tris)	7	hepta	11	undeca
4	tetra (tetrakis)	8	octa	12	dodeca

Number of ligands

- Two kinds of multiplicative prefix are available
 - Prefixes **di, tri, etc.** are generally used with the names of **simple ligands**. Enclosing marks are not required.
 - Prefixes **bis, tris, tetrakis**, etc. are used with **complex ligand names** and in order to avoid ambiguity, **enclosing marks must be placed around the multiplicand**.
 - **for $(\text{NH}_3)_2$**
 - **diammine, or**
 - **bis(methylamine)**

Representing ligands in names

- Names of anionic ligands: modified to end in ‘o’.
- In general, if the anion name ends in ‘ide’, ‘ite’ or ‘ate’, the final ‘e’ is replaced by ‘o’, giving ‘ido’, ‘ito’ and ‘ato’, respectively.
 - **alcoholates, thiolates, phenolates, carboxylates, phosphanes, etc.**
- neutral and cationic ligands, including organic ligands, are used without modification

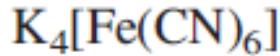
naming the central metal

- If the complex ion is a cation, the metal is named same as the element.
 - Co in a complex cation is called cobalt.
- If the complex ion is an anion, the name of the metal ends with the suffix –ate.
 - Co in a complex anion is called cobaltate.
- For some metals, the Latin names are used in the complex anions
 - Fe is called ferrate (not ironate).

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argenate
Gold	Aurate
Tin	Stannate

Charge numbers and oxidation numbers

- The **oxidation number of the central atom**: a **Roman numeral** appended in parentheses to the central atom name (including the ending ‘ate’, if applicable)
- **Arabic zero** indicates the oxidation number zero.
- **Alternatively, the charge on a coordination entity may be indicated.**
- The net charge is written in **arabic numbers**, with the number preceding the charge sign, and enclosed in parentheses.
- It follows the name of the central atom (including the ending ‘ate’, if applicable) without the intervention of a space.



potassium hexacyanidoferrate(II), or
potassium hexacyanidoferrate(4–), or
tetrapotassium hexacyanidoferrate



hexaamminecobalt(III) chloride



pentaamminechloridocobalt(2+) chloride

Exceptions ...

- For historic reasons, some coordination compounds are called by their common names.
- For example, $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are named ferricyanide and ferrocyanide respectively
- $\text{Fe}(\text{CO})_5$ is called iron carbonyl.

Formulae of coordination compounds

- A (line) formula of a compound:
 - provides basic information about the constitution of the compound in a concise and convenient manner
 - The central atom symbol is listed first
 - The ligand symbols are then listed in alphabetical order
 - single letter symbols precede two letter symbols.
 - Example: CO precedes Cl

sodium amminebromidochloridonitrito- κN -platinate(1-)



Formulae of coordination compounds

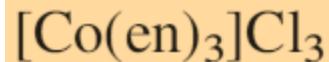
- Use of enclosing marks
 - **Square brackets:** []
 - formula for the entire coordination entity, whether charged or not
 - **Parentheses:** ()
 - polyatomic ligands formulae and abbreviations of ligands.



sodium amminebromidochloridonitrito- κN -platinate(1-)



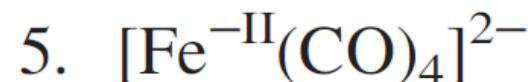
hexakis(methyl isocyanide)iron(II) bromide



tris(ethane-1,2-diamine)cobalt(III) trichloride

Ionic charges and oxidation numbers

- If the **formula** of a charged coordination entity is to be written **without any counterion**, the charge is indicated outside the square bracket as a right superscript (number before the sign).
- The **oxidation number** of a central atom *may be* represented by a Roman numeral, which should be placed as a right superscript on the element symbol.



Specifying donor atoms

- Cases where specification of the donor atom is not required for a ligand that can bind to a central atom in more than one way
 - monodentate O-bound carboxylate groups
 - monodentate C-bound cyanide (ligand name ‘cyanido’)
 - monodentate C-bound carbon monoxide (ligand name ‘carbonyl’)
 - monodentate N-bound nitrogen monoxide (ligand name ‘nitrosyl’).

Specifying donor atoms

- The kappa convention
 - Single ligating atoms are indicated by the italicized element symbol preceded by a Greek kappa, κ
 - Placing the symbol κ
 - κ placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found



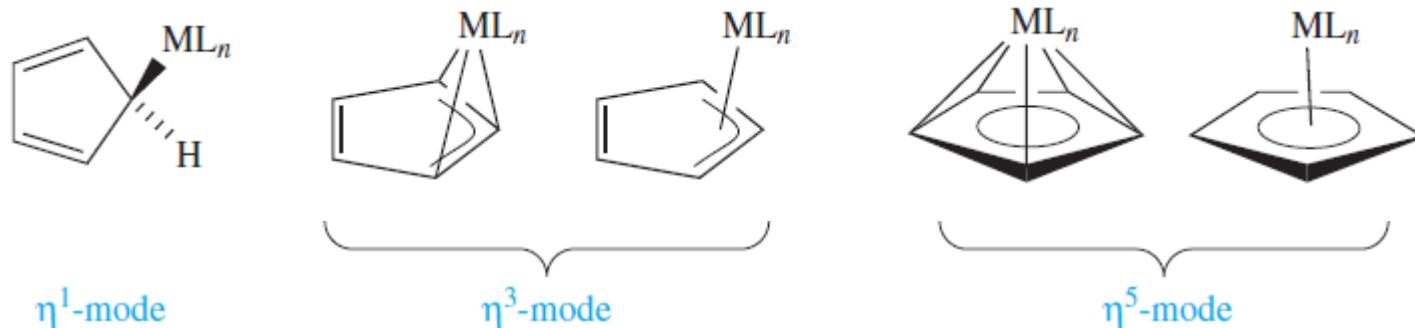
dibromido[ethane-1,2-diylbis(dimethylphosphane- κP)]nickel(II)

Specifying donor atoms

- The kappa convention
 - thiocyanato- κN for nitrogen-bonded NCS
 - thiocyanato- κS for sulfur-bonded NCS.
 - Nitrogen-bonded nitrite is named nitrito- κN
 - Oxygen-bonded nitrite is named nitrito- κO , as in pentaamminenitrito- κO -cobalt(III)

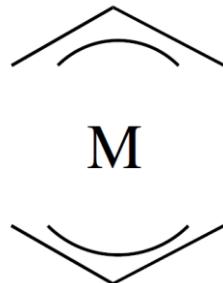
hapticity of a ligand

- The hapticity of a ligand is the number of atoms that are directly bonded to the metal centre



Specifying donor atoms

- The eta (η) convention: ('hapticity')
 - applied in cases where adjacent donor atoms within a given ligand are involved in bonding to a central atom



4 electron donor and anionic

bis- η^3 -allyl nickel, or $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2]$



Metal–metal bonds



bis(tetrabromidorhenium)(*Re*—*Re*)(2+)

2.



nonacarbonyl-1κ⁵ C,2κ⁴ C-rheniumcobalt(*Re*—*Co*)



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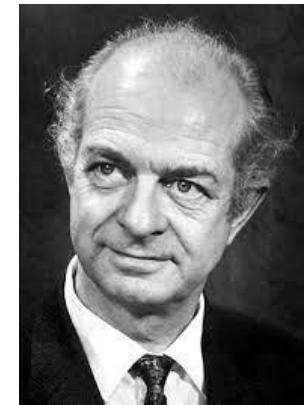
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Bonding in d-block metal complexes:

valence bond,
crystal field and
molecular orbital theories

Valence Bond Theory (VBT)

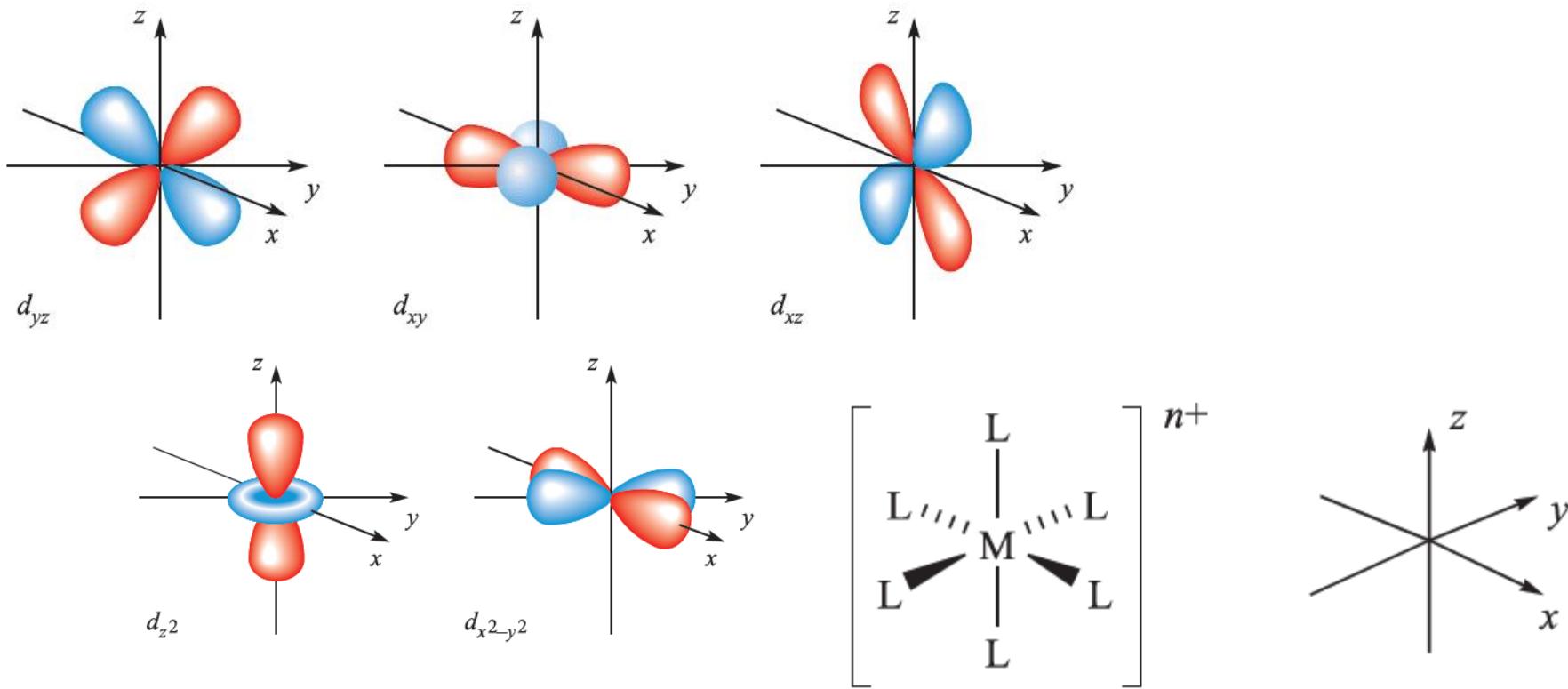


- developed by Pauling in the 1930s
- uses hybridization schemes to describe the bonding in d-block metal complexes
- the use of sp^3d , sp^3d^2 and sp^2d hybridization schemes in trigonal pyramidal, square-based pyramidal, octahedral and square planar molecules

Valence Bond Theory (VBT)

- Describes hybridization schemes for the σ -bonding frameworks of different geometrical configurations of ligand donor atoms.
- an empty hybrid orbital on the metal centre can accept a pair of electrons from a ligand to form a sigma (σ)-bond.
- The choice of particular p- or d- atomic orbitals depends on the definition of the axes with respect to the molecular framework

Spatial orientation of d-orbitals



consequence of this difference: the d orbitals in the presence of ligands are split into groups of different energies, the type of splitting and the magnitude of the energy differences depend on the arrangement and nature of the ligands.

the applications and limitations of VBT

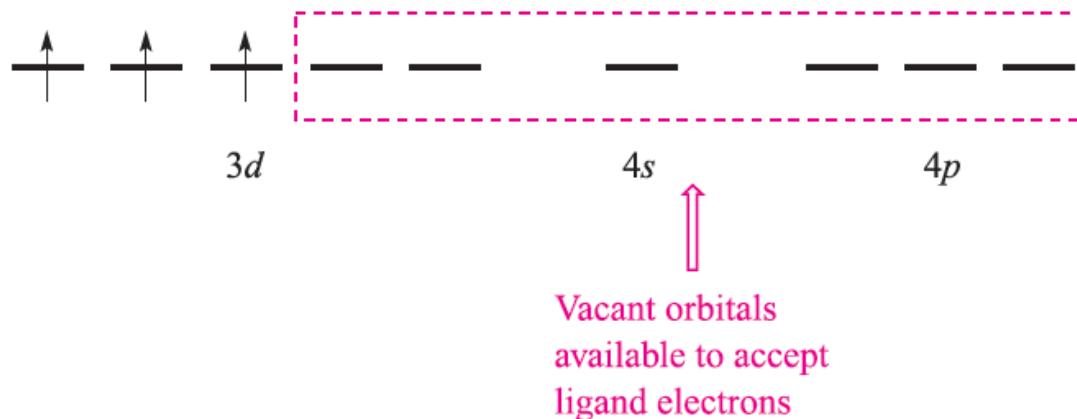
- We will consider the following :
- octahedral complexes of Cr(III) (d^3) and Fe(III) (d^5) and
- octahedral, tetrahedral and square planar complexes of Ni(II) (d^8)
- Which atomic orbitals are required for hybridization in an octahedral complex?
- $3d_{z^2}$, $3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$
- Any other requirement?
- For octahedral complex: these orbitals must be unoccupied so as to be available to accept six pairs of electrons from the ligands.

VB Theory

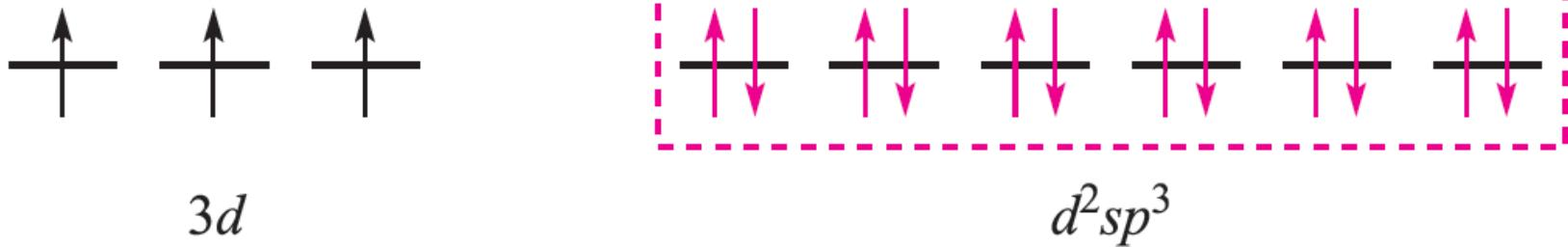
- According to VBT,
- complexes in which the **electronic configuration** of the metal ion was the **same** as that of the free gaseous atom were **called ionic complexes**,
- while those in which the **electrons had been paired** up as far as possible were called **covalent complexes**.
- First row metal complexes in which **ligand electrons entered 3d orbitals** (as in $[\text{Fe}(\text{CN})_6]^{3-}$) were termed **inner orbital complexes**,
- those in which **4d orbitals were occupied** (as in $[\text{FeF}_6]^{3-}$) were **outer orbital complexes**.
- **high-spin complex = ionic complex = outer orbital complex**
- **low-spin complex = covalent complex = inner orbital complex**

Chromium (III): Octahedral

$$Z = 24$$

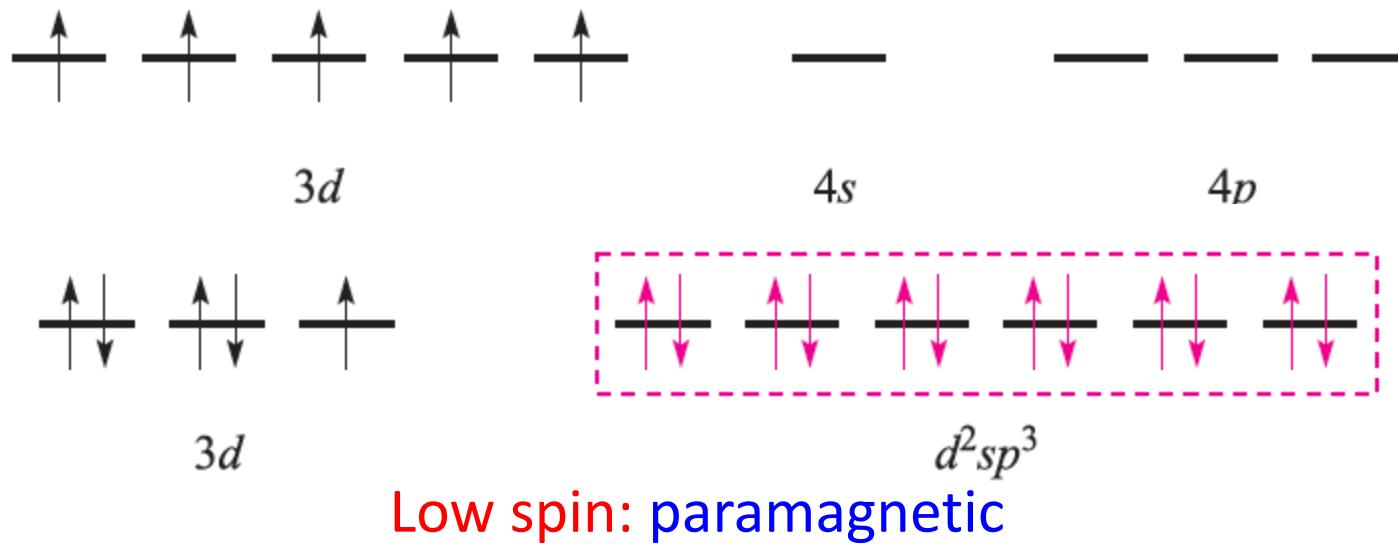


With the electrons from the ligands included and a hybridization scheme applied for an octahedral complex, the diagram becomes ...



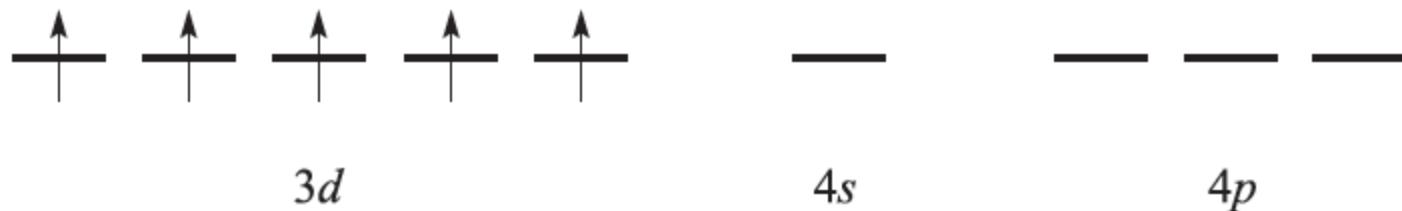
Fe³⁺ ion: Octahedral

we must account for the existence of both high- and low-spin complexes.

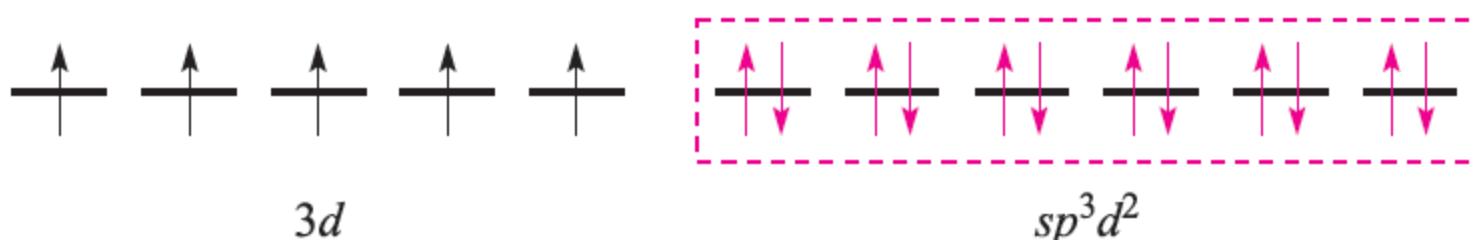


Fe³⁺ ion: Octahedral

we must account for the existence of both high- and low-spin complexes.



This scheme is unrealistic because the 4d orbitals are at a significantly higher energy than the 3d atomic orbitals.



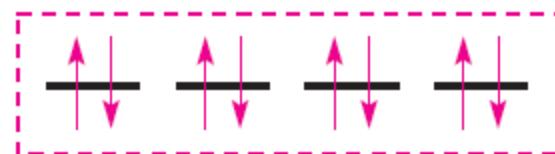
High spin, but **unrealistic: paramagnetic**

Ni²⁺ ion: Octahedral vs Tetrahedral

- Nickel(II) (d⁸) forms **paramagnetic** tetrahedral
- and **paramagnetic** octahedral complexes.



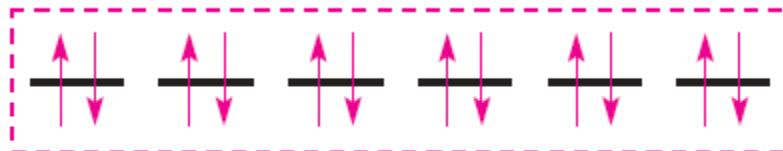
3d



sp³



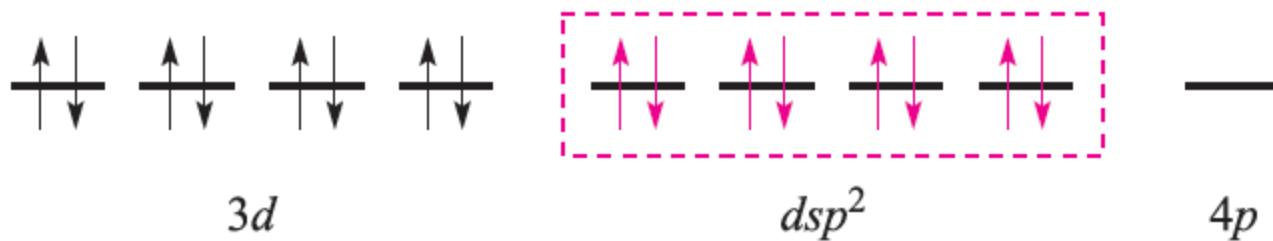
3d



sp³d²

Ni²⁺ ion: Square Planar

- Nickel(II) (d^8) forms **diamagnetic** square planar complexes.



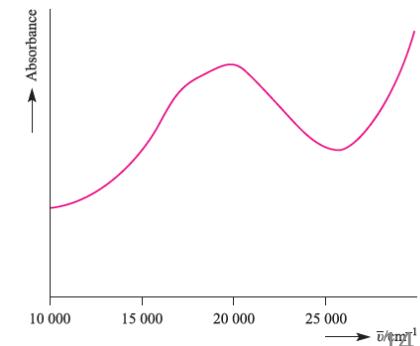
valence bond theory

Coordination number	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[\text{Ag}(\text{NH}_3)_2]^+$
3	Trigonal planar	s, p_x, p_y	sp^2	$[\text{HgI}_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[\text{FeBr}_4]^{2-}$
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	sp^2d	$[\text{Ni}(\text{CN})_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d	$[\text{CuCl}_5]^{3-}$
5	Square-based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d	$[\text{Ni}(\text{CN})_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2	$[\text{Co}(\text{NH}_3)_6]^{3+}$
6	Trigonal prismatic	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yz}$	sd^5 or sp^3d^2	$[\text{ZrMe}_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^3	$[\text{V}(\text{CN})_7]^{4-}$
7	Monocapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3	$[\text{NbF}_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	sp^3d^3f	$[\text{PaF}_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$	sp^3d^4	$[\text{Mo}(\text{CN})_8]^{4-}$
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	sp^3d^4	$[\text{TaF}_8]^{3-}$
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5	$[\text{ReH}_9]^{2-}$

Limitations

- It can say nothing about **electronic spectroscopic properties**.
- **Chemical reactivity** can't be predicted
 - kinetic inertness that is a characteristic of the low-spin d^6 configuration.
- Furthermore, it cannot tell us why certain ligands are associated with the **formation of high- (or low-)spin complexes**.

Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$





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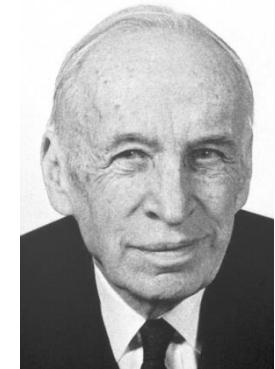
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crystal field theory



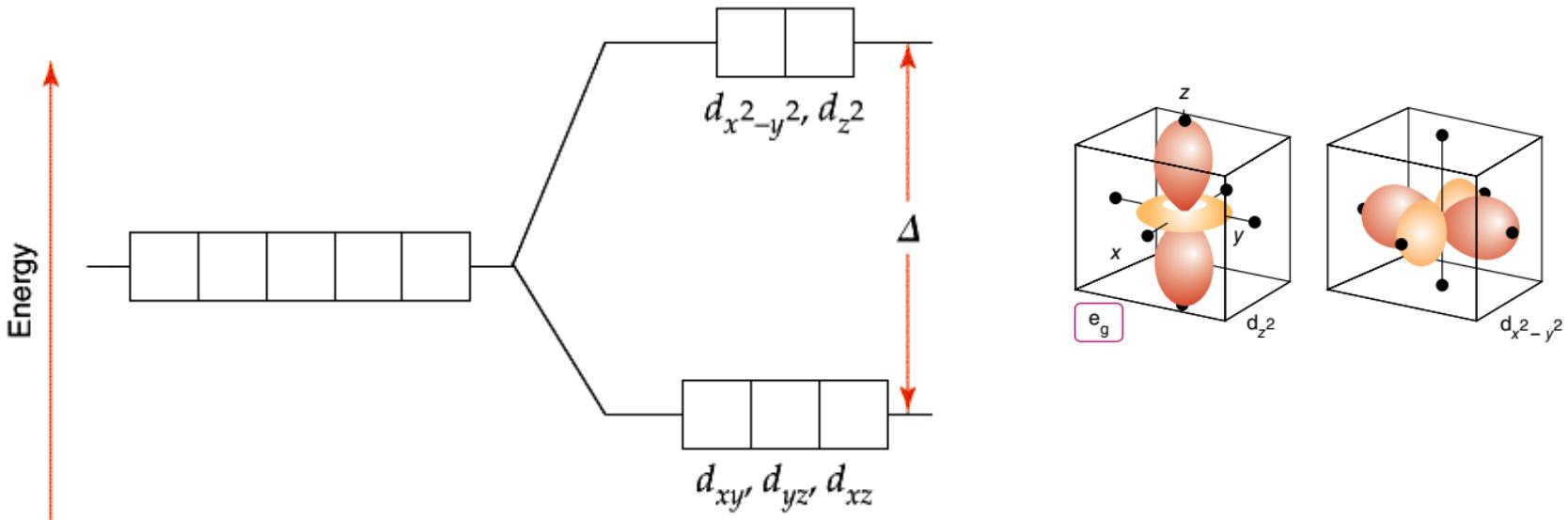
- Proposed by Bethe and Van Vleck
- Crystal field theory was originally developed to describe the electronic structure of metal ions in crystals
- metal ions in crystals are surrounded by anions that create an electrostatic field
- The energies of the *d orbitals of the metal ions* are split by the electrostatic field,
- approximate values for these energies can be calculated.

Crystal field theory (CFT)

- This is an **electrostatic model** and simply uses the ligand electrons to create an electric field around the metal centre.
- **Ligands** are considered as **point charges** and there are no metal–ligand covalent interaction.
- Predicts that the **d orbitals** in a metal complex are **not degenerate**.
- **pattern of splitting of the d orbitals** depends on the crystal field, this being determined by the arrangement and **number/type of ligands**

Splitting of the d-Orbitals

Octahedral field Splitting Pattern



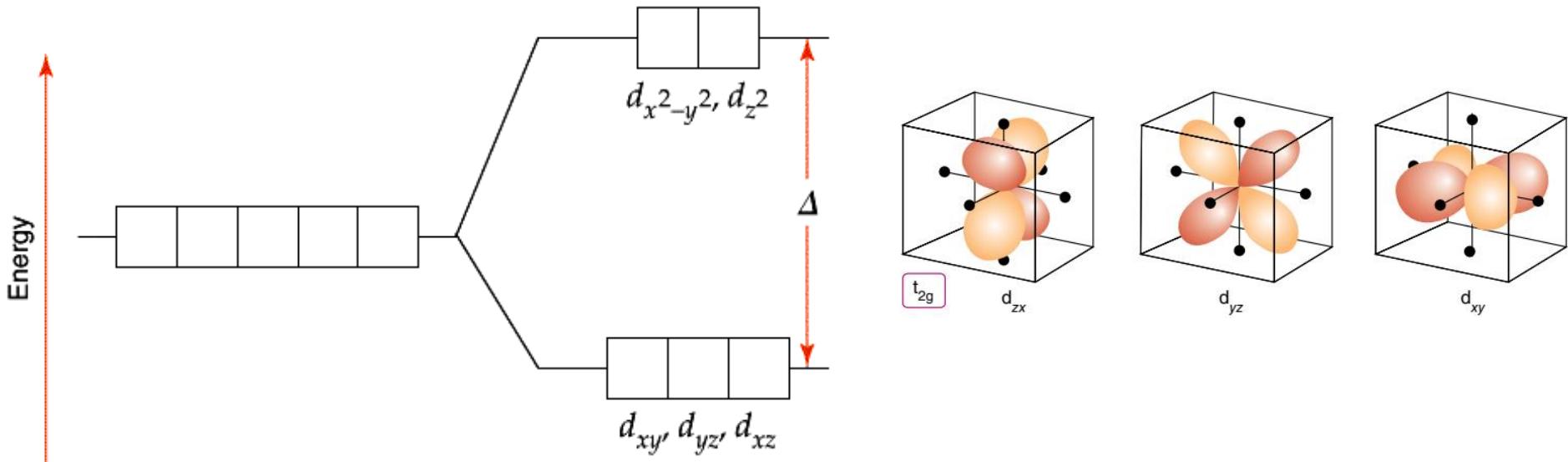
The d_z^2 and $d_{x^2-y^2}^2$ orbitals lie on the same axes as negative charges.

Therefore, there is a large, unfavorable interaction between ligand orbitals and d-orbitals.

These orbitals form the degenerate high energy pair of energy levels.

Splitting of the d-Orbitals

Octahedral field Splitting Pattern



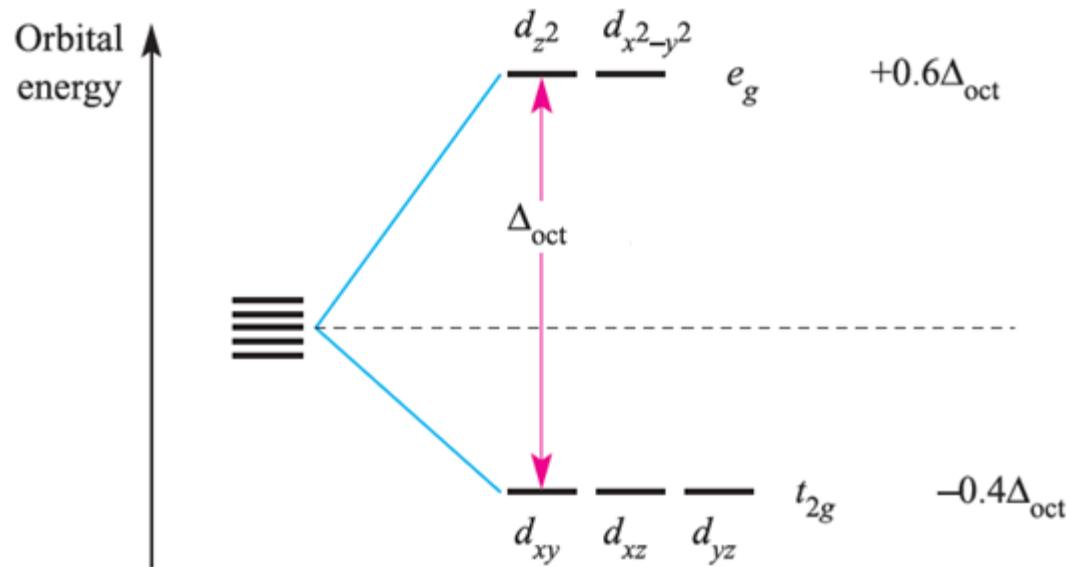
The d_{xy} , d_{yx} and d_{xz} orbitals bisect the negative charges.

Therefore, there is a smaller repulsion between ligand & metal for these orbitals.

These orbitals form the degenerate low energy set of energy levels.

Splitting of the d orbitals in an octahedral crystal field

The energy difference between the actual distribution of electrons and that for the hypothetical configuration with all electrons in the uniform (or spherical) field level is called the **crystal field stabilization energy (CFSE)**



Magnitude of CF Splitting (Δ_O)

Color of the complex depends on magnitude of Δ

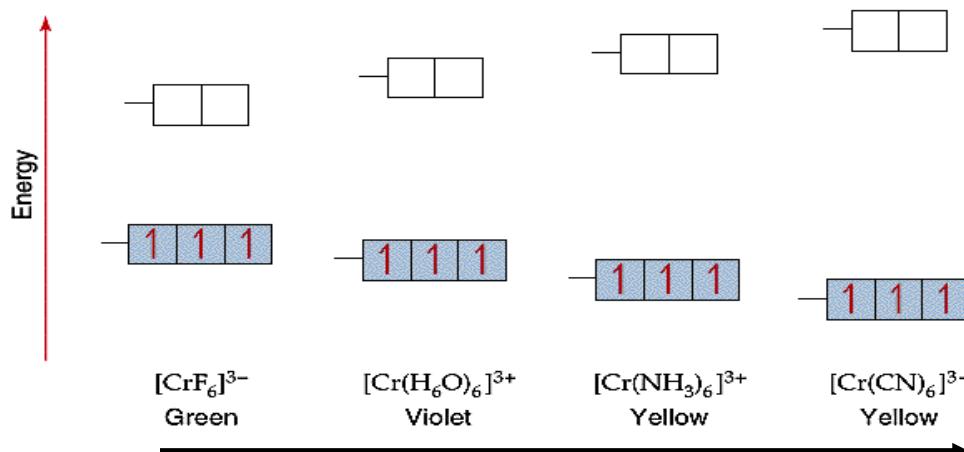
1. Metal ion: Larger metal ion \rightarrow larger Δ
Higher Oxidation State \rightarrow larger Δ

2. Ligand: Spectrochemical series



Weak field Ligand: Low electrostatic interaction: small CF splitting.

High field Ligand: High electrostatic interaction: large CF splitting.

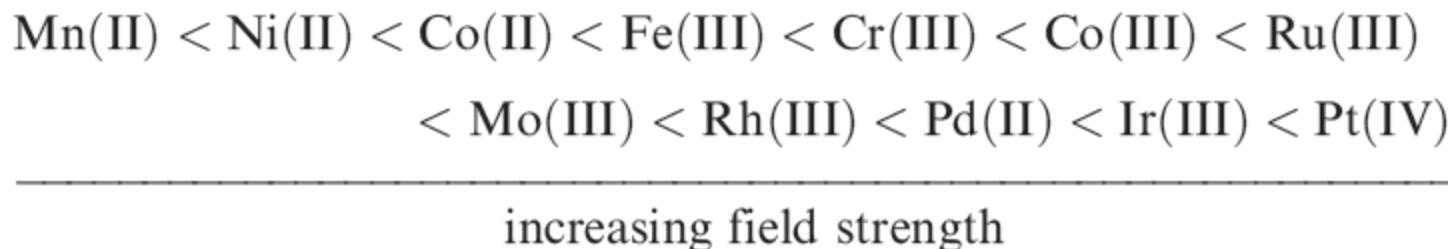
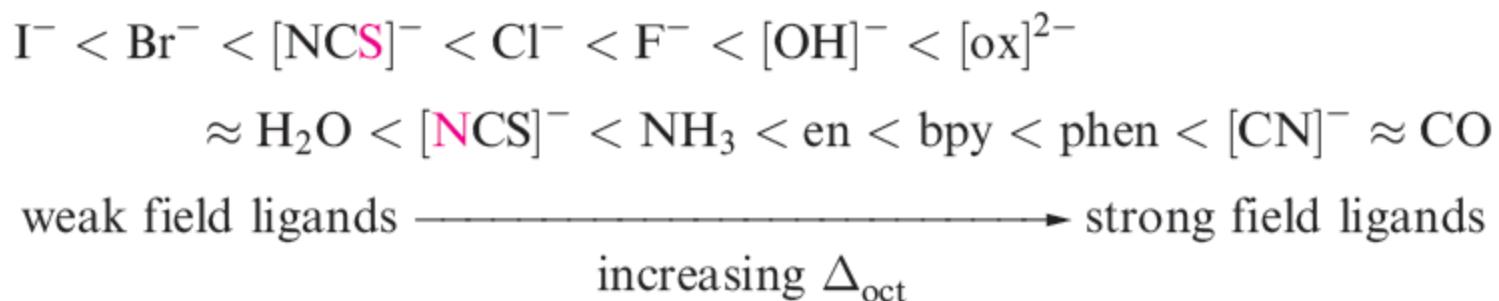


Spectrochemical series:
Increasing Δ

Spectrochemical Series

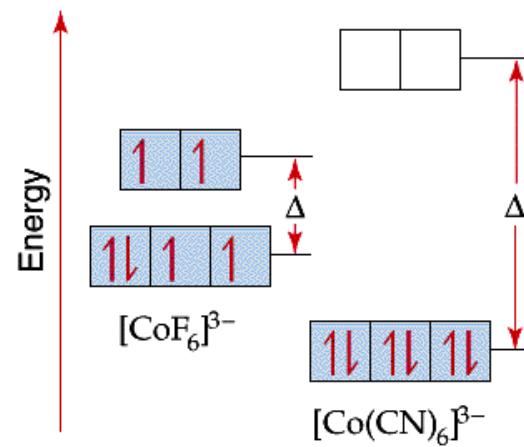
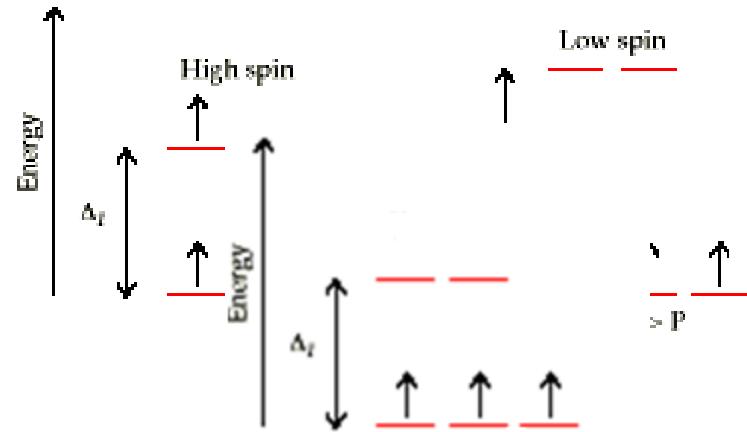
Weak and Strong field

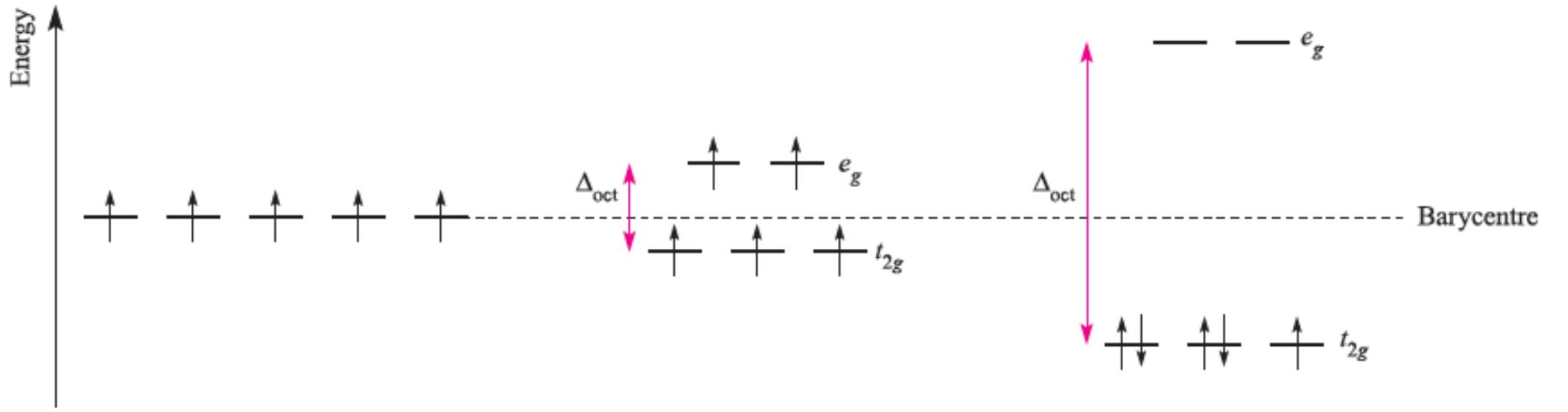
$$\Delta_{\text{oct}}(\text{weak field}) < \Delta_{\text{oct}}(\text{strong field})$$



Electron Configuration in Octahedral Field

- Electron configuration of metal ion:
- s-electrons are lost first.
- Ti^{3+} is a d¹, V^{3+} is d², and Cr^{3+} is d³
- **Hund's rule:**
 - First three electrons are in separate orbitals with their spins parallel.
 - Fourth e- has choice:
 - Higher orbital if Δ is small; **High spin**
 - Lower orbital if Δ is large: **Low spin**.
- **Weak field ligands**
 - Small Δ , High spin complex
- **Strong field Ligands**
 - Large Δ , Low spin complex





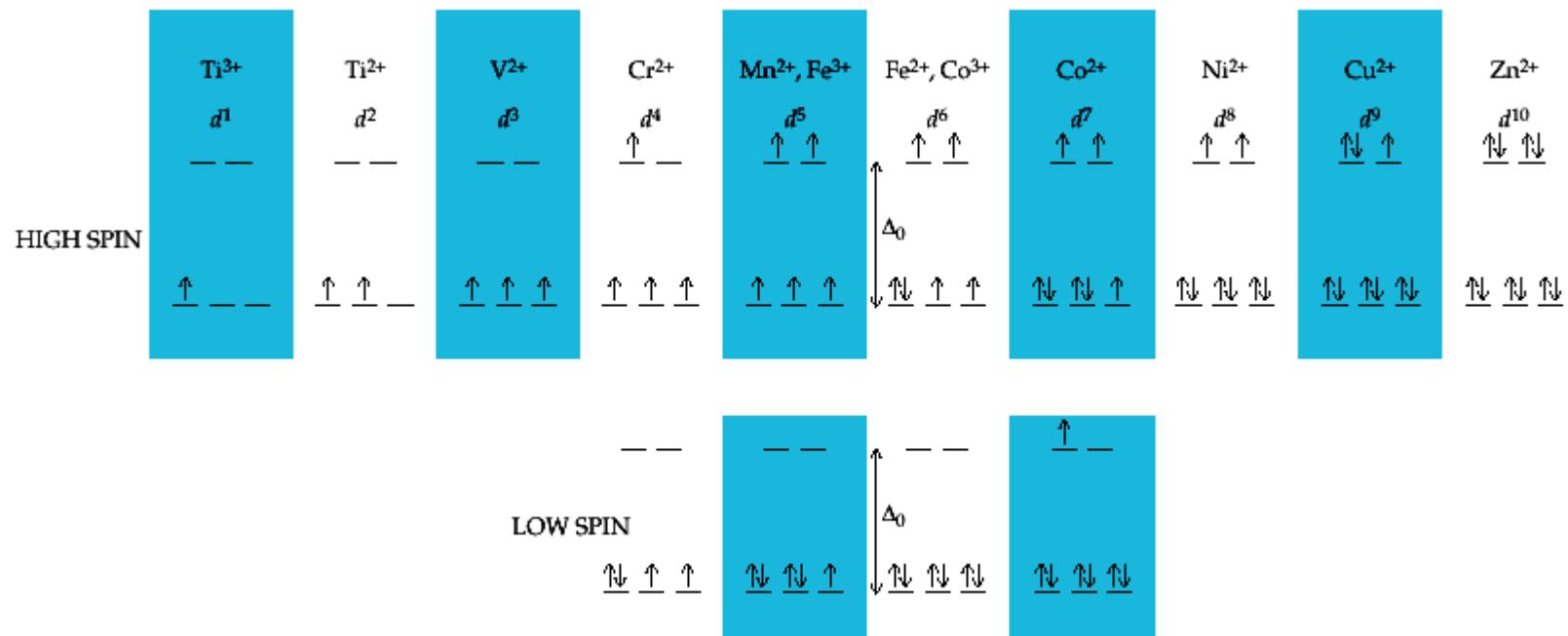
Gaseous ion

Weak field
(high-spin)
complex
e.g. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Strong field
(low-spin)
complex
e.g. $[\text{Fe}(\text{CN})_6]^{3-}$

High Spin Vs. Low Spin (d^1 to d^{10})

- Electron Configuration for Octahedral complexes of metal ion having d^1 to d^{10} configuration $[M(H_2O)_6]^{+n}$.
- **Only the d^4 through d^7 cases have both high-spin and low spin configuration.**



Pairing Energy and Δ_{oct} .



For high-spin: $\Delta_{\text{oct}} < P$

For low-spin: $\Delta_{\text{oct}} > P$

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{\text{oct}}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{\text{oct}}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{\text{oct}}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{\text{oct}}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{\text{oct}} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{\text{oct}} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{\text{oct}}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{\text{oct}} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{\text{oct}}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{\text{oct}} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{\text{oct}}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{\text{oct}}$		
d^{10}	$t_{2g}^6 e_g^4$	0		



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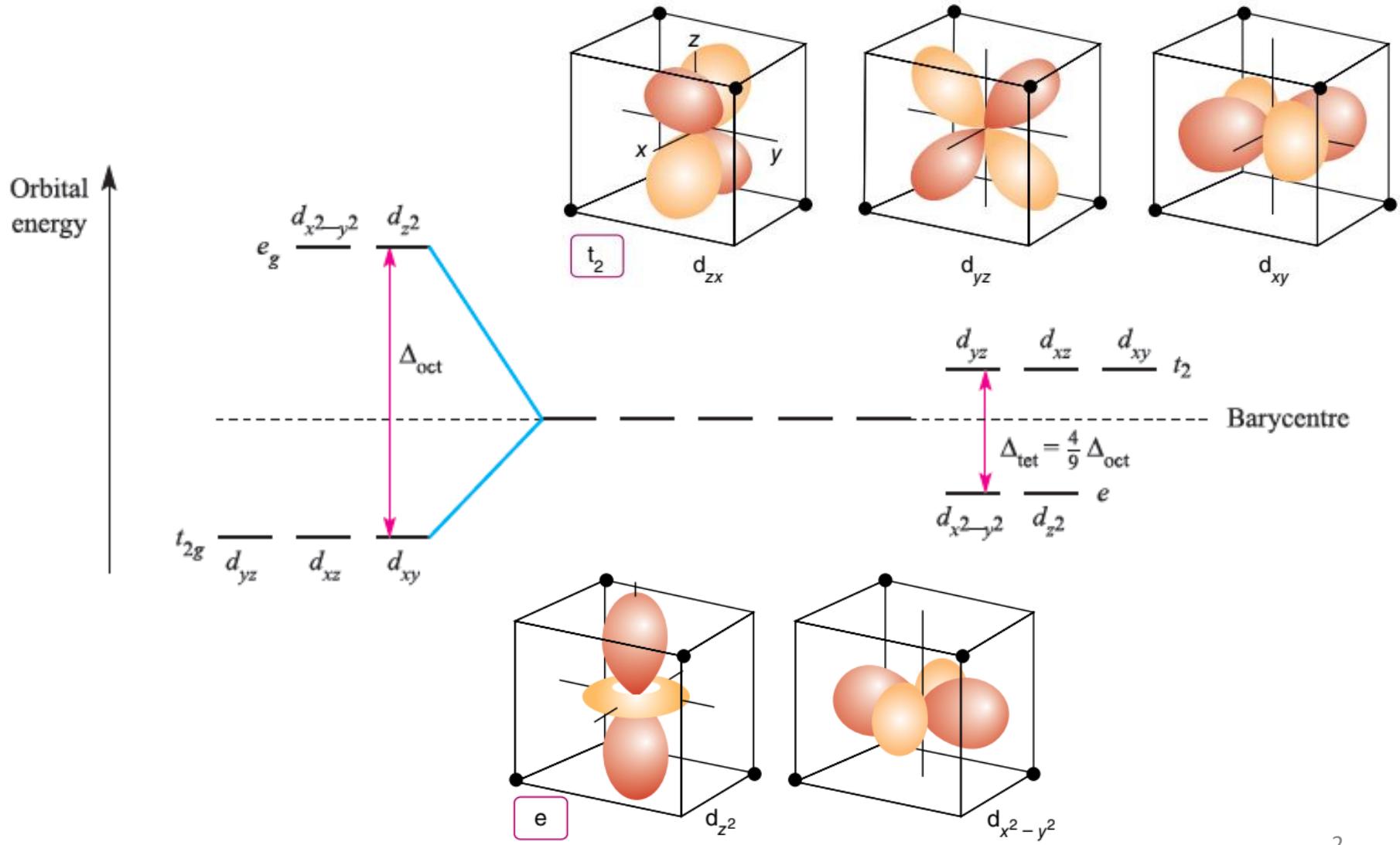
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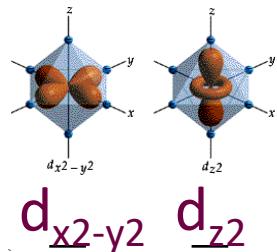
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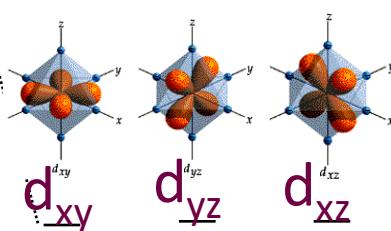
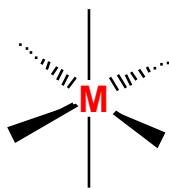
Octahedral vs Tetrahedral



Octahedral, Tetrahedral & Square Planar



Octahedral

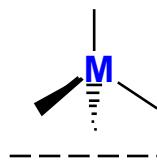


Pairing energy Vs. Δ

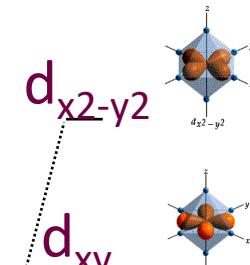
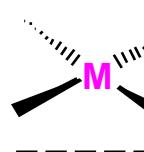
Weak field $\Delta < Pe$

Strong field $\Delta > Pe$

Tetrahedral



Square planar



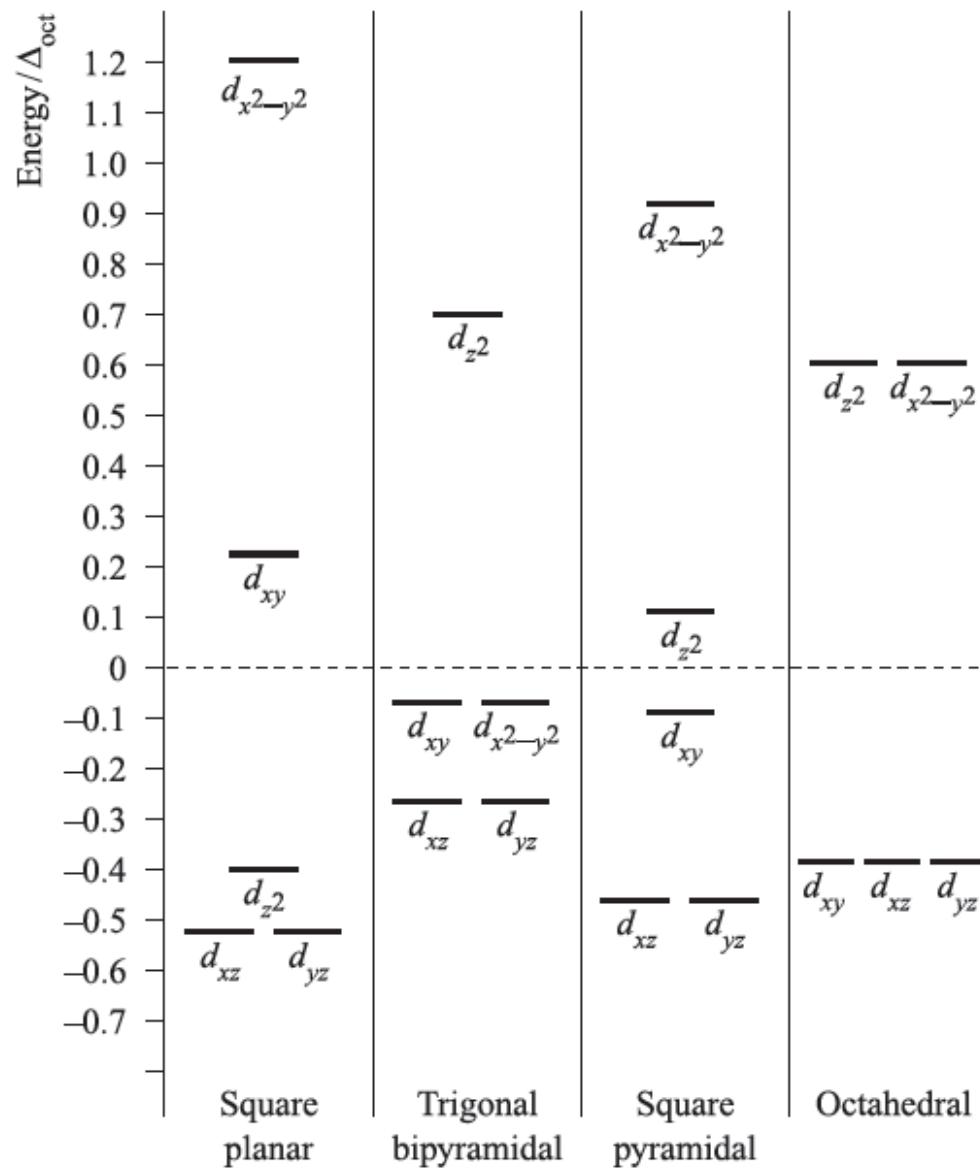
Mostly d^8

Pd^{2+} , Pt^{2+} , Ir^+ , Au^{3+}

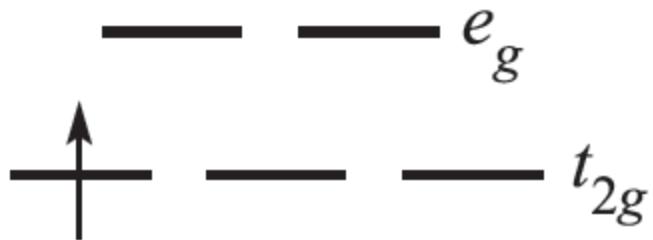
(Majority Low spin)

Strong field ligands

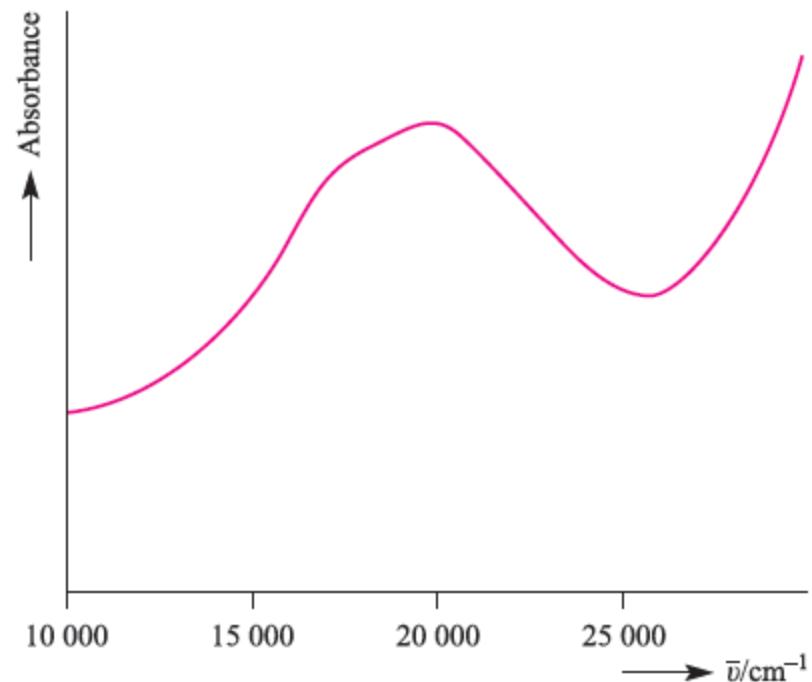
Crystal Field Splittings



Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

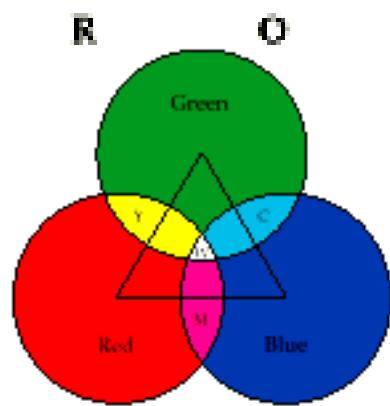
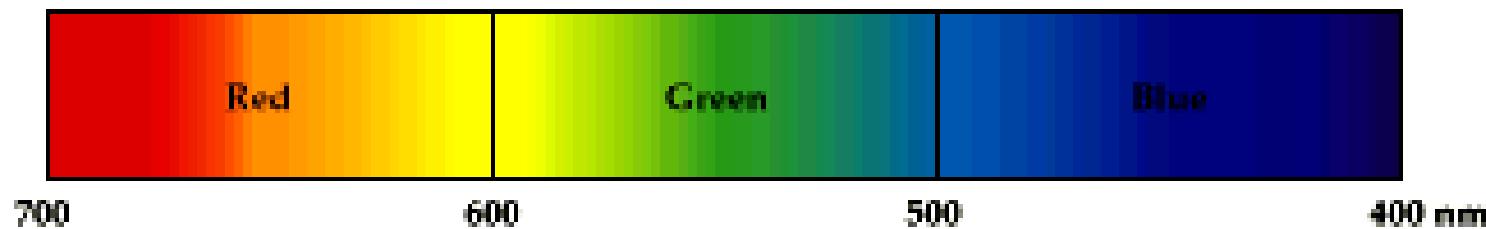


$$\Delta_{\text{oct}} = 243 \text{ kJ mol}^{-1}$$



$$\lambda_{\max} = 20\ 300 \text{ cm}^{-1}$$

Colors & How We Perceive it

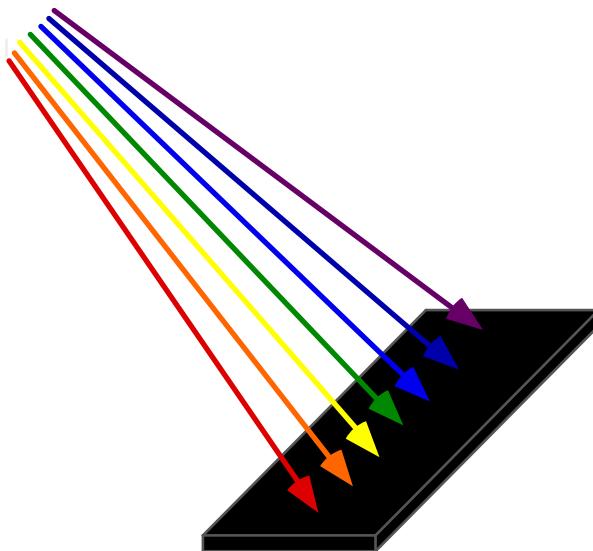


Artist color wheel
showing the colors which
are complementary to one
another and the wavelength
range of each color.

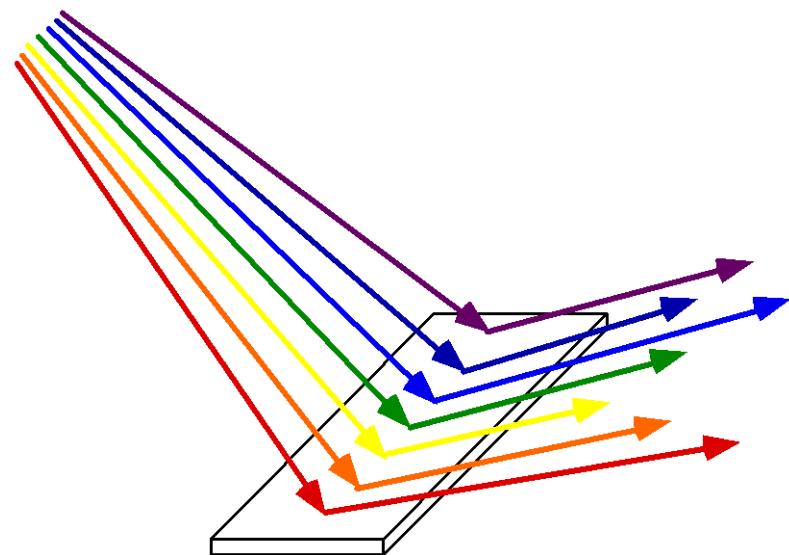


Black & White

- When a sample absorbs light, what we see is the sum of the remaining colors that strikes our eyes.

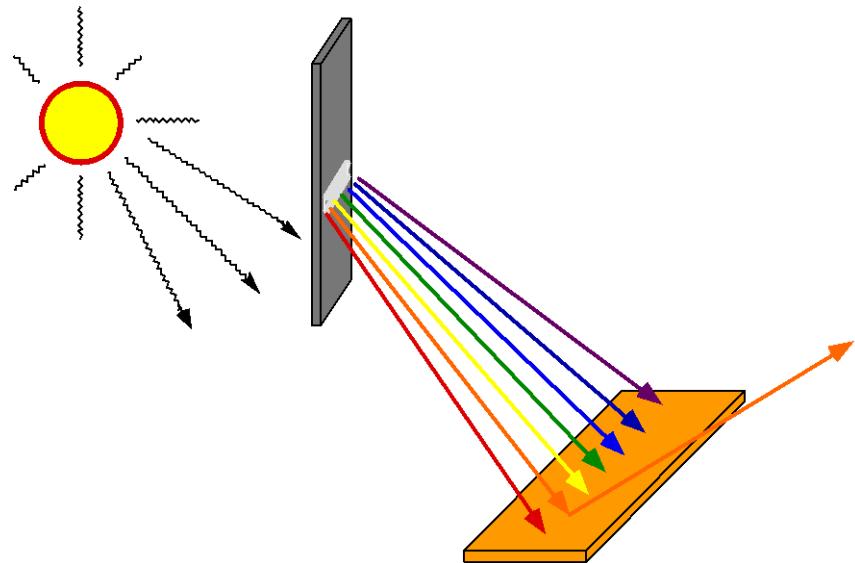


If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample. Consequently, it appears black.



If the sample absorbs no visible light, it is white or colorless.

Absorption and Reflection



- If the sample absorbs all but orange, the sample appears orange.

if the sample absorbed only orange, it would appear blue; blue and orange are said to be complementary colors.



Complex Influence on Color

Compounds of Transition metal complexes solution.



Color Absorption of Co³⁺ Complexes

The wavelengths refer to the center of that absorption band.

Complex Ion	Wavelength of light absorbed	Color of Light Absorbed	Color of Complex
[CoF ₆] ³⁺	700 (nm)	Red	Green
[Co(C ₂ O ₄) ₃] ³⁺	600, 420	Yellow, violet	Dark green
[Co(H ₂ O) ₆] ³⁺	600, 400	Yellow, violet	Blue-green
[Co(NH ₃) ₆] ³⁺	475, 340	Blue, violet	Yellow-orange
[Co(en) ₃] ³⁺	470, 340	Blue, ultraviolet	Yellow-orange
[Co(CN) ₆] ³⁺	310	Ultraviolet	Pale Yellow



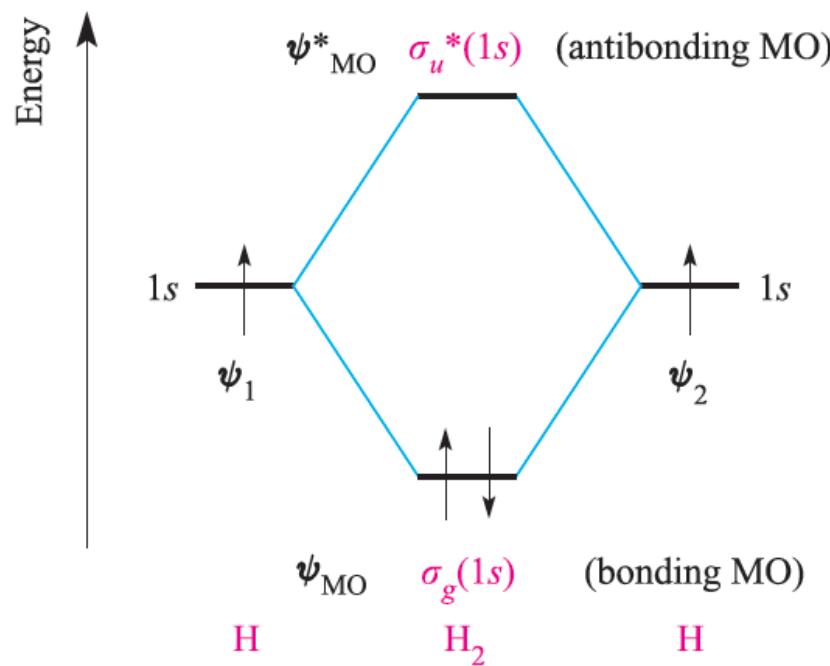
Crystal field theory: uses and limitations

- Crystal Field Theory provides a basis for explaining many features of transition-metal complexes.
- Examples include
 - why transition metal complexes are highly colored,
 - why some are paramagnetic while others are diamagnetic.
 - The spectrochemical series for ligands explains nicely the origin of color and magnetism for these compounds.
- crystal field theory provides no explanation as to why particular ligands are placed in the spectrochemical series.
- There is evidence to suggest that the **metal-ligand bond has covalent character** which explains why these complexes are very stable. Molecular Orbital Theory can also be used to describe the bonding scheme in these complexes.

Molecular Orbital Theory (MOT)

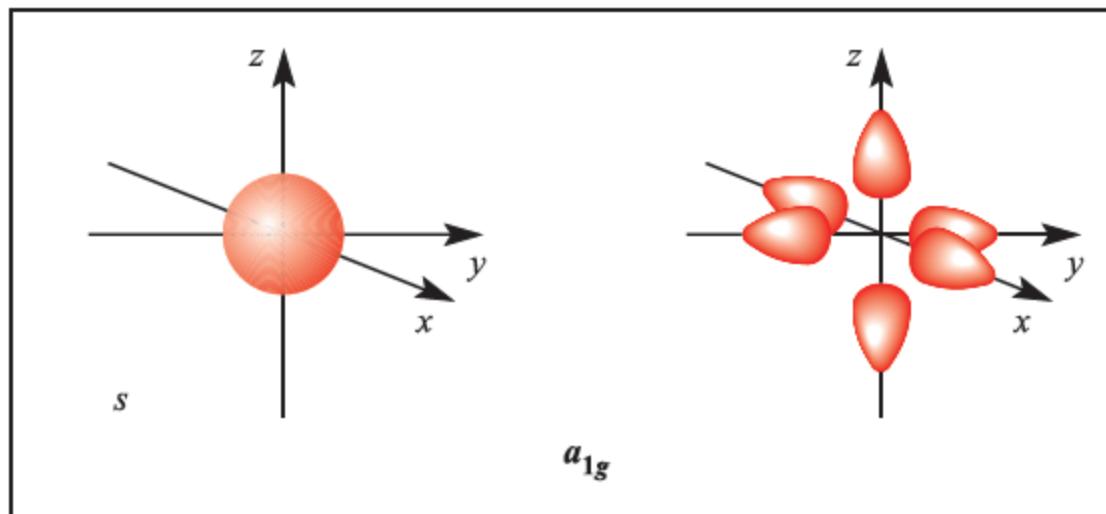
- considers **covalent interactions** between the metal centre and ligands
- In molecular orbital (MO) theory, we begin by placing the nuclei of a given molecule in their equilibrium positions and then calculate the molecular orbitals (i.e. regions of space spread over the entire molecule) that a single electron might occupy.
- **Each MO arises from interactions between orbitals of atomic centres in the molecule, and such interactions are:**
- **allowed** if the symmetries of the atomic orbitals are compatible with one another;
- **efficient** if the region of overlap between the two atomic orbitals is significant;
- **efficient** if the atomic orbitals are relatively close in energy.

- the number of MOs that can be formed must equal the number of atomic orbitals of the constituent atoms.
- construct the orbital interaction diagram first and then put in the electrons according to the aufbau principle.



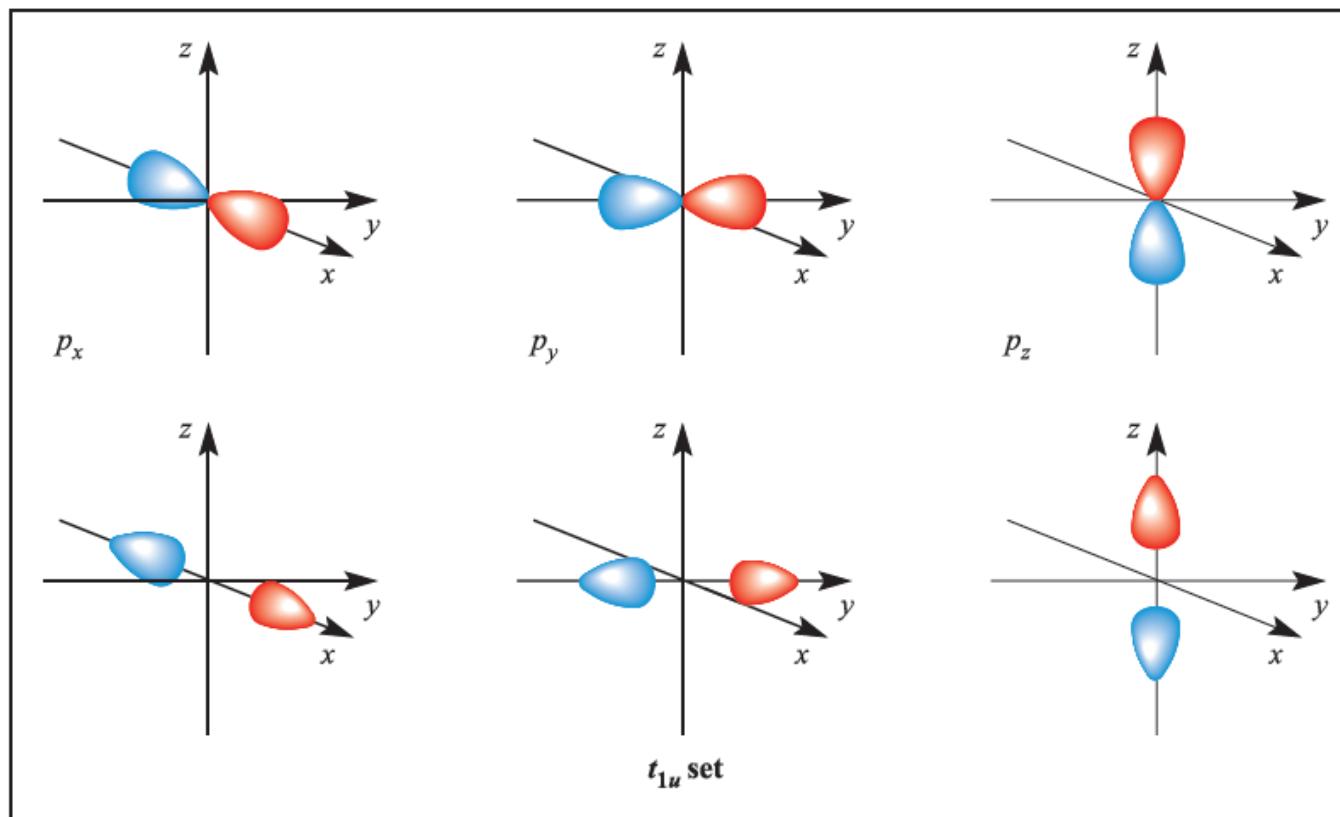
MO diagram : O_h [ML₆]ⁿ⁺

- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p



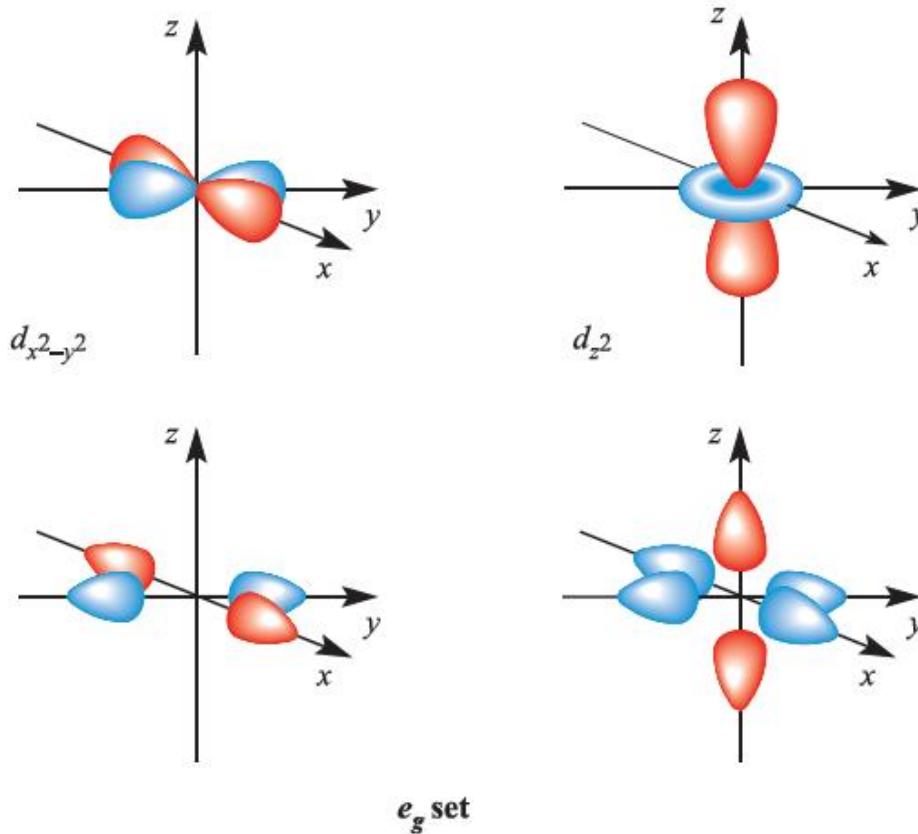
MO diagram : O_h [ML₆]ⁿ⁺

- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p

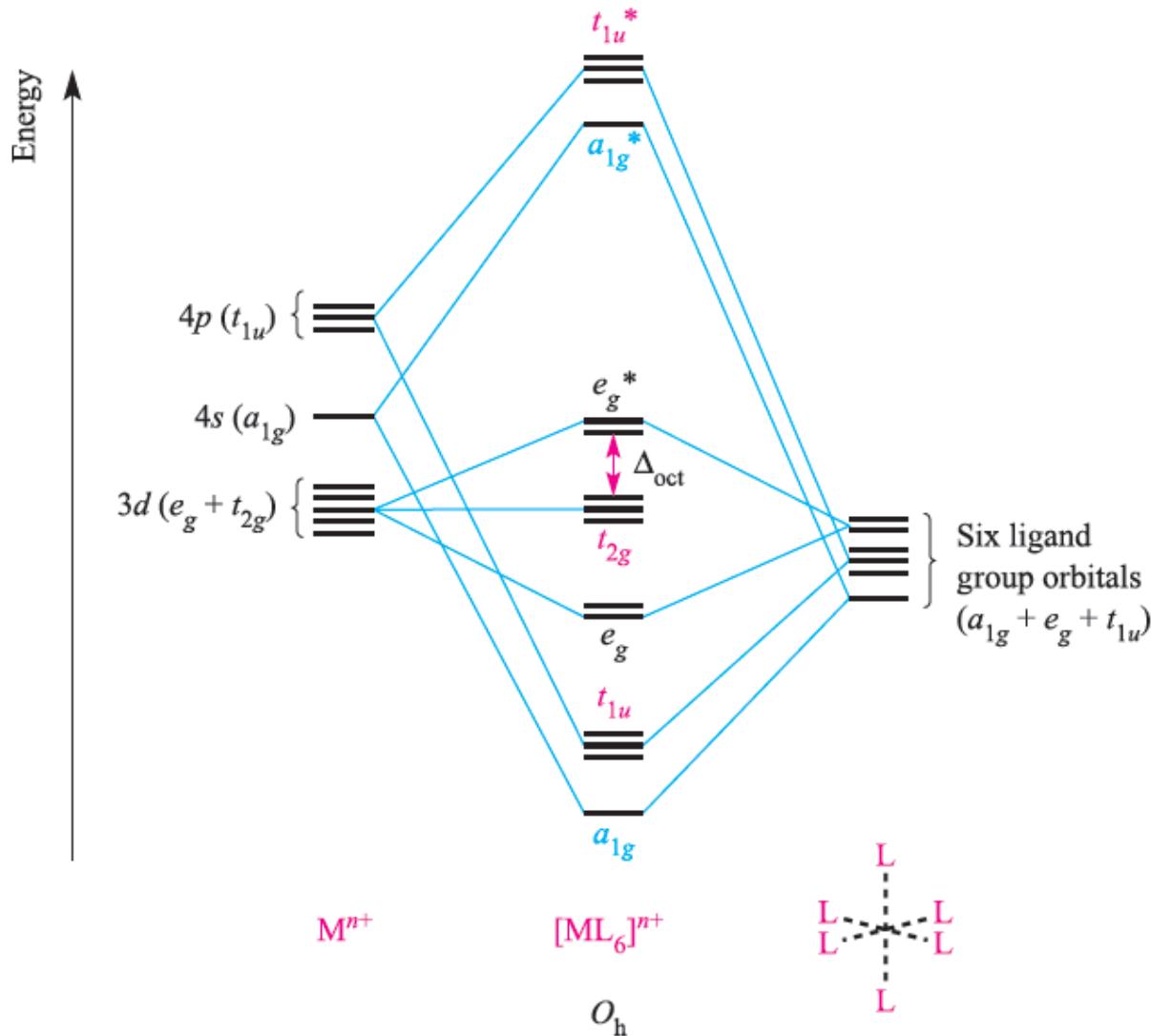


MO diagram : O_h [ML₆]ⁿ⁺

- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p



MO diagram: O_h [ML₆]ⁿ⁺ no metal-ligand π bonding





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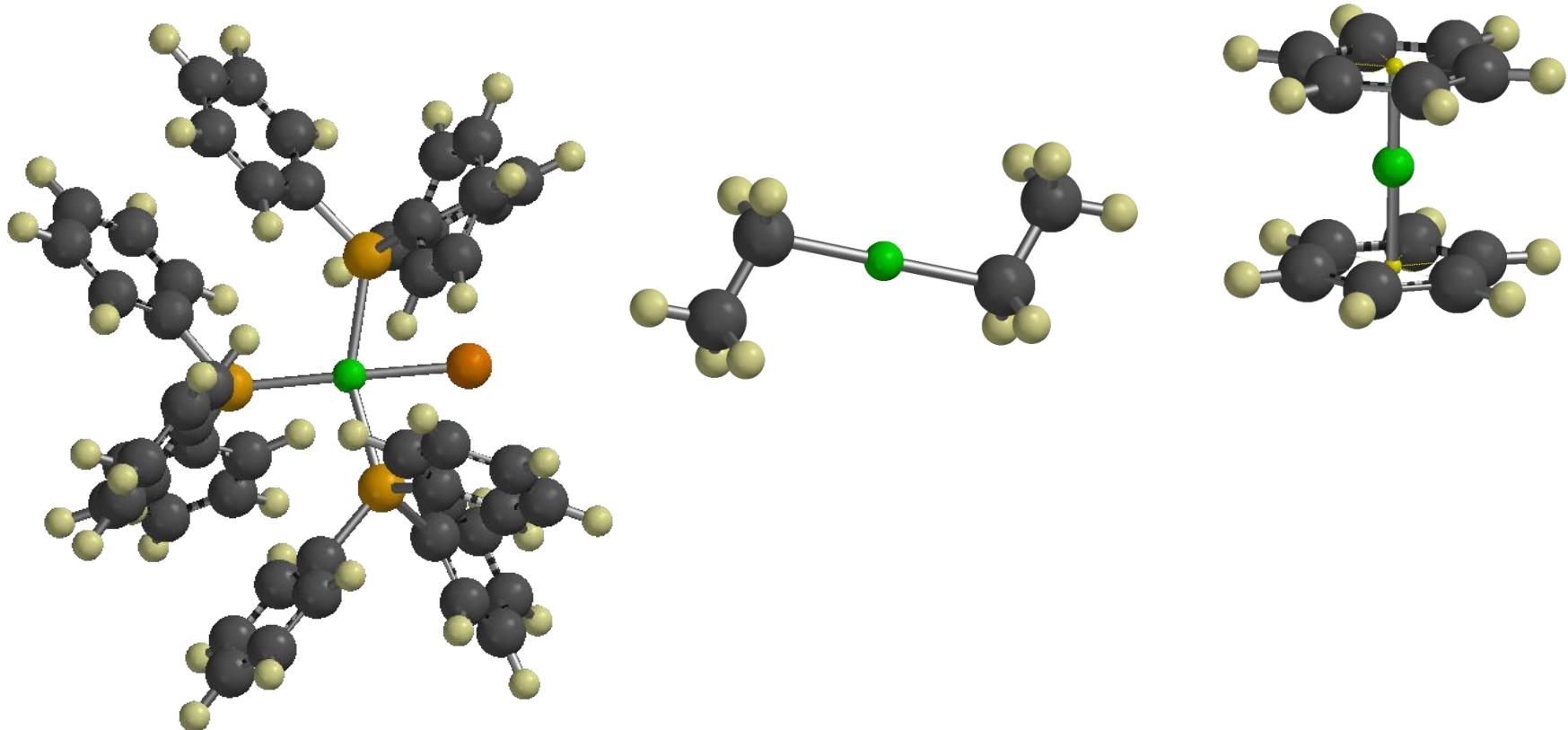
CH 103

Instructor: Dr. Neeladri Das
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Rm-215, Block-IV
Chemistry department
IIT Patna

Organometallic Chemistry

between organic and inorganic



Frontiers in Organometallic Chemistry

- *Definition* of organometallic chemistry: transformations of organic compounds using metals.
- Organometallic chemistry is at the interface between inorganic and organic chemistry.
 - Inorganic: subset of coordination chemistry
 - Organic: subset of synthetic methods
- Other interdisciplinary areas
 - Bioorganometallic chemistry
 - Surface organometallic chemistry

Why should you care ?

- Organometallic chemistry is the basis of *homogeneous catalysis*, which is the method of choice for clean and efficient synthesis of fine chemicals, pharmaceuticals and many larger-scale chemicals.
- Many *plastics* (polythene, polypropene, butadiene rubber, ...) and *detergents* are made via organometallic catalysis.
- Organometallic compounds are used on a large scale as precursors for *generation of semiconductors* (AlN, GaAs, etc).

Real life Example: Acetic Acid synthesis

Acetic acid is an important industrial chemical.

- What is the traditional synthetic method?
- bio-oxidation of ethanol obtained via fermentation:

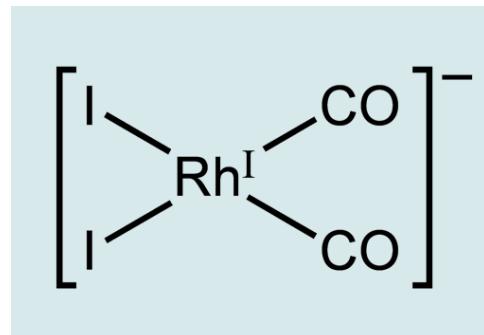


This is *not* a clean and efficient process!

Industrial acetic acid synthesis:

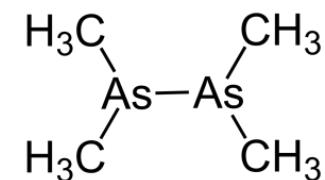


Catalyzed by a rhodium complex.

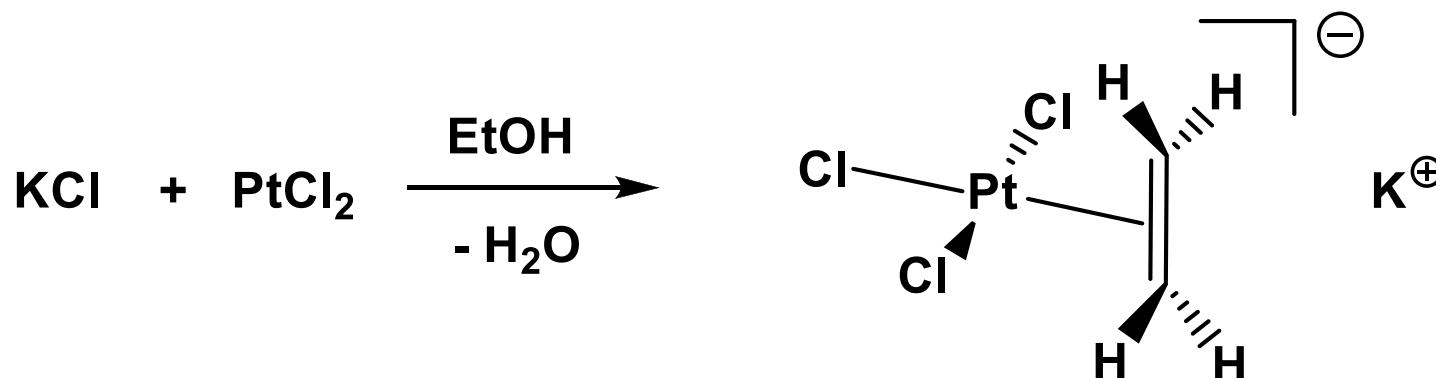


History: earlier organometallic compounds

- 1760 Louis Claude Cadet de Gassicourt (Paris) isolates cacodyl from cobalt minerals containing arsenic (CoAs_2 and CoAsS_2) :
- What is cacodyl?

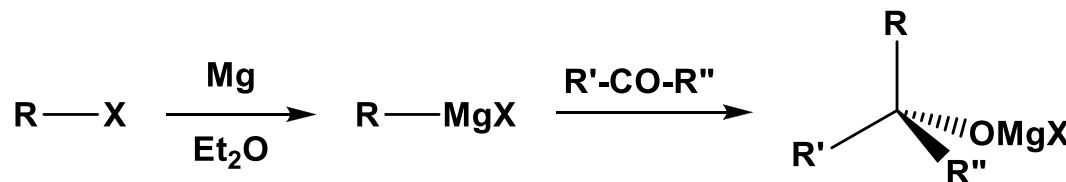


1827 : Zeise's salt
the first organometallic complex with a transition metal

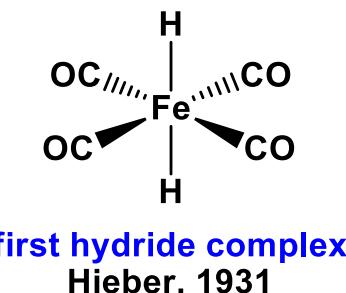
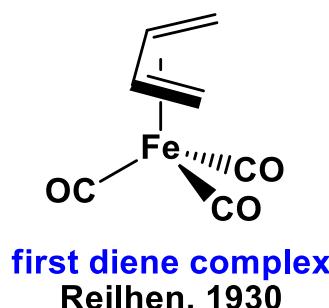
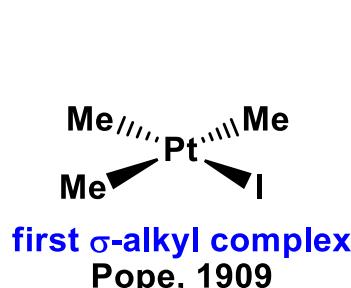


History: organometallic compounds

- 1863 Charles Friedel and James Crafts prepared organochlorosilanes
- 1899 introduction of Grignard reagents

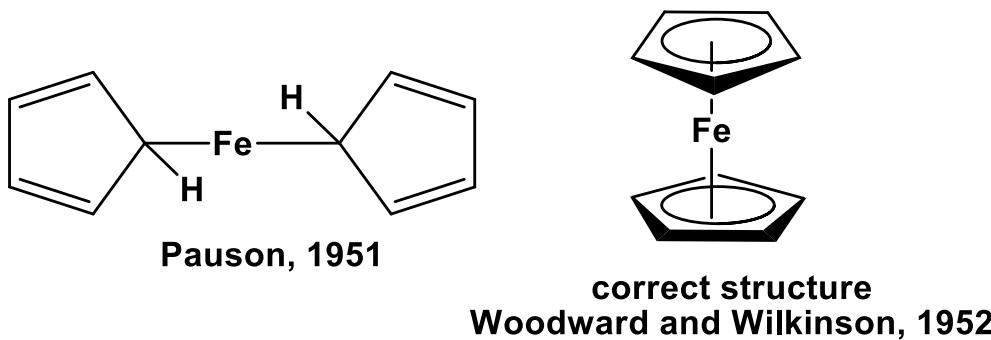


- 1912 Nobel prize Victor Grignard and Paul Sabatier
- 1930 Gilman reported organolithium preparation alkyl halide metallation



History: 1950 – 1960

- 1951 – 1952 Discovery of ferrocene, $(\eta^5\text{-Cp})_2\text{Fe}$



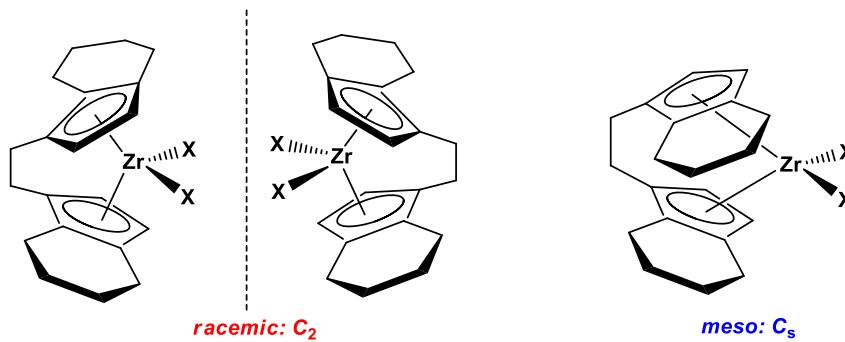
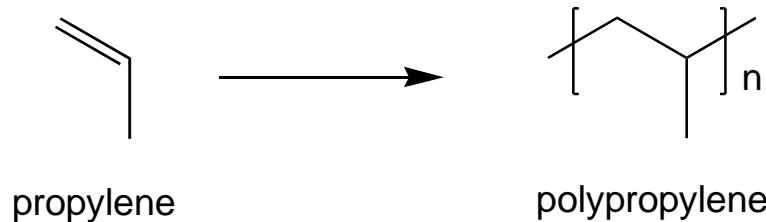
–1973 Nobel prize : Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds

1955 : Ziegler and Natta develop olefin polymerization at low pressure using mixed metal catalysts (transition metal halide / AlR_3)



Ziegler/Natta polymerization

- polymerization of olefins such as ethylene, propylene and styrene.
- polymerization of unsubstituted alkene : yields various polymers
- polypropylene was made up of two fractions: **amorphous (atactic)** and **crystalline (tactic)**.
- ***Polypropylene is not produced in radical initiated reactions.***



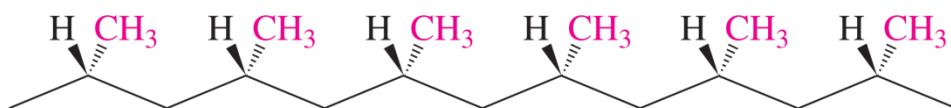
1963 Nobel prize : Karl Ziegler and Giulio Natta on Ziegler-Natta catalysts

The substituents in an **atactic polymer** are randomly oriented

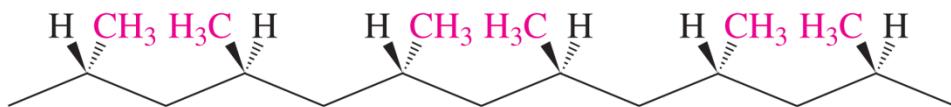
An **isotactic polymer** has all of its substituents on the same side of the fully extended carbon chain.

In a **syndiotactic polymer** (*syndio* means “alternating”), the substituents regularly alternate on both sides of the carbon chain.

isotactic configuration (same side)

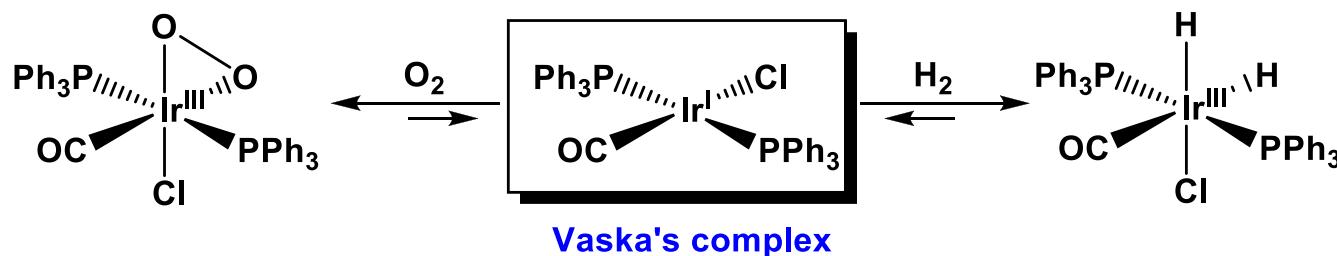


syndiotactic configuration (both sides)

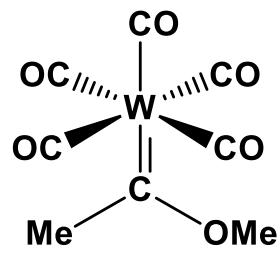


History: 1960 – 1980: catalysis

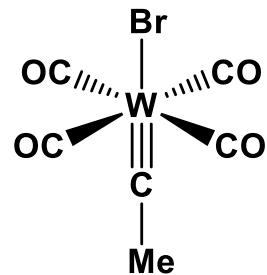
- 1962: Vaska's complex



- 1964: Fischer reports the first metal carbene.



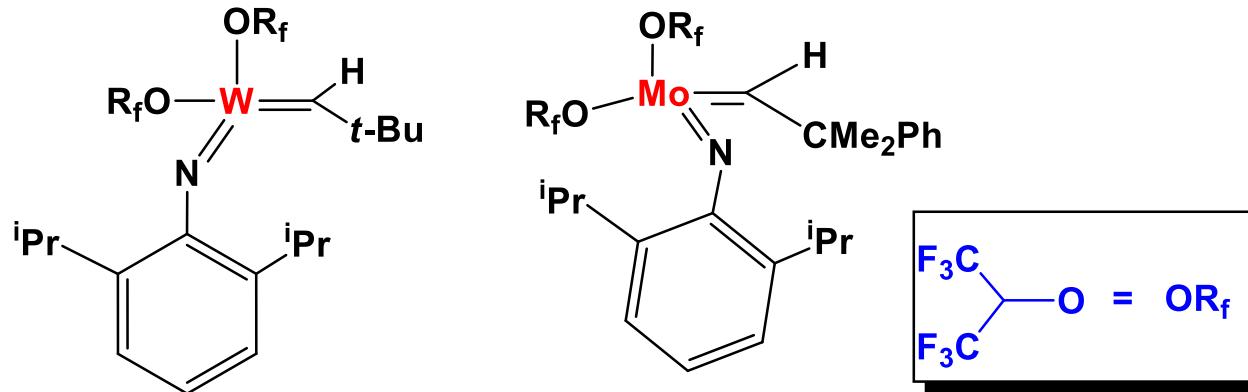
stabilized carbene complex
Fischer, 1964



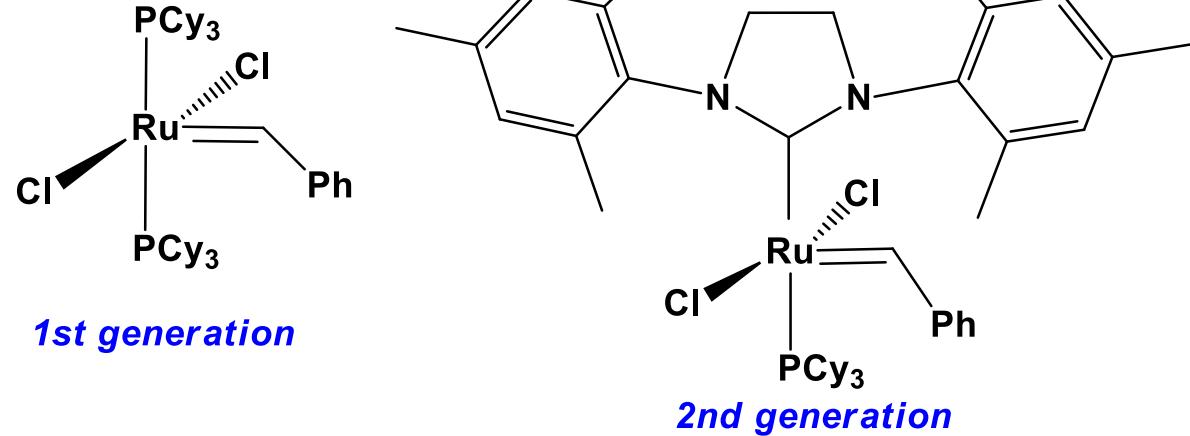
carbyne complex
Fischer, 1973

2005 Nobel prize in chemistry

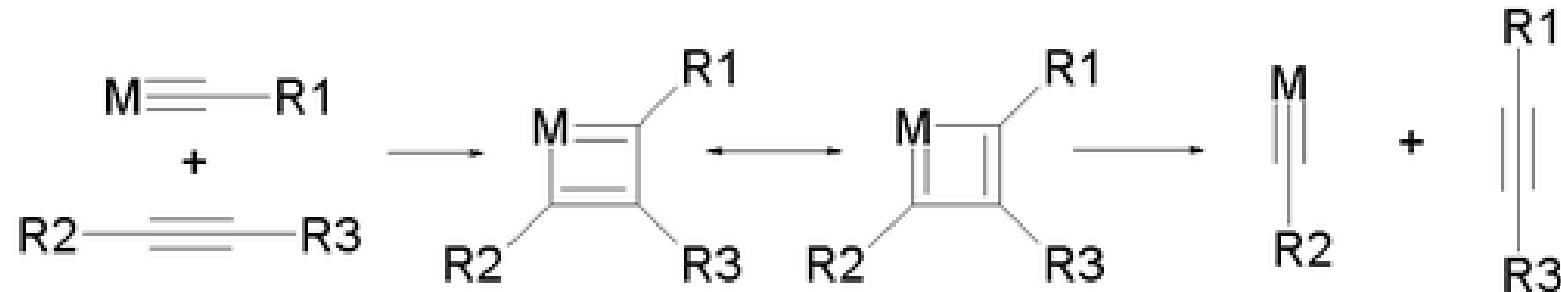
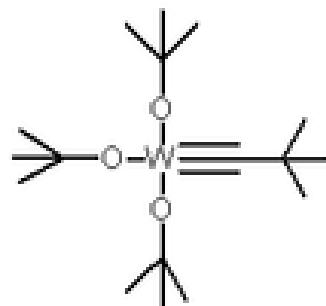
Schrock catalysts



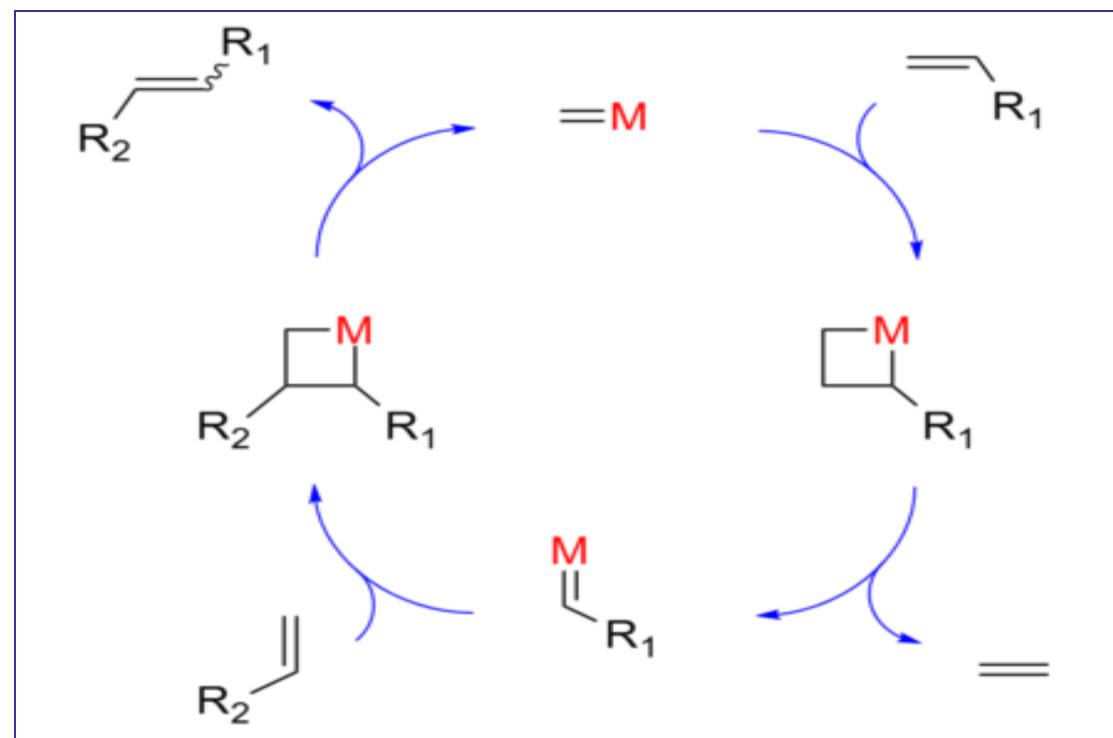
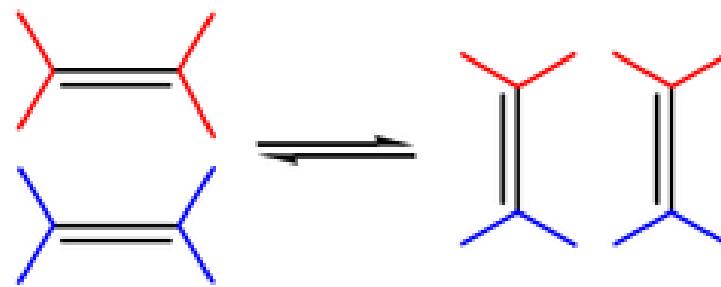
Grubbs catalysts



SCHROCK CATALYST AND ALKYNE METATHESIS



GRUBB'S CATALYST is used in organic synthesis to achieve **olefin metathesis**.



C–H activation

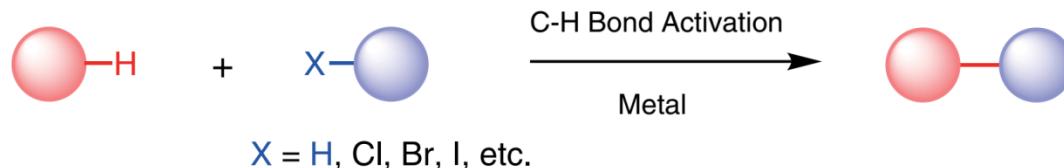
A methodology for directly forming carbon–carbon bonds by activating a carbon hydrogen bond

Why is it important?

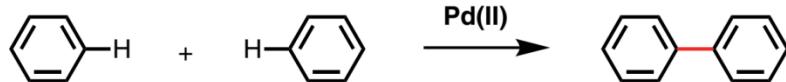
C–H bonds generally have relatively high energy;

therefore, the formation of a carbon–carbon or carbon–heteroatom bond by dissecting C–H bonds has been believed to be difficult.

C–H Bond Activation Reaction

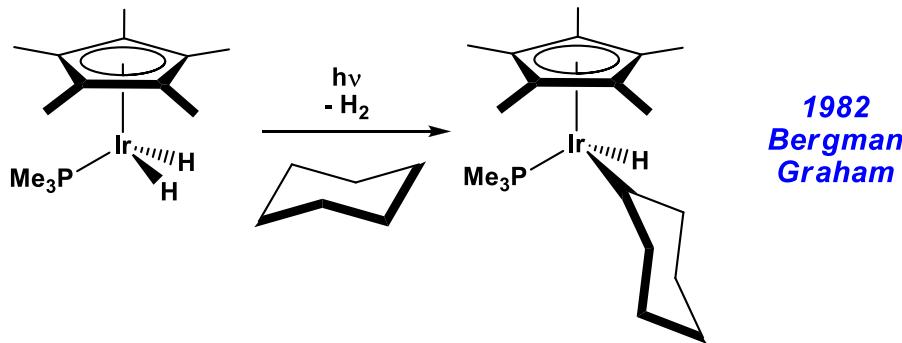


(example)

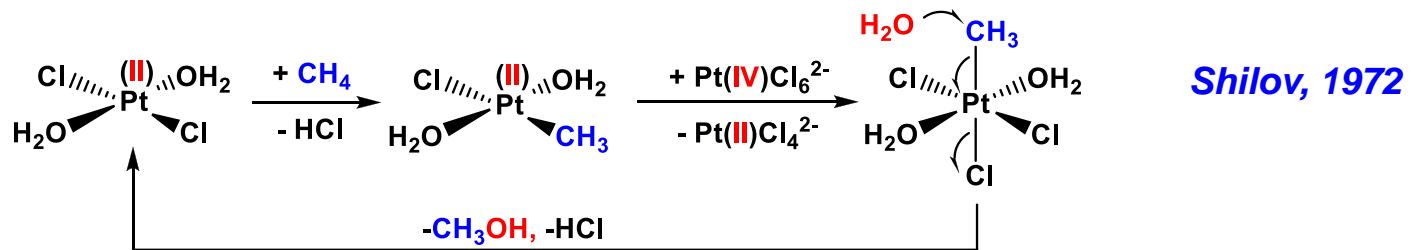


C–H activation

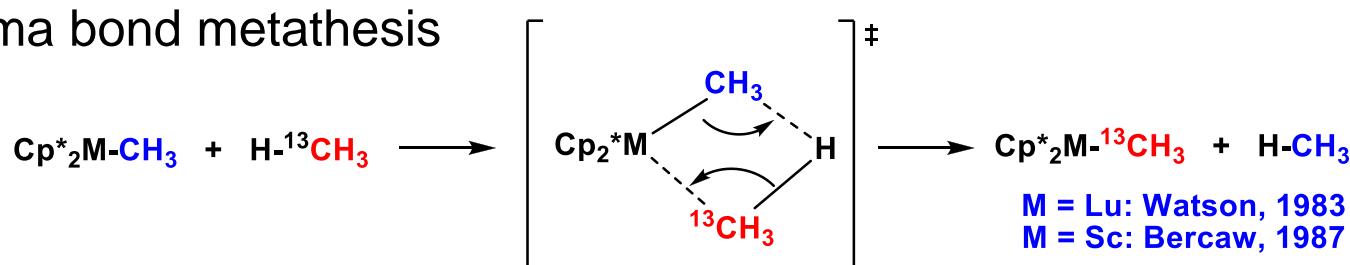
- Oxidative addition



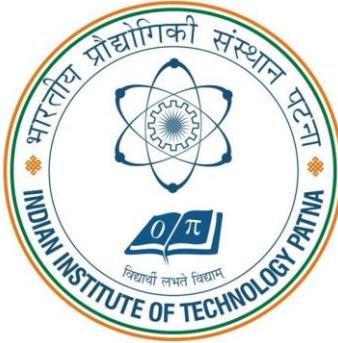
- Electrophilic activation



- Sigma bond metathesis



C–H activation requires very reactive species.



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Organolithium Compounds

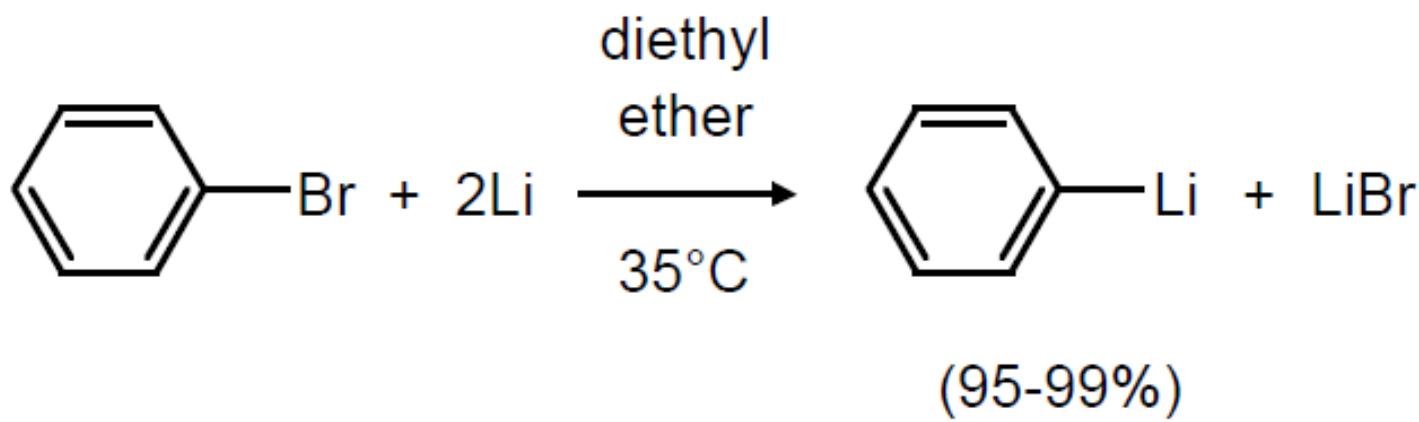
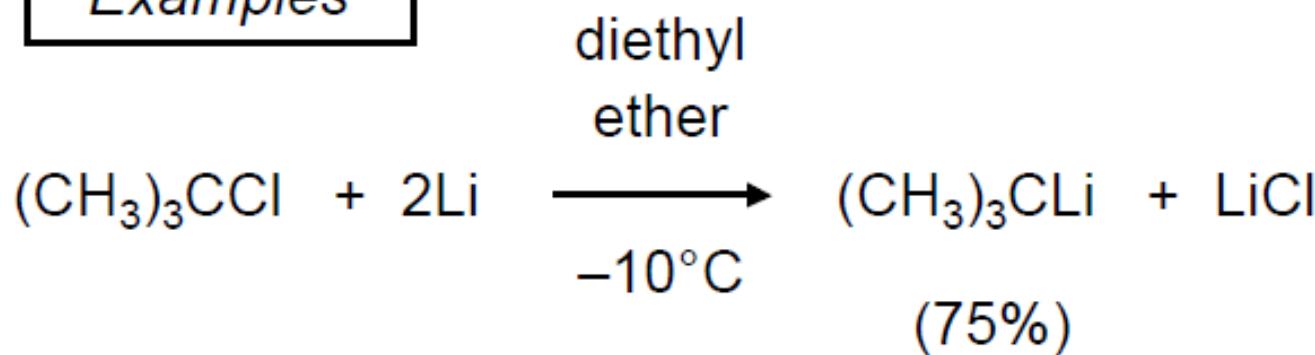
normally prepared by reaction of alkyl halides
with lithium



same for Ar—X

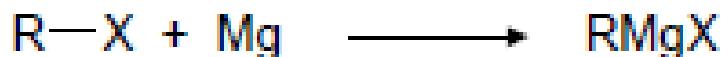
is an oxidation-reduction reaction: carbon
is reduced

Examples



Grignard Reagents

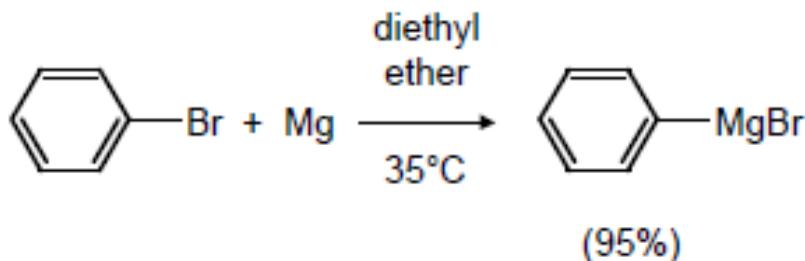
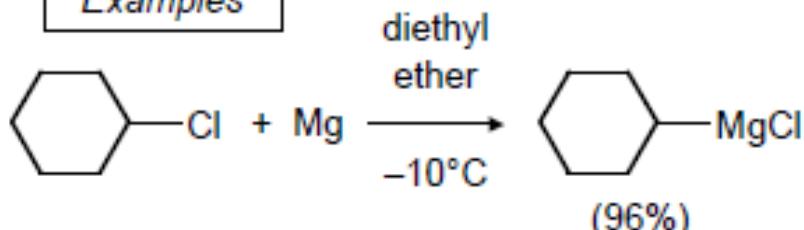
prepared by reaction of alkyl halides
with magnesium



same for Ar-X

Diethyl ether is most often used solvent.
Tetrahydrofuran is also used.

Examples



Grignard reagents react with:

- formaldehyde to give primary alcohols
- aldehydes to give secondary alcohols
- ketones to give tertiary alcohols
- esters to give tertiary alcohols

18 electron rule

1920s: N.V. Sidgwick

- ❖ Used for predicting formulas for stable metal complexes.
- ❖ Valence shells of a transition metal consists of nine valence orbitals, which collectively can accommodate 18 electrons either as nonbinding electron pairs or as bonding electron pairs.
- ❖ When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas at the end of the period.
- ❖ The 18-electron rule is sometimes referred to as the **effective atomic number or EAN rule**.

Rules for Electron counting

- Two models
- **neutral-ligand method** (sometimes called the *covalent method*)
- **donor-pair method** (sometimes known as the *ionic method*).

Rules for Electron counting

- **donor-pair method** (sometimes known as the *ionic method*).
- The *oxidation number* of the metal atom is the total charge of the complex minus the charges of any ligands.
- The *number of electrons* the metal provides is its group number minus its oxidation number.
- The *total electron count* is the sum of the number of electrons on the metal atom and the number of electrons provided by the ligands.

Common Ligands and Their Electron Counts

Ligand	Type	Covalent Model	Ionic Model
Me, Cl, Ph, Cl, η^1 -allyl, NO (bent) ^a	X	1e	2e
Lone-pair donors: CO, NH ₃	L	2e	2e
π -Bond donors: C ₂ H ₄	L	2e	2e
σ -Bond donors: (H ₂)	L	2e	2e
M–Cl (bridging)	L	2e	2e
η^3 -Allyl, κ^2 -acetate	LX	3e	4e
NO (linear) ^a		3e	2e ^a
η^4 -Butadiene	L ₂	4e	4e
=O (oxo)	X ₂	4e	2e
η^5 -Cp	L ₂ X	5e	6e
η^6 -Benzene	L ₃	6e	6e

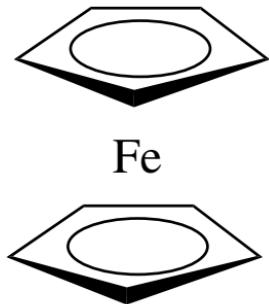
^aLinear NO is considered as NO⁺ on the ionic model

Validity of the 18-electron rule for d-metal organometallic compounds

- $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$ $\text{Ni}(\text{CO})_4$ follow 18 electron rule
- Most organometallic compounds of the Group 4 metals have fewer than 18 electrons and are air- and moisture-sensitive.
- Square-planar complexes are particularly common for the heavier elements in Groups 9 and 10, especially for Rh(I), Ir(I), Pd(II), and Pt(II) : **16-electron complexes**

Usually less than 18 electrons			Usually 18 electrons			16 or 18 electrons	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

C_5H_5^-	6e
C_5H_5^-	6e
Fe^{2+}	$\frac{6e}{18e}$



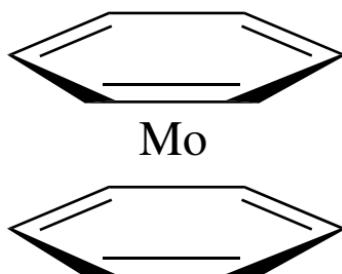
$\text{C}_5\text{H}_5^\bullet$	5e
$\text{C}_5\text{H}_5^\bullet$	5e
Fe	$\frac{8e}{18e}$

Mo^{4+}	2e
$4 \times \text{H}^-$	8e
$4 \times \text{PR}_3$	$\frac{8e}{18e}$



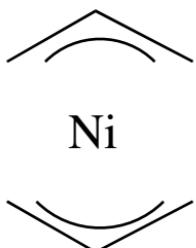
Mo	6e
$4 \times \text{H}^\bullet$	4e
$4 \times \text{PR}_3$	$\frac{8e}{18e}$

Mo	6e
$2 \times \text{C}_6\text{H}_6$	$\frac{12e}{18e}$



Mo	6e
$2 \times \text{C}_6\text{H}_6$	$\frac{12e}{18e}$

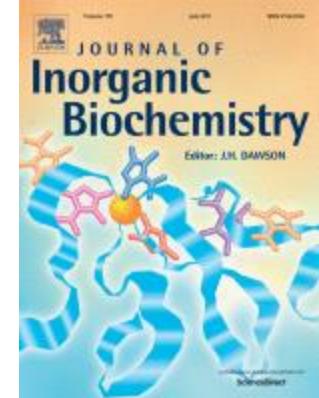
Ni^{2+}	8e
$2 \times \text{C}_3\text{H}_5^-$	$\frac{8e}{16e}$



Ni	10e
$2 \times \text{C}_3\text{H}_5^\bullet$	$\frac{6e}{16e}$



Bioinorganic chemistry



Topics

1. Trace elements in biology,
 2. heme and non-heme oxygen carriers,
 3. haemoglobin and myoglobin
- What is bioinorganic chemistry?
 - Study of role of metal species in biological systems
 - Interface of biology and inorganic chemistry
 - Metal ions are present in various enzymes and proteins
 - Bioinorganic chemistry *aka* Inorganic biochemistry

Polypeptides and Proteins

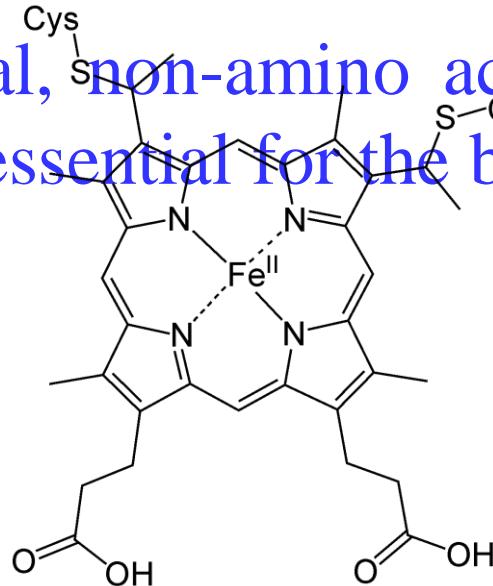
- A **polypeptide**: condensation, in varying sequences, of the 20 naturally occurring **α -amino acids**
- **Proteins**: high molecular mass polypeptides with complex structures.
- **Enzymes**: proteins that catalyze the biochemical reactions. May contain metal ions that are responsible for catalysis (**metalloenzymes**)
- All enzymes are proteins but all proteins are not enzymes

Some Terminology in Proteins

- **Globular proteins:** the polypeptide chains are coiled into near-spherical structures
- **Metalloproteins:** Metal containing proteins
- **Oxygenases:** enzymes that insert oxygen into other molecules
- **Nitrogenases:** Nitrogen fixation by bacteria involves the reduction of N₂ to NH₃
$$\text{N}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2$$
- **Apoprotein:** metalloprotein minus metal
 - Metal free species

The prosthetic group

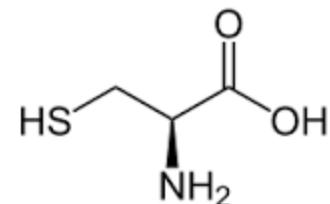
- It is an additional, non-amino acid component of a protein which is essential for the biological activity of the protein.



- We shall be concerned with prosthetic groups containing metal centres, e.g. haem is the prosthetic group in haemoglobin and myoglobin.

Fundamental elements

- building blocks of biomolecules (e.g. amino acids, peptides, carbohydrates, proteins, lipids and nucleic acids) are **C**, **H**, **N** and **O**,
- **P**: ATP and DNA and **S** being the key to the coordinating abilities of cysteine residues in proteins.



less abundant elements

- **Na, K and Cl**: osmotic control and nerve action as electrolytes in body.
- Mg^{2+} in chlorophyll and Mg^{2+} containing enzymes involved in phosphate hydrolysis,
- Ca^{2+} : structural functions (e.g. bones, teeth, shells) and triggering actions of in muscles.

trace metals essential for growth for most organisms

- **V**: Enzymes (nitrogenases, haloperoxidases)
- **Cr**: essential in glucose metabolism in higher mammals
- **Mn**: Enzymes (phosphatase, mitochondrial superoxide dismutase, glycosyl transferase); Photosynthesis
- **Fe**: Electron-transfer systems (Fe–S proteins, cytochromes); O₂ storage and transport (haemoglobin, myoglobin, haemerythrin); Fe storage (ferritin, transferritin); Fe transport proteins (siderophores); in enzymes (e.g. nitrogenases, hydrogenases, oxidases, reductases)



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CH 103

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Other trace metals

- **Co**: Vitamin B12 coenzyme
- **Ni**: Enzymes (urease, some hydrogenases)
- **Cu**: Electron transfer systems (blue copper proteins); O₂ storage and transport (haemocyanin); Cu transport proteins (ceruloplasmin)
- **Zn**: Acts as a Lewis acid (e.g. in hydrolysis processes involving carboxypeptidase, carbonic anhydrase, alcohol dehydrogenase); structural roles
- **Mo**: Enzymes (nitrogenases, reductases, hydroxylases)

Trace Nonmetals

- **B**: essential to green algae and higher plants
- **Si**: exoskeletons of marine diatoms composed of hydrated silica
- **Se**: essential to mammals and some higher plants;
- **F**: deficiency causes dental caries;
- **I**: essential to many organisms
 - constituent of the thyroid hormones
 - thyroxine (T4) and triiodothyronine (T3)

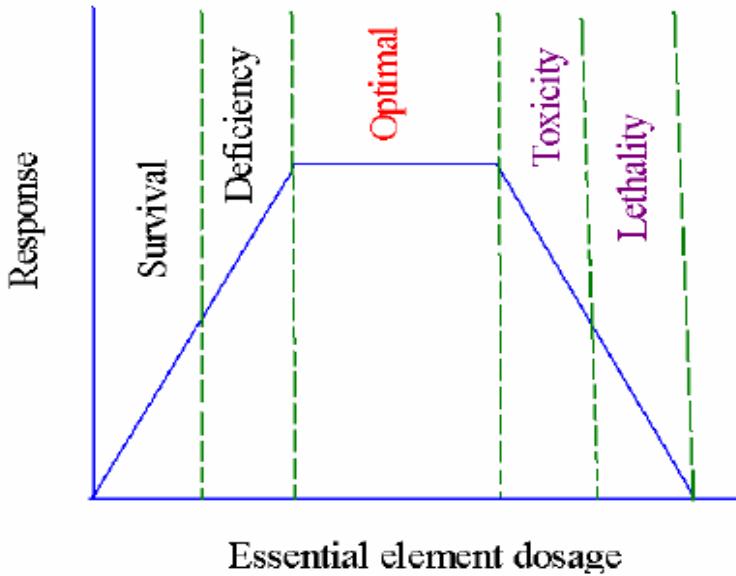
Chemical elements essential to life forms can be divided into the following

- (i) Bulk elements:** C, H, N, O, P, S
- (ii) Macrominerals and ions:** Na, K, Mg, Ca, Cl, PO_4^{3-} , SO_4^{2-}
- (iii) Trace elements:** Fe, Zn, Cu
- (iv) Ultratrace elements comprises of**
 - (a) non-metals:** F, I, Se, Si, As, B
 - (b) metals:** Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li

Essentiality of elements is defined by

- (1) A physiological deficiency appears when the element is removed from the diet
- (2) The deficiency is relieved by the addition of that element to the diet
- (3) A specific biological function is associated with the element

Every essential element follows a dose-response curve



At lowest dosages organism does not survive

In deficiency regions, the organism exists with less than optimal functions

After optimal dosage (plateau region), higher dosage cause toxic effects in the organism eventually leading to lethality

Metal Toxicity

Aluminum

Target tissues are bones, brain, kidneys, and stomach. Signs and symptoms include colic, dementia, gastroenteritis, kidney damage, and liver damage.

Arsenic

Chronic toxic effects are fatigue, loss of energy, G.I. disturbance, nasal septum perforation, ulceration in folds of skin, increased pigmentation of skin, appearance of small “corns” or “warts” on the palms, soles, exfoliative dermatitis, rashes, muscular paralyses and atrophy, sensory disturbances, visual disturbances and blindness, degeneration of liver (cirrhosis) and kidneys.

Barium:

Difficulties in breathing; increased blood pressure; changes in heart rhythm (digitalis-like toxicity) and ventricular fibrillation, extra systoles; stomach irritation; brain swelling (cerebral cortex--digitalis-like effect); convulsive tremors and muscle weakness; damage to liver, kidney, heart, and spleen

Lead:

In the central nervous system, lead causes edema, and its effects are often irreversible. Reduced IQ, learning and behavioral difficulties in children, Neurological and behavioral effects, peripheral neuropathy, (leading to weakness and palsy with wrist drop).

Zinc:

cause stomach cramps, nausea, and vomiting. Taken longer, it can cause anemia, pancreas damage

Chromium:

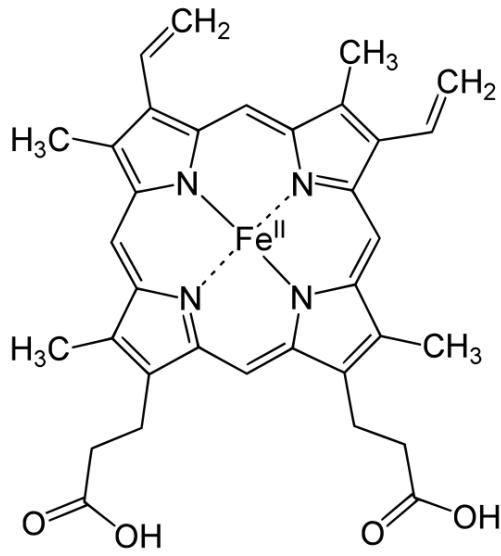
Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death.

Bioinorganic chemistry of Fe

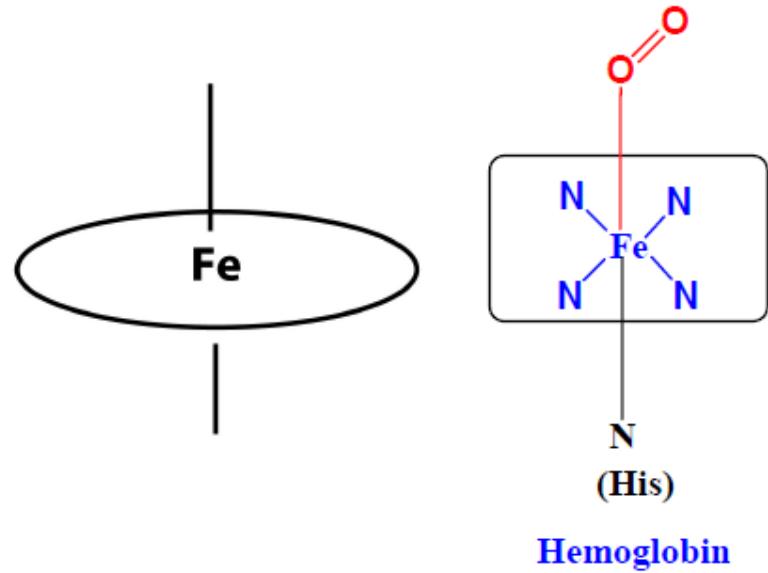
- Fe: the most important trace metal in humans.
- dietary intake (typically 6–40 mg per day)
- There is no excretory loss of Fe
 - a phenomenon not shared by other metals present in the body.
- the mammalian system is very effective at (storing and transporting) recycling Fe

Haemoglobin and myoglobin

- Haemoglobin:
 - carrying O₂ in blood stream
- Myoglobin:
 - storing O₂ in tissues



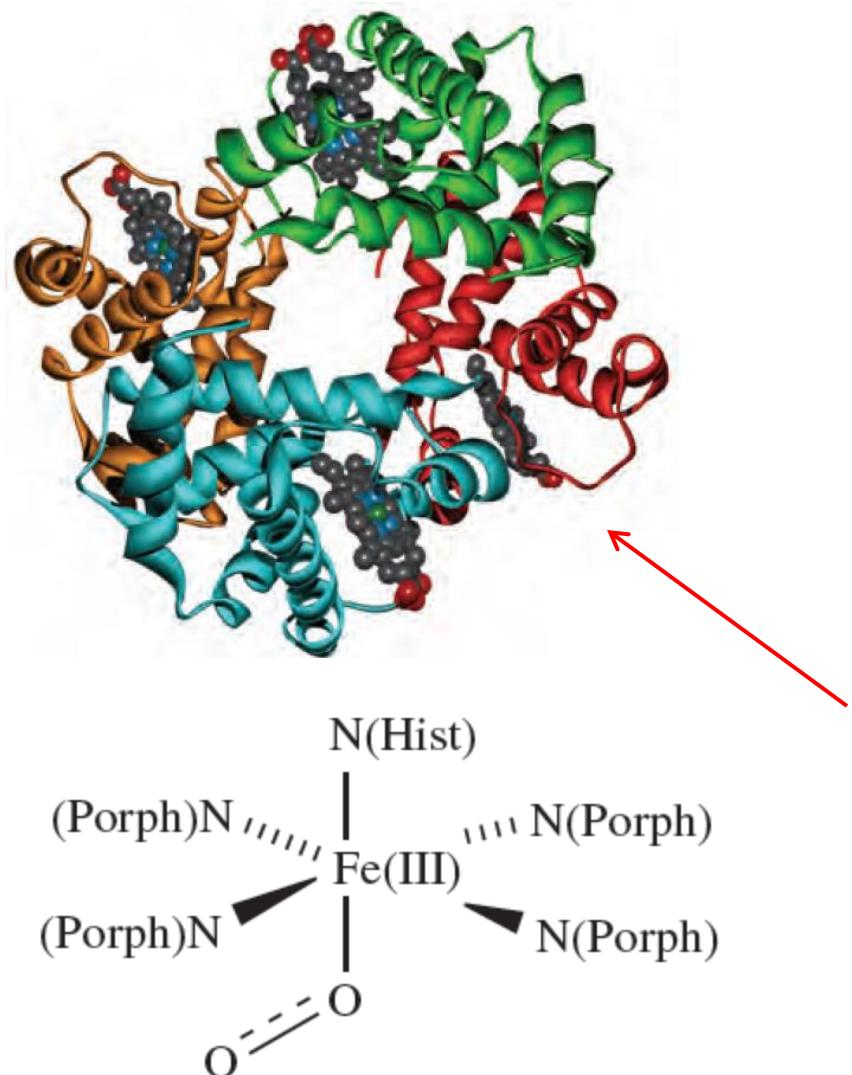
haem group



Hemoglobin

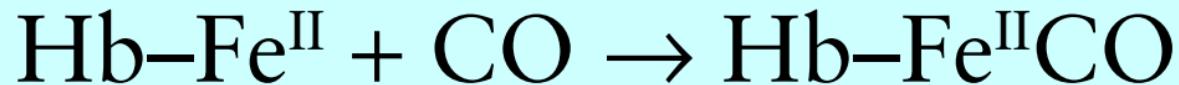
Haemoglobin (tetrameric)

- The Fe(II) centre is in a **square-based pyramidal** environment when in its '**rest state**', also referred to as the **deoxy-form**
 - the binding (and release) of O₂ is a **cooperative process**



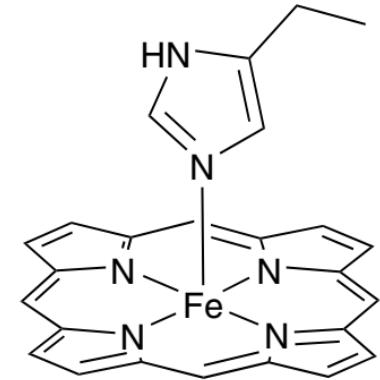
CO toxicity

- The toxicity of carbon monoxide to animals is an example of a Lewis acid–base reaction.
- Normally, oxygen forms a bond to the Fe(II) atom of haemoglobin and does so reversibly
- carbon monoxide is a much better Lewis acid than O₂
- CO forms such a stable bond with the iron(II)
- the complexation of Fe and CO is almost irreversible.
- excluding the attachment of O₂ : victim suffocates



Myoglobin

- the oxygen transport protein
- It is an Fe protein that coordinates O_2 reversibly and controls its concentration in tissue
- Structure of the active centre of myoglobin
- the Fe atom is located in the plane of the ring
- Geometry: square pyramidal
- The fifth ligand to the Fe is provided by a histidine-N, and the sixth position is the site at which O_2 is coordinated
- Deoxymyoglobin (Mb) is bluish red and contains Fe(II)—the oxidation state that binds O_2 reversibly to give the familiar bright red oxymyoglobin (oxyMb)



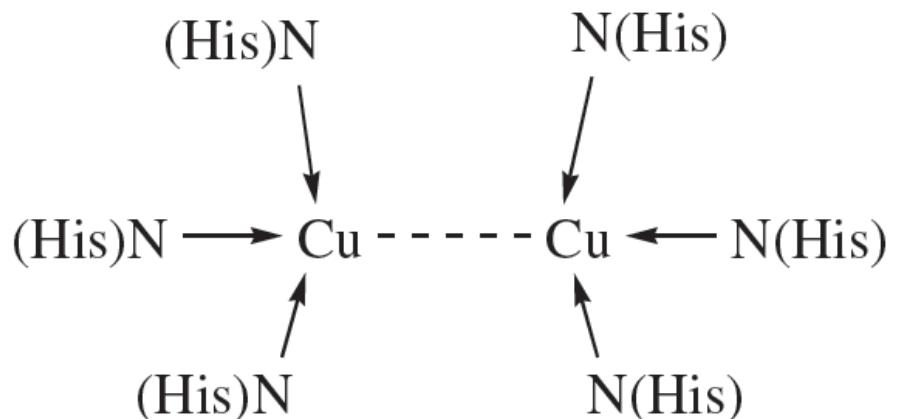


Haemocyanin

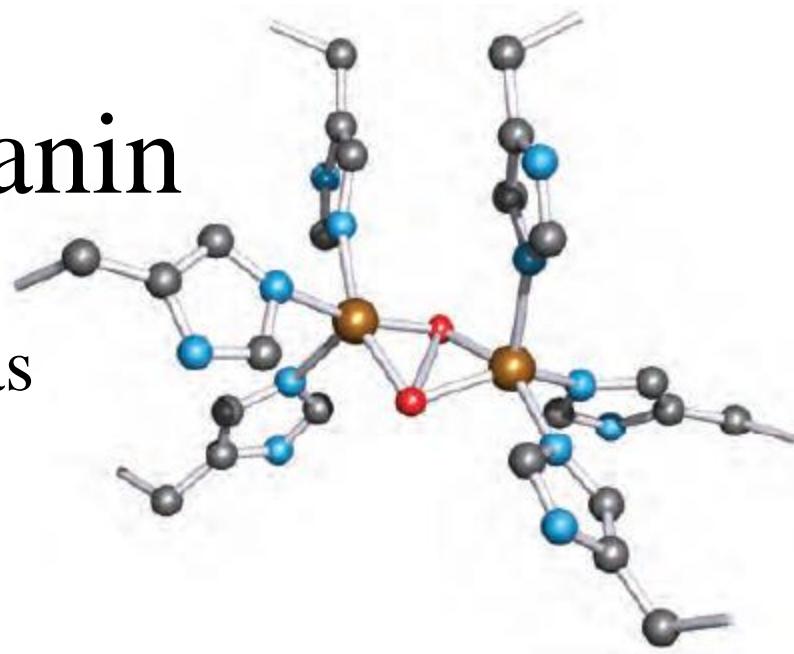


- **O₂-carrying copper**-containing proteins in **molluscs** (e.g. snails, squid) and **arthropods** (e.g. lobsters, crabs, shrimps, horseshoe crabs, scorpions)
- deoxy-form (colourless)
 - contains Cu(I), : d^{10}
- O₂ binding results in the **blue** colour
 - Contains Cu(II) form : d^9

- **Cu \cdots Cu = 360 pm**



Haemocyanin

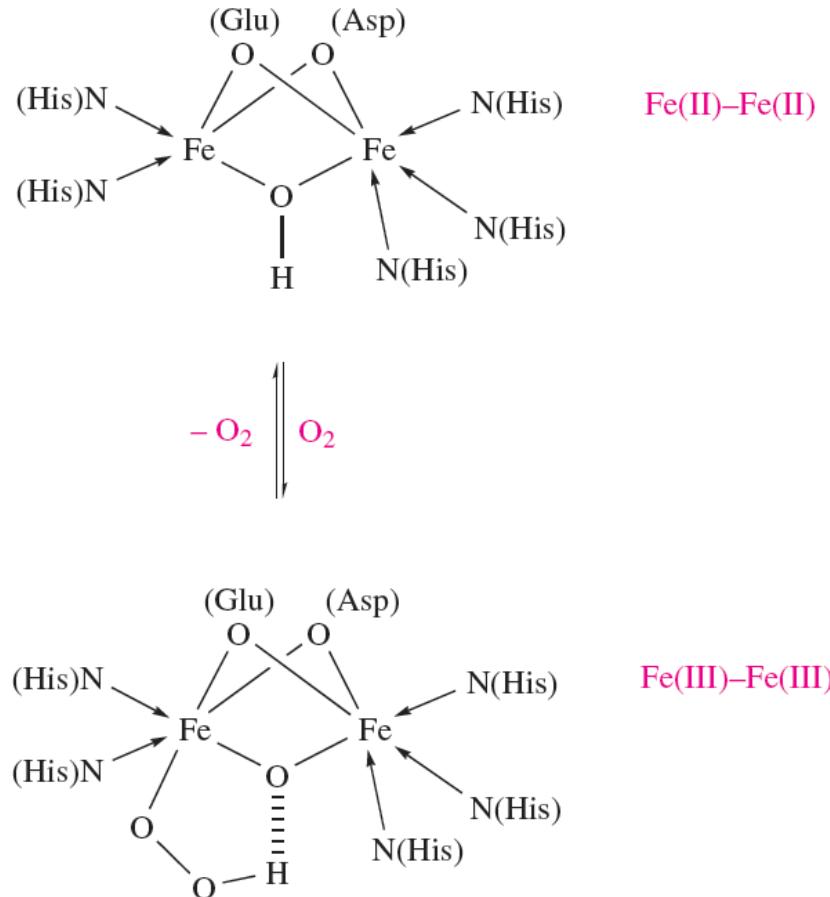


- O₂-binding site is formulated as
- Cu(II)-[O₂]²⁻-Cu(II)
 - O₂ bond length: 140 pm
 - Molecular oxygen: 120 pm



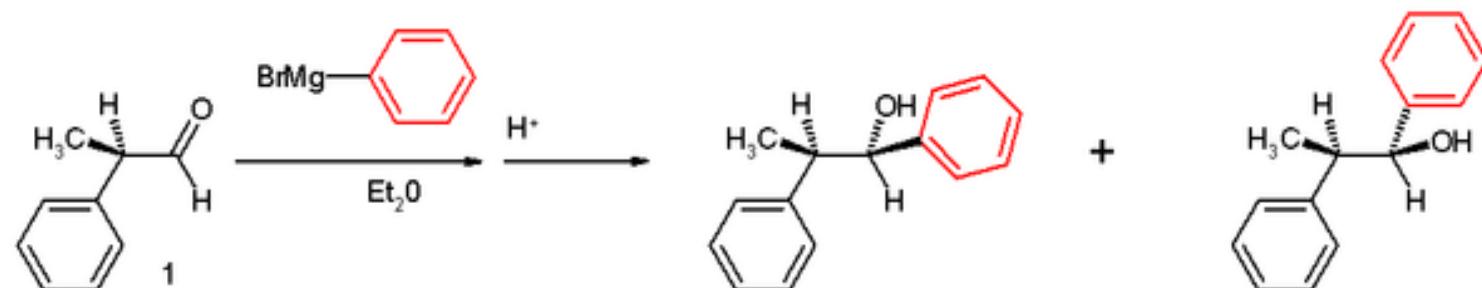
Haemerythrin

- A non-haem Fe-containing protein
- O_2 is transported in marine invertebrates such as annelids (segmented worms)

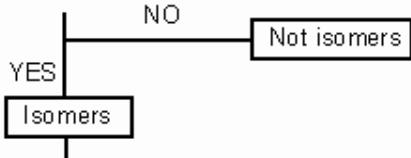


Stereochemistry

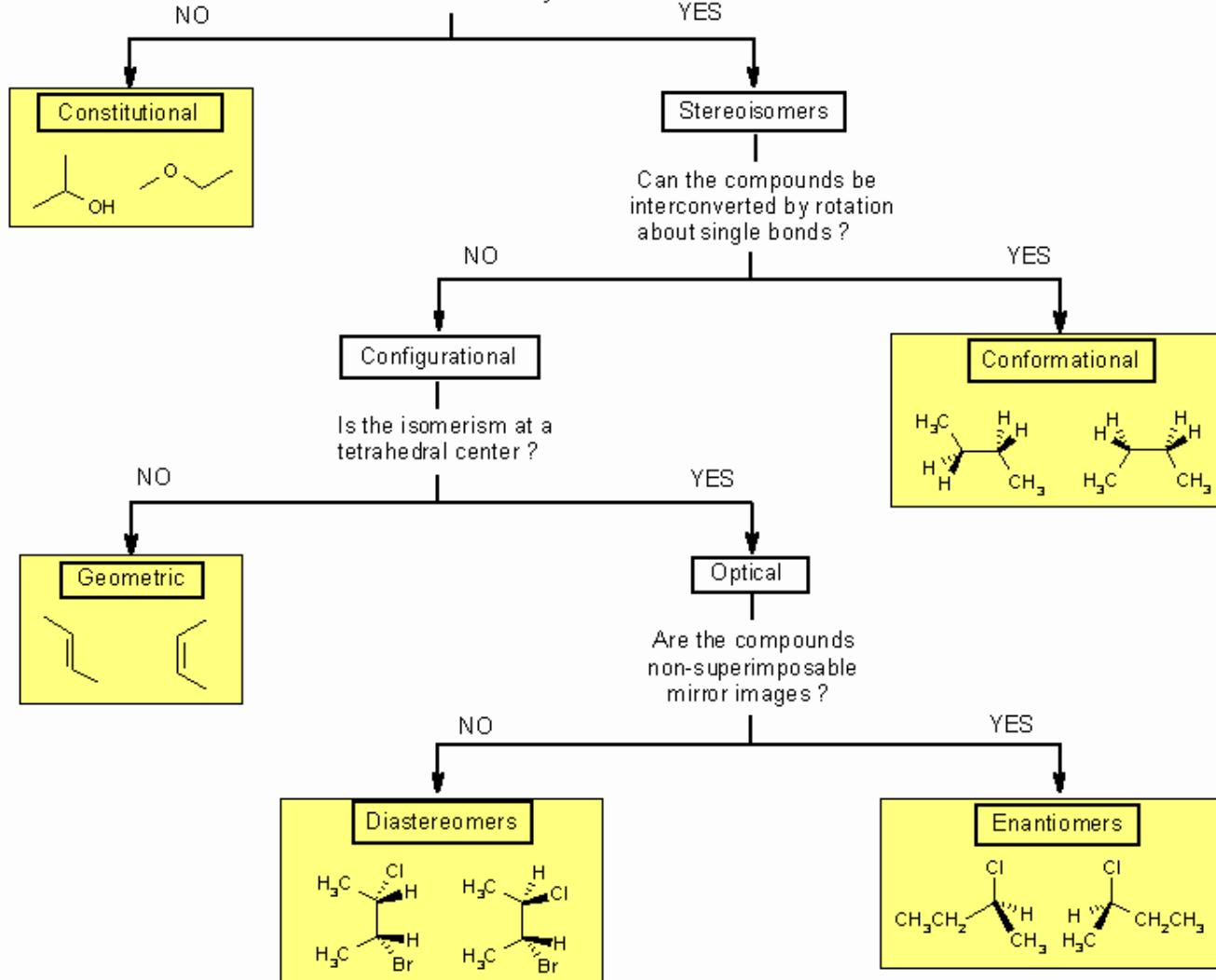
refers to the 3-dimensional properties and reactions of molecules.



Do the compounds
have the same molecular
formulae ?



Do the compounds have
the same connectivity ?



Definitions

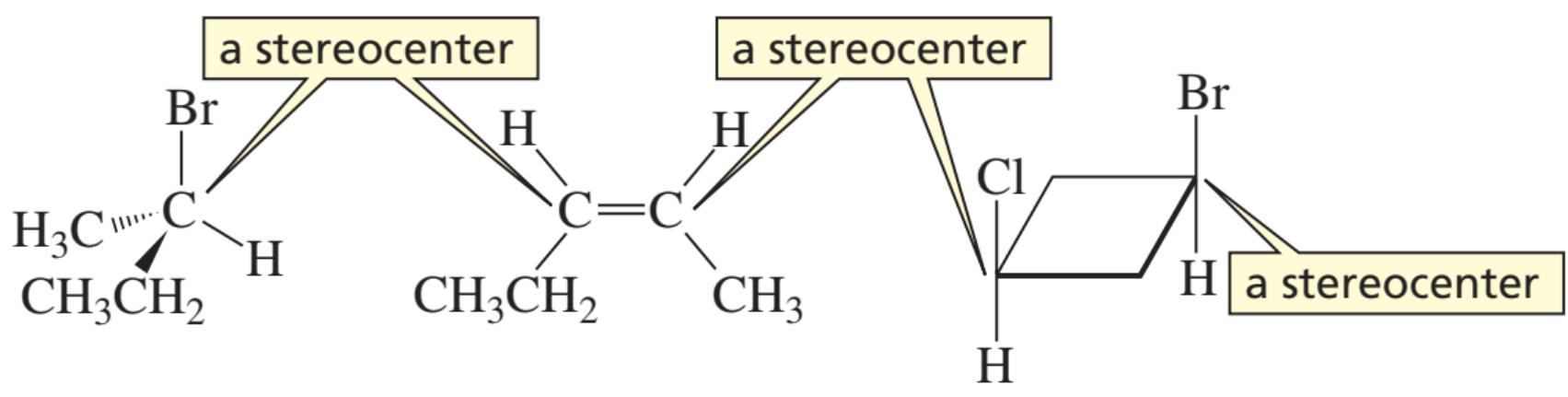
- **Stereoisomers** – compounds with the same connectivity, different arrangement in space
- **Enantiomers** – stereoisomers that are non-superimposable mirror images; only properties that differ are direction (+ or -) of optical rotation
- **Diastereomers** – stereoisomers that are not mirror images; different compounds with different physical properties

More Definitions

- **Asymmetric center** – sp^3 carbon with 4 different groups attached
- **Optical activity** – the ability to rotate the plane of plane-polarized light
- **Chiral compound** – a compound that is optically active (**achiral compound** will not rotate light)
- **Polarimeter** – device that measures the optical rotation of the chiral compound

Stereocenter

- Aka stereogenic center
- an atom at which the interchange of two groups produces a stereoisomer.



Specific Rotation, $[\alpha]$

$$[\alpha]_T = \frac{\alpha}{l \times c}$$

α = observed rotation

c = concentration in g/mL

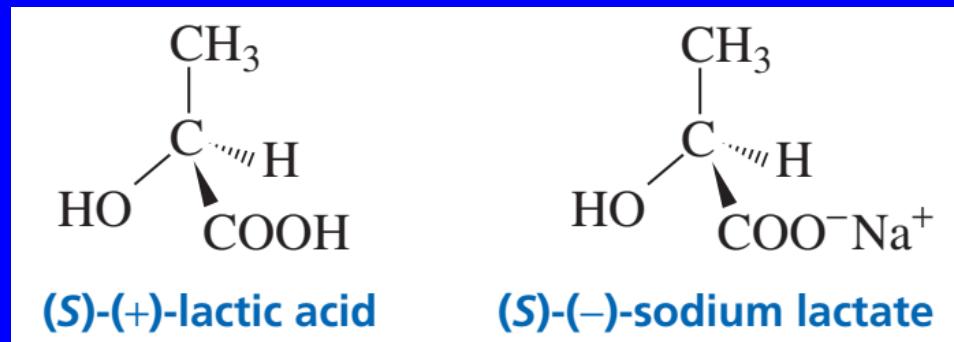
l = length of tube in dm

Dextrorotary designated as *d* or (+), clockwise rotation

Levorotary designated as *l* or (-), counter-clockwise rotation

R/S vs D/L

- Knowing whether a chiral molecule has the *R* or the *S* configuration does not tell us the direction the compound rotates the plane of polarization.
- because some compounds with the *R* configuration rotate the plane to the right and some rotate the plane to the left
- We can tell by looking at the structure of a compound whether it has the *R* or the *S* configuration, but the only way we can tell whether a compound is dextrorotatory or levorotatory is to **put the compound in a polarimeter**.
- (*S*)-lactic acid and (*S*)-sodium lactate have the same configuration, but (*S*)-lactic acid is dextrorotatory whereas (*S*)-sodium lactate is levorotatory

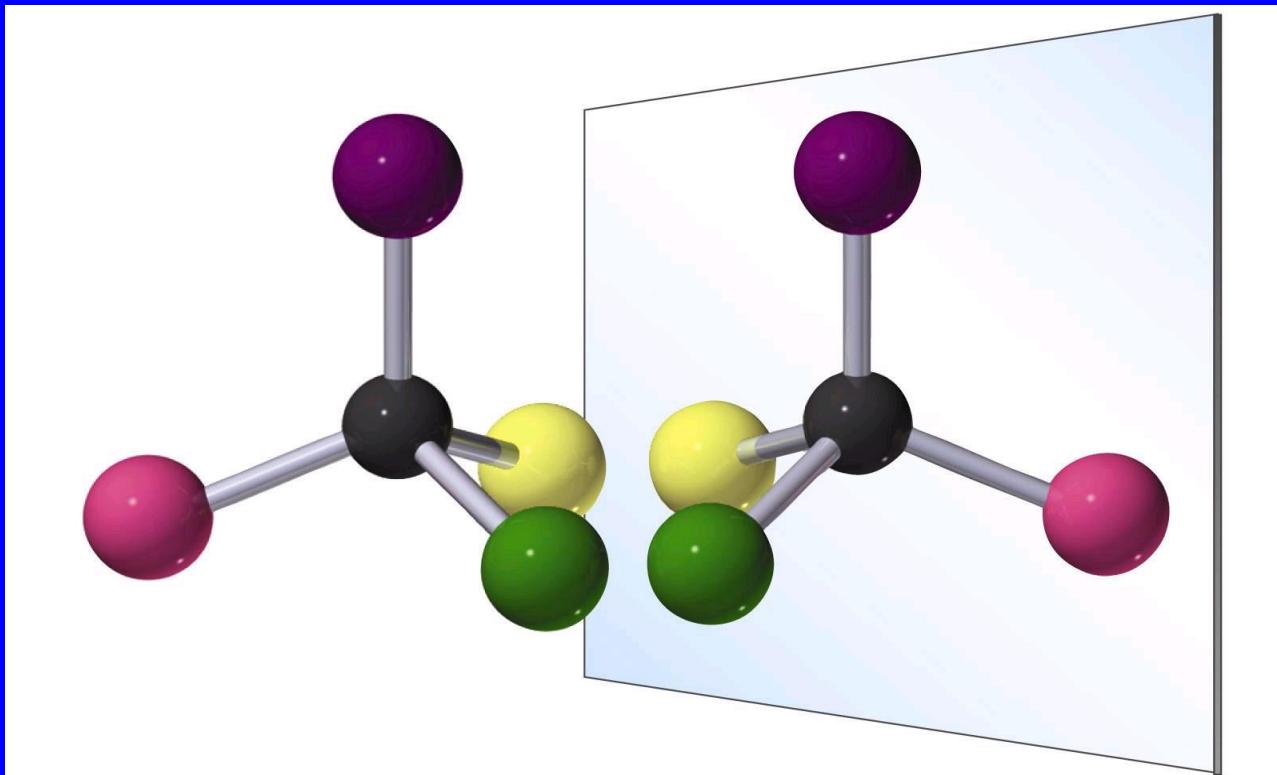


Specific Rotations of some Common Organic Compounds

<u>Compound</u>	[a]	<u># * centers</u>
Sucrose	+66.5	10
Camphor	+44.3	2
MSG	+25.5	1
Cholesterol	-31.3	8
Morphine	-132.0	5

Chirality Center

Carbon has four different groups attached

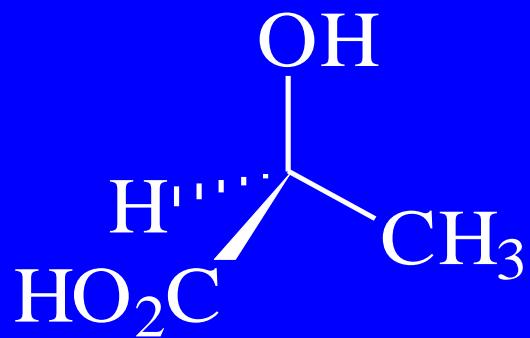


nonsuperimposable
mirror images

Enantiomers

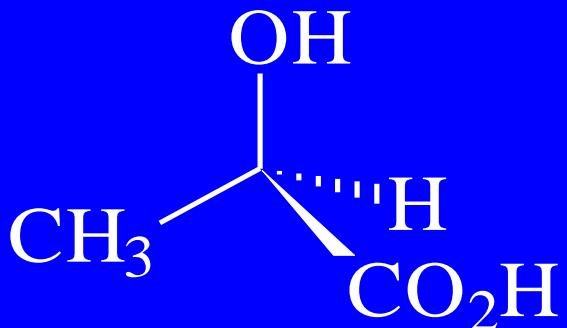
nonsuperimposable mirror images

mirror
plane



(S)(+) lactic acid

from muscle tissue
 $[\alpha] = +13.5^\circ$

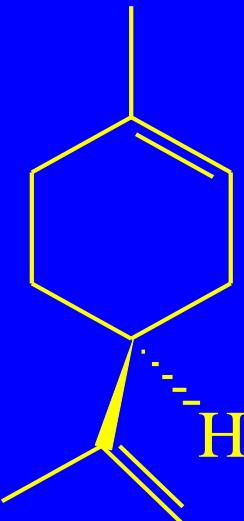


(R)(-) lactic acid

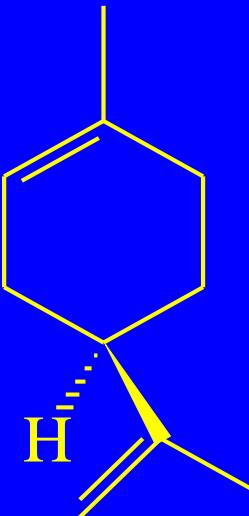
from milk
 $[\alpha] = -13.5^\circ$

Enantiomeric Excess (Optical Purity)

$$\frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} \times 100 = \text{enantiomeric excess (e.e.)}$$



(S)-(-) Limonene
 $[\alpha] = -123.0^\circ$
from lemons



(R)(+) Limonene
 $[\alpha] = +123.0^\circ$
from oranges

observed rotation = $+109^\circ$

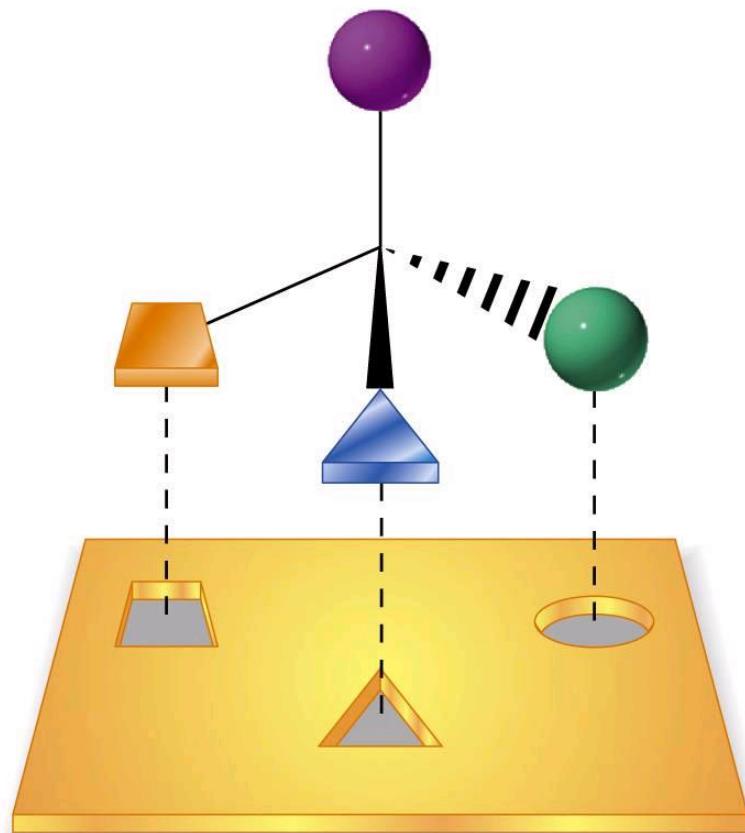
$$\text{e.e.} = \frac{109.0}{123.0} \times 100$$

= 88.6% e.e.

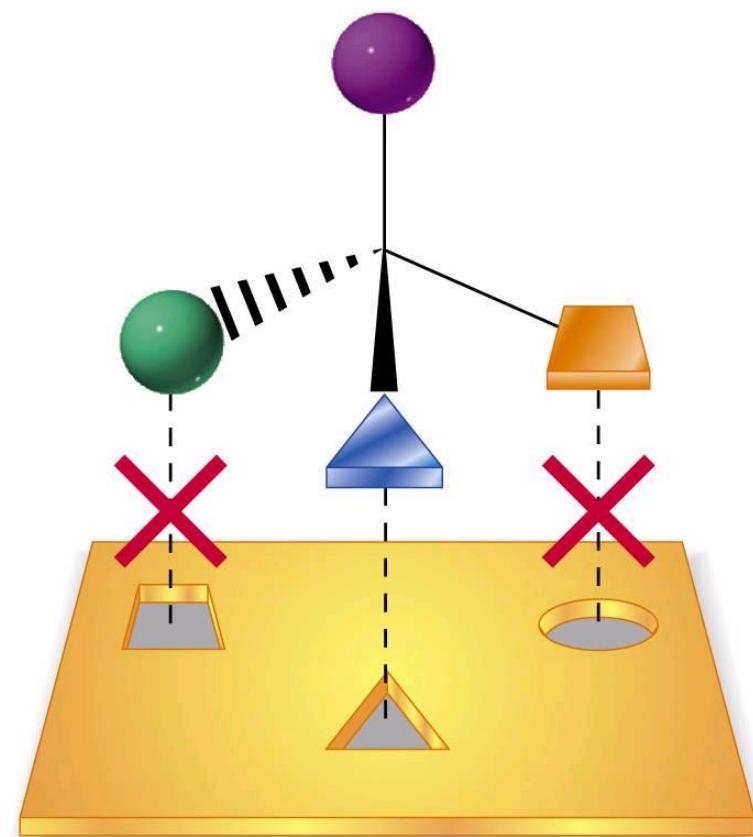
88.6% (+)
11.4% racemic

actually 94.3% (+)

R enantiomer



S enantiomer

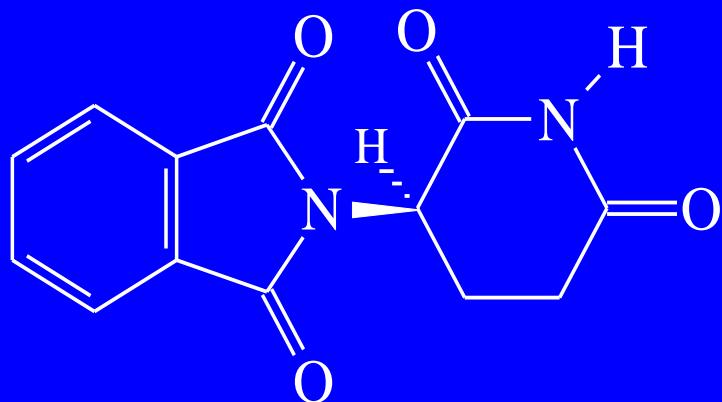


binding site of the receptor

binding site of the receptor

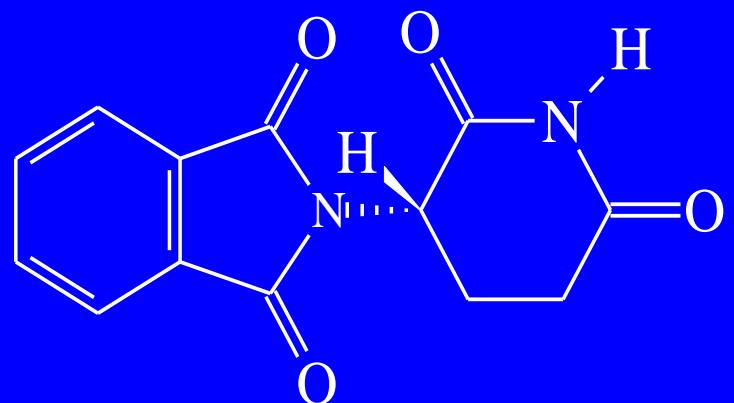
Biological Activity

(R)(+) Thalidomide



a sedative and hypnotic

(S)(-) Thalidomide



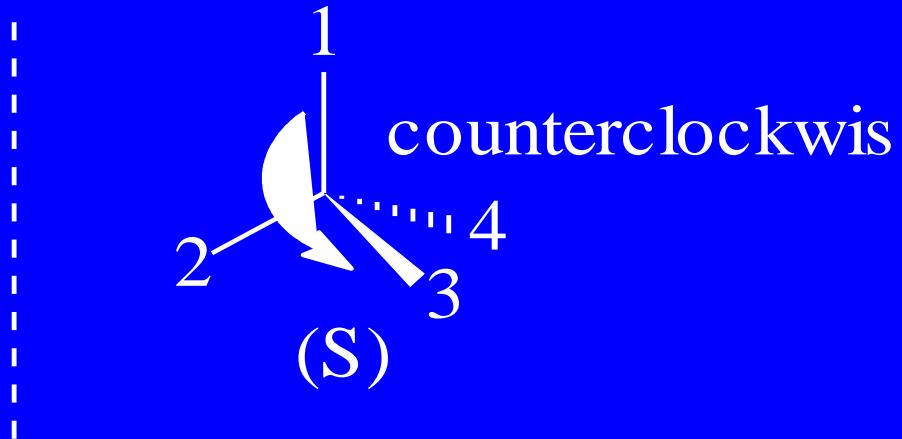
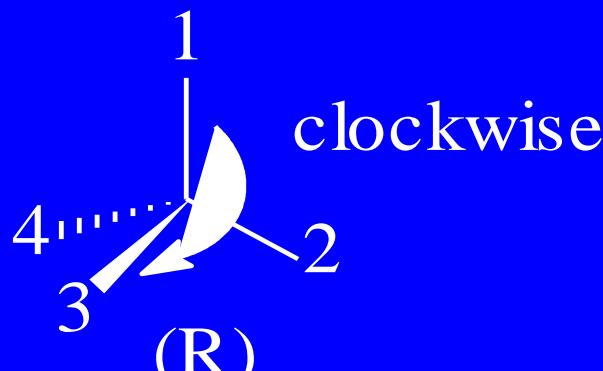
a teratogen

A teratogen is any agent that causes an abnormality following fetal exposure during pregnancy

Absolute Configuration

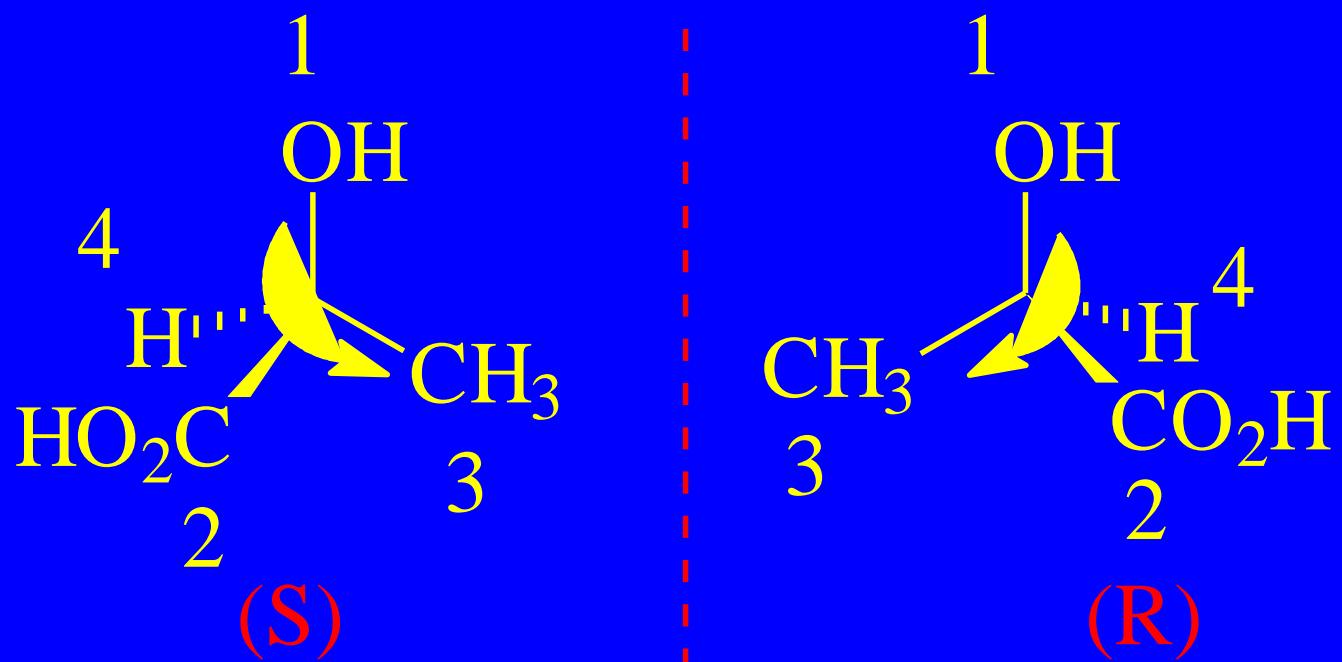
Use Cahn, Ingold, Prelog priorities

Place the lowest priority group back
(focus down C - 4 bond)
draw arrow from 1-2-3

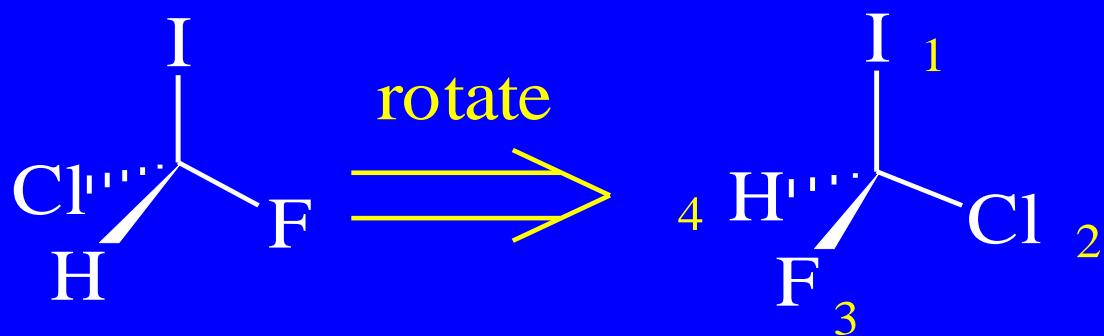


R is for *rectus* (Latin for “right”) *S* is for *sinister* (Latin for “left”)

Lactic Acid



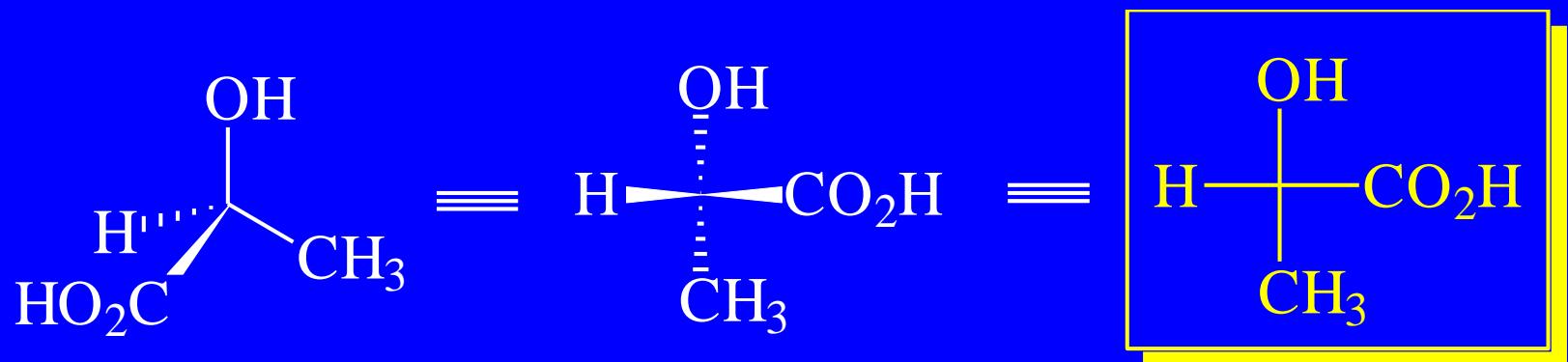
Assign Priority to each Group on Asymmetric Center



focus down C-4 bond

If the group with the lowest priority (**4**) is NOT bonded by a dashed wedge, then rotate molecule such that so lowest priority group **4** is bonded by a hatched wedge.

Fischer Projections

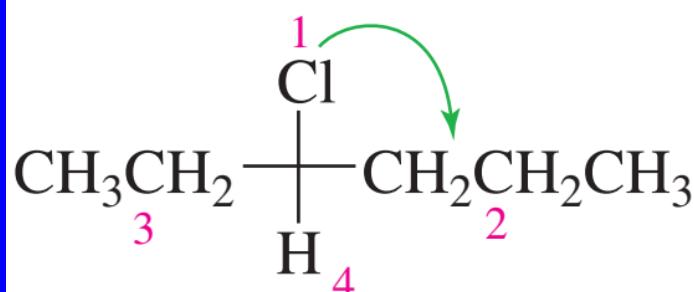


Horizontal bonds approach you (wedge bonds)

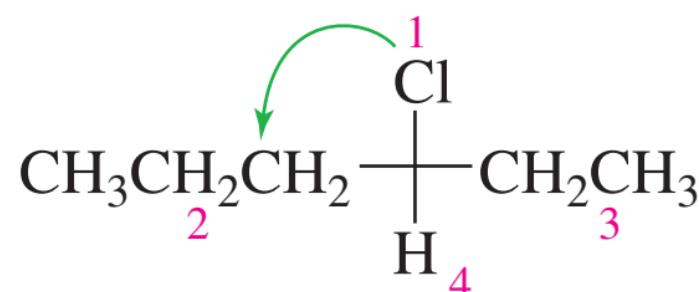
Vertical bonds move away (dashed bonds)

Fischer Projections

- *Check:* The group with the lowest priority (4) is on a vertical bond.
- Draw an arrow from the group (or atom) with the highest priority (1) to the group (or atom) with the next highest priority (2).
- If the arrow points clockwise, the enantiomer has the *R* configuration; if it points counterclockwise, the enantiomer has the *S* configuration



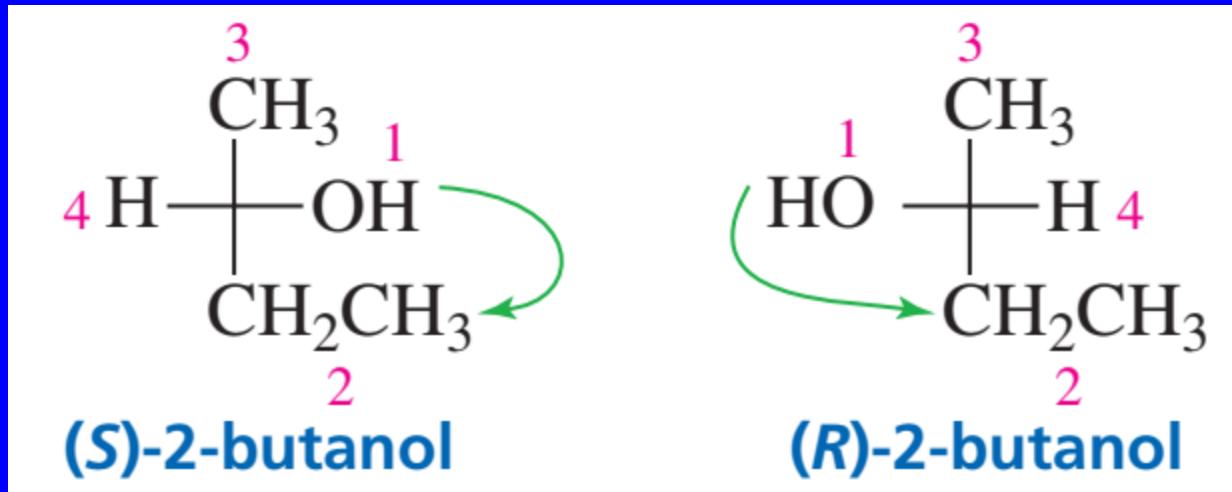
(*R*)-3-chlorohexane



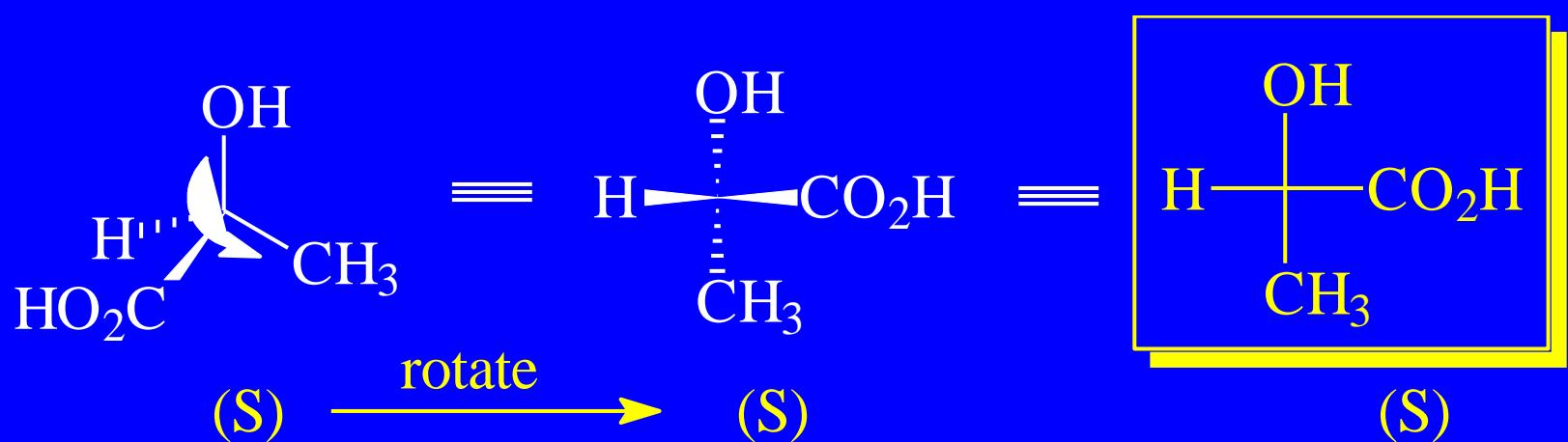
(*S*)-3-chlorohexane

Fischer Projections

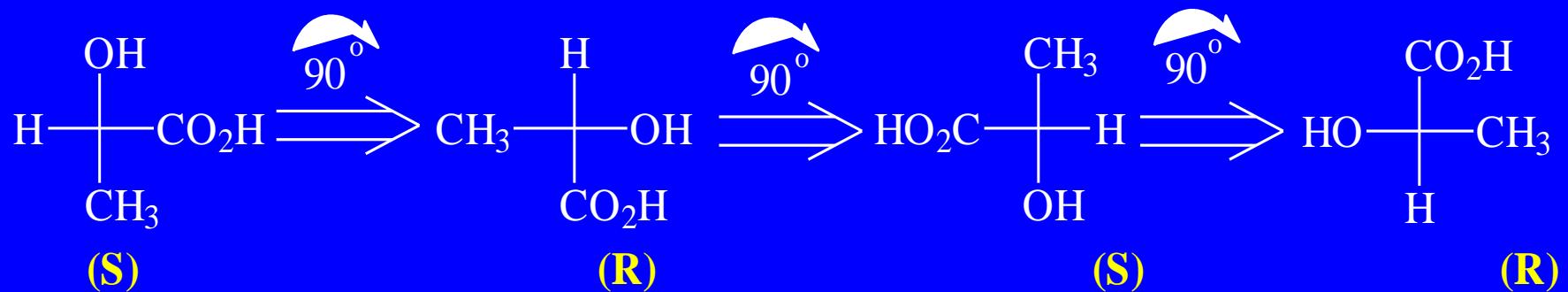
- If the group (or atom) with the lowest priority is on a *horizontal* bond, the answer you get from the direction of the arrow will be the opposite of the correct answer.
- For example, if the arrow points clockwise, suggesting that the asymmetric carbon has the *R* configuration, it actually has the *S* configuration
- if the arrow points counterclockwise, suggesting that the asymmetric carbon has the *S* configuration, it actually has the *R* configuration.



Assigning Absolute Configuration to Fischer Projections



Rotation of the Projection 90° Reverses Absolute Configuration



C.I.P. Priorities

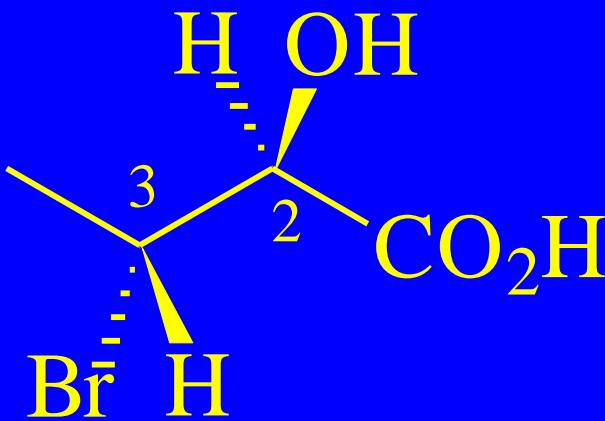
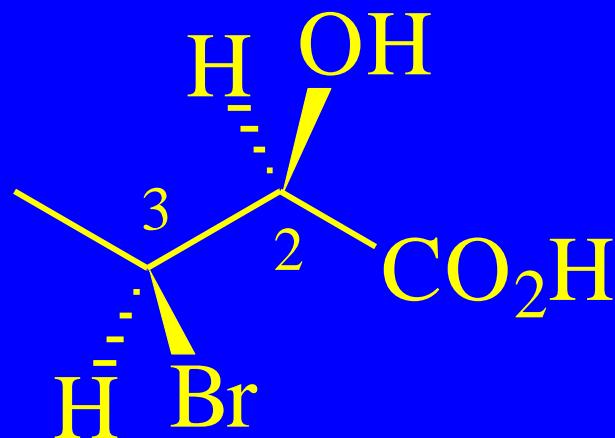
Ranking the groups (or atoms) bonded to the asymmetric carbon in order of priority.

The atomic numbers of the atoms directly attached to the asymmetric carbon determine the relative priorities. The higher the atomic number, the higher the priority.

<u>Low</u>	<u>High</u>
— CH ₂ CH ₂ CH ₃	— CH(CH ₃) ₂
— CH ₂ CH ₂ OH	— CH ₂ CH=O
— CH ₂ CH ₂ CH ₃	— CH=CH ₂
— CO ₂ H	— CH ₂ Cl
— CH ₂ CH ₂ Br	— CH(CH ₃) ₂

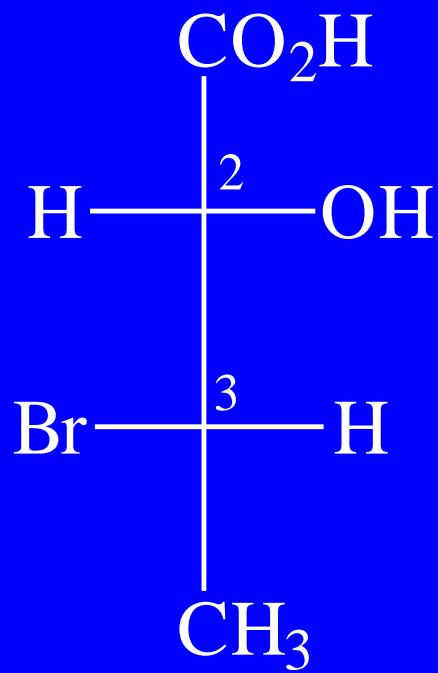
Diastereomers

Stereoisomers That Are Not Mirror Images

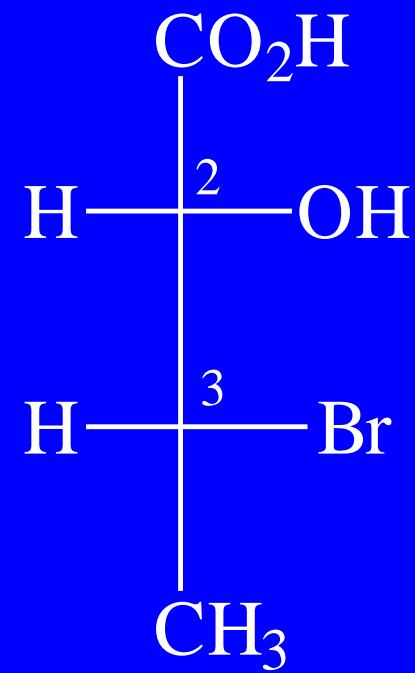


same stereochemistry at C₂ (S)
opposite stereochemistry at C₃

Fischer Projections with 2 Chiral Centers

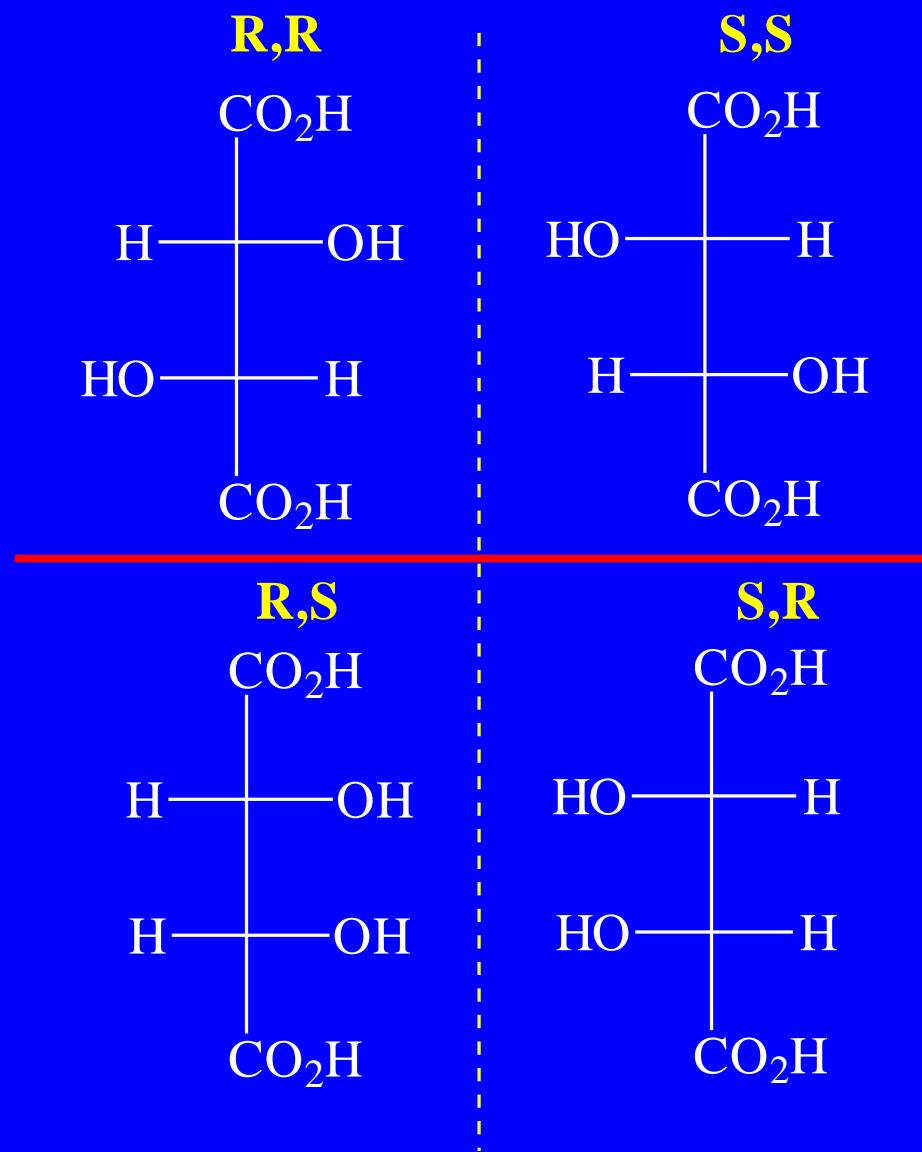


$(2S,3S)$

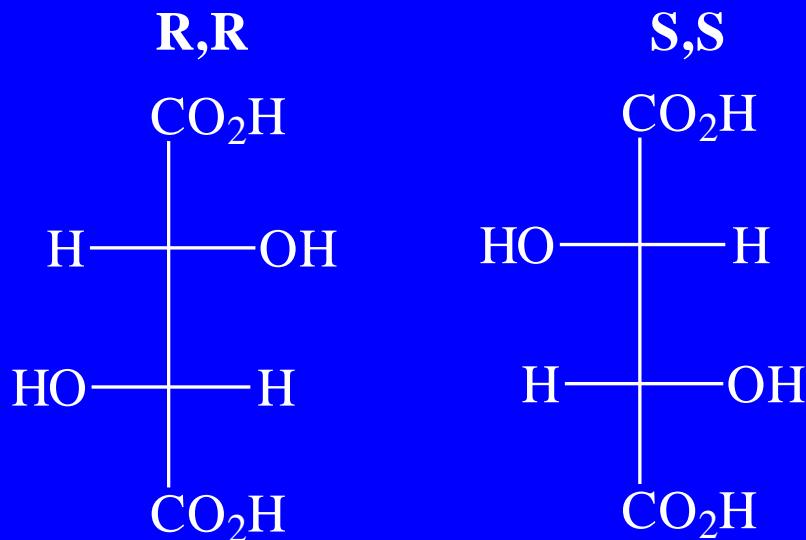


$(2S,3R)$

Tartaric Acids



Racemic Mixture



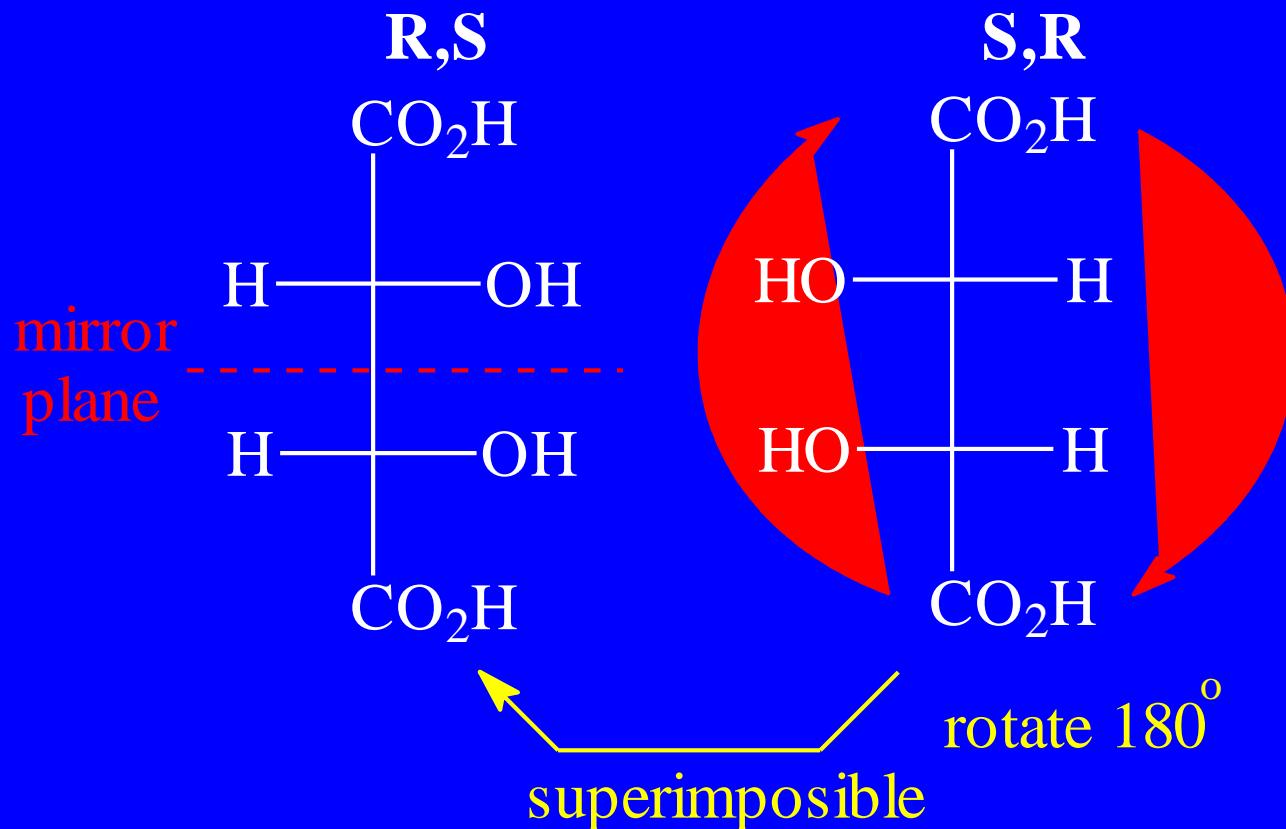
Racemic Mixture (Racemate): 50/50 mixture of enantiomers

	(R,R) Tartaric acid	(S,S) Tartaric Acid	(+/-) Tartaric acid
m.p. C	168-170	168-170	210-212
[α] (degrees)	- 12	+ 12	0
ρ (g/mL)	1.7598	1.7598	1.7723

Meso Compound

Internal Plane of Symmetry

Optically Inactive

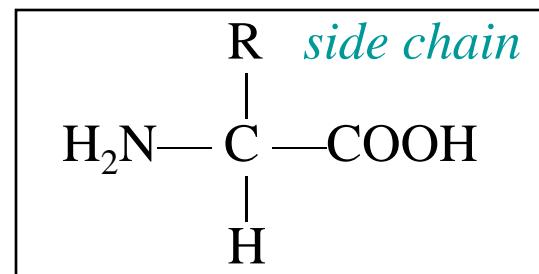


Amino Acids, Peptides, and Proteins



Amino Acids

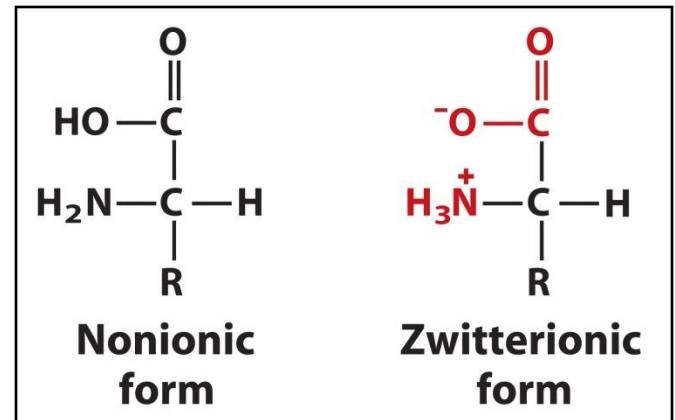
- The building blocks of proteins
- Also used as single molecules in biochemical pathways
- 20 standard amino acids (α -amino acids)
- Two functional groups:
 - carboxylic acid group
 - amino group
 - Both on the same carbon
- Have different side groups (R)
 - Properties dictate behavior of AAs



Zwitterions

- Both the $-\text{NH}_2$ and the $-\text{COOH}$ groups in an amino acid undergo ionization in water.
- At physiological pH (7.4), a **zwitterion** forms

- Both + and – charges
- Overall neutral
- Amphoteric
 - Amino group is protonated
 - Carboxyl group is deprotonated



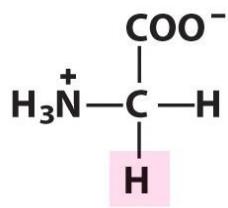
- Soluble in polar solvents due to ionic character
- Structure of R also influence solubility

Classification of Amino Acids

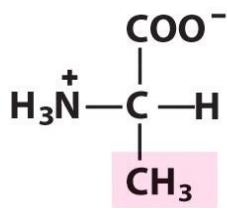
- Based on structure of R
 - Nonpolar
 - Polar
 - Aromatic
 - Acidic
 - Basic

Nonpolar Amino Acids

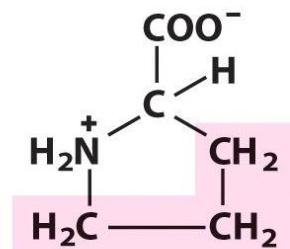
- Hydrophobic, neutral, aliphatic



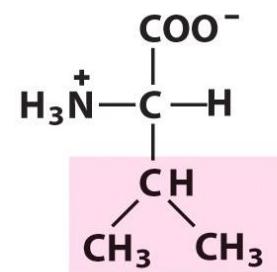
Glycine



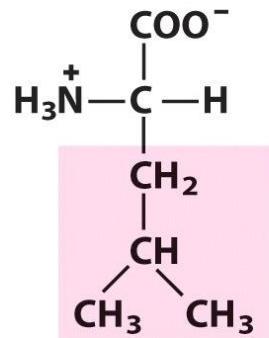
Alanine



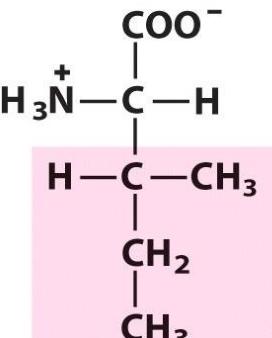
Proline



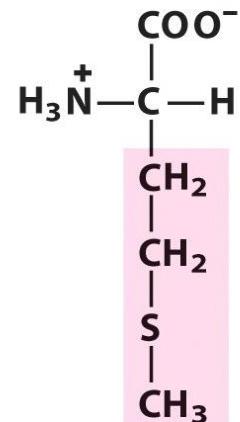
Valine



Leucine



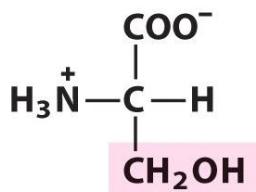
Isoleucine



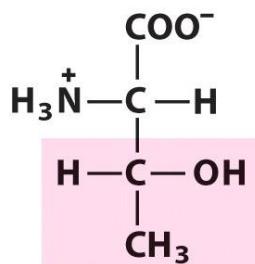
Methionine

Polar Amino Acids

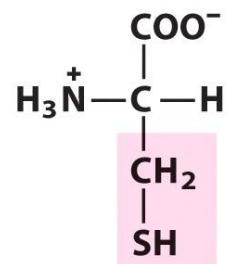
- Hydrophilic, neutral, typically H-bond



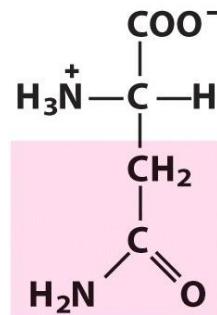
Serine



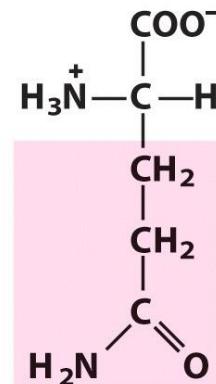
Threonine



Cysteine



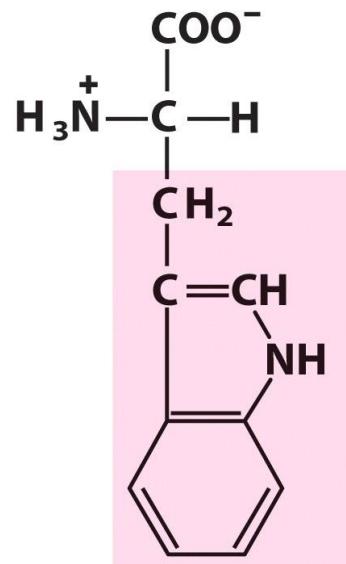
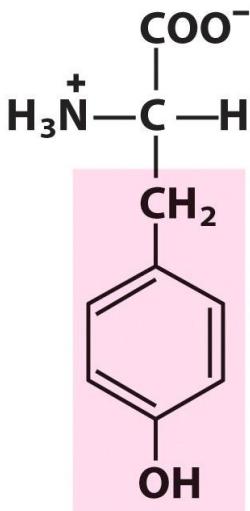
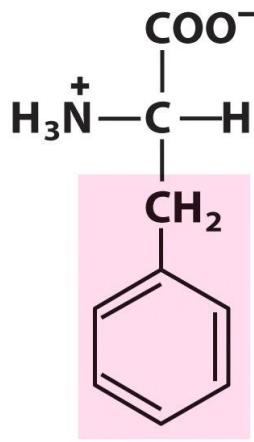
Asparagine



Glutamine

Aromatic Amino Acids

- Bulky and neutral,
- polarity depend on R



Phenylalanine

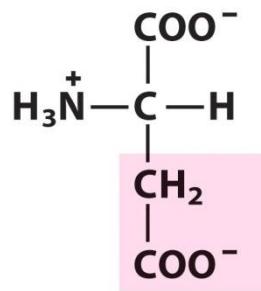
Tyrosine

Tryptophan

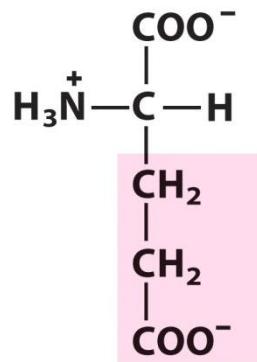
Acidic and Basic Amino Acids

- **Acidic**

- R group = carboxylic acid
- Donates H⁺
- Negatively charged



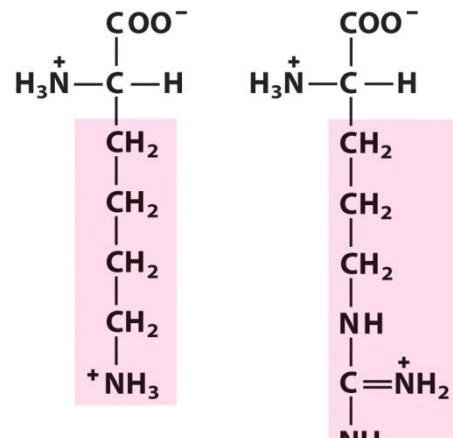
Aspartate



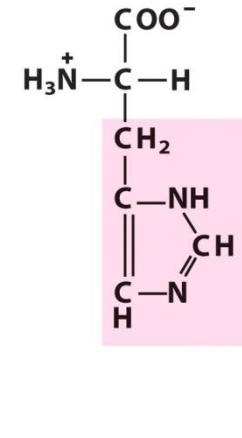
Glutamate

- **Basic**

- R group = amine
- Accepts H⁺
- Positively charged
- Histidine ionizes at pH 6.0



Lysine

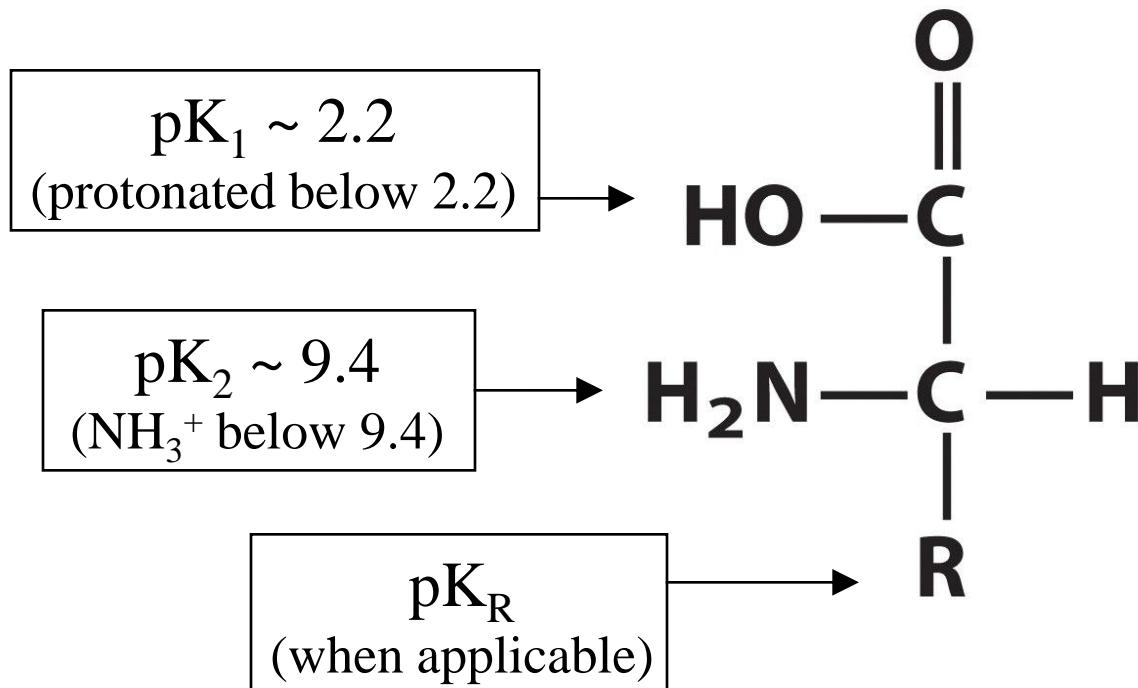


Arginine

Histidine

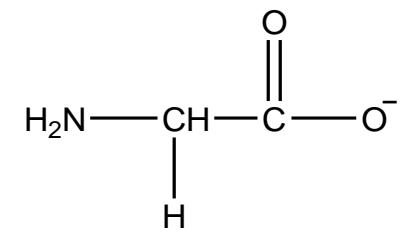
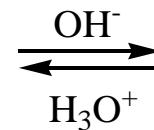
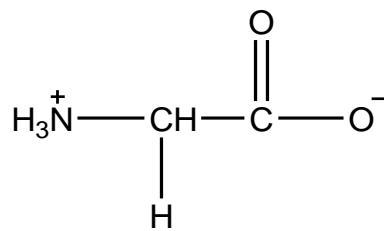
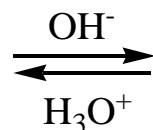
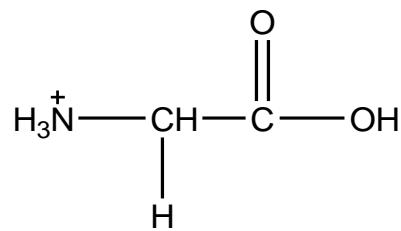
Acid-base Properties

- Remember H_3PO_4 (multiple pK_a 's)
- AAs also have multiple pK_a 's due to multiple ionizable groups



pH and Ionization

- Consider glycine:



Glycine ion at
acidic pH
(charge = 1+)

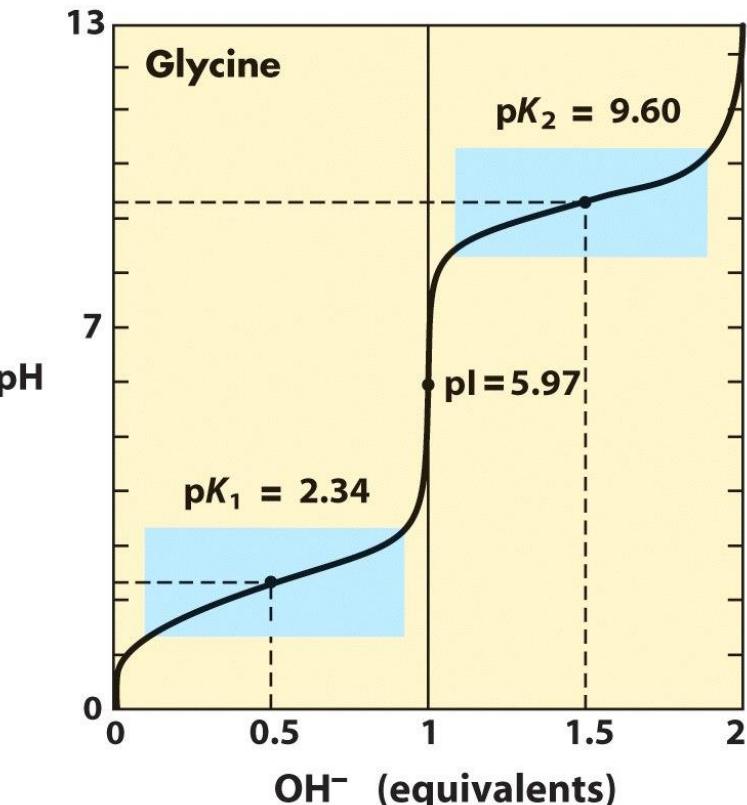
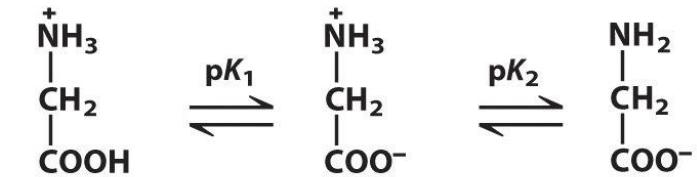
Zwitterion of glycine
(charge = 0)

Glycine ion at
basic pH
(charge = 1-)

- Note that the uncharged species never forms

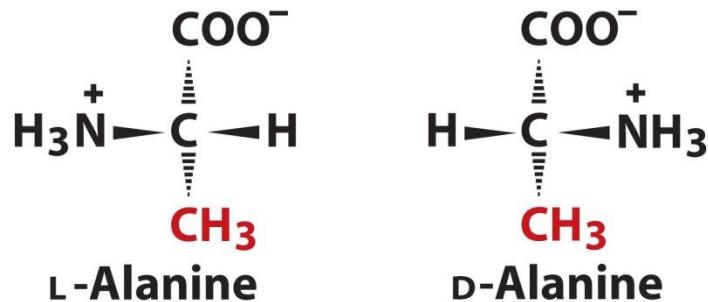
Titration of Glycine

- pK_1
 - $[\text{cation}] = [\text{zwitterion}]$
- pK_2
 - $[\text{zwitterion}] = [\text{anion}]$
- First equivalence point
 - Zwitterion
 - Molecule has no net charge
 - $\text{pH} = \text{pI}$ (Isoelectric point)
 - $\text{pI} = \text{average of } pK_a \text{'s} = \frac{1}{2} (pK_1 + pK_2)$
 - $\text{pI}_{\text{glycine}} = \frac{1}{2} (2.34 + 9.60) = 5.97$

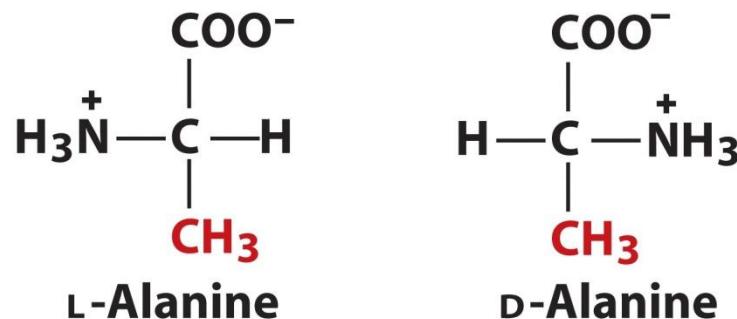


Stereochemistry of AAs

- All amino acids (except glycine) are optically active

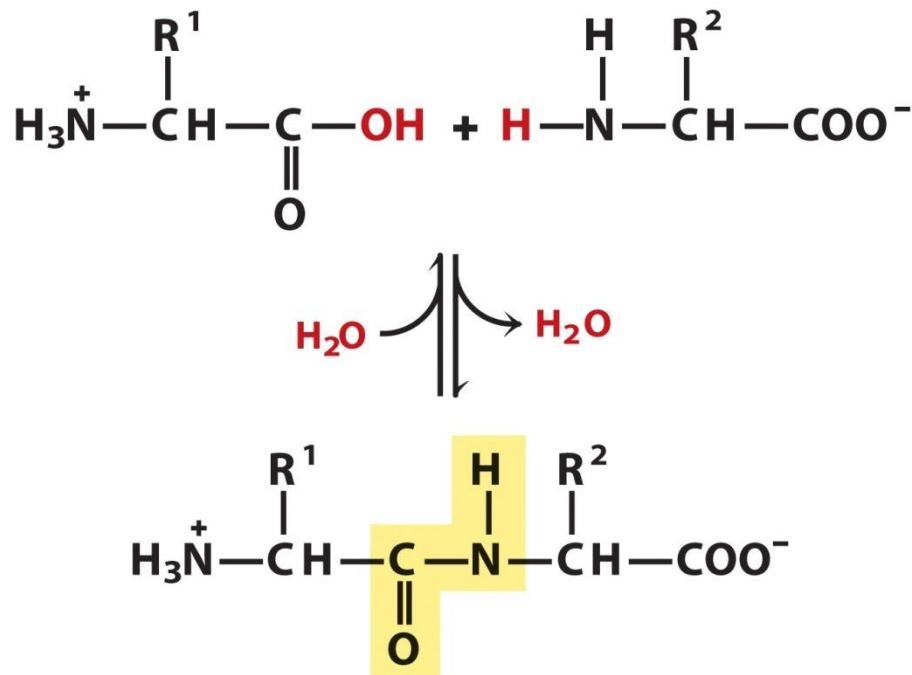


- Fischer projections:

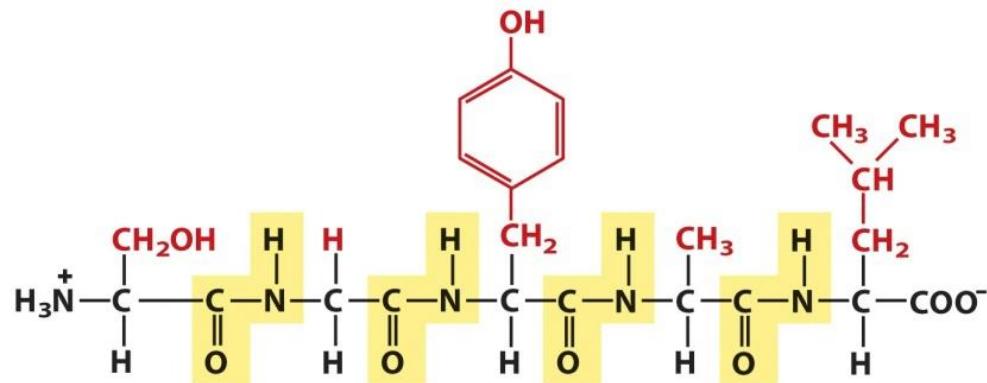


The Peptide Bond

- Chain of amino acids = peptide or protein
- Amino acid residues connected by **peptide bonds**
- Residue = AA – H₂O



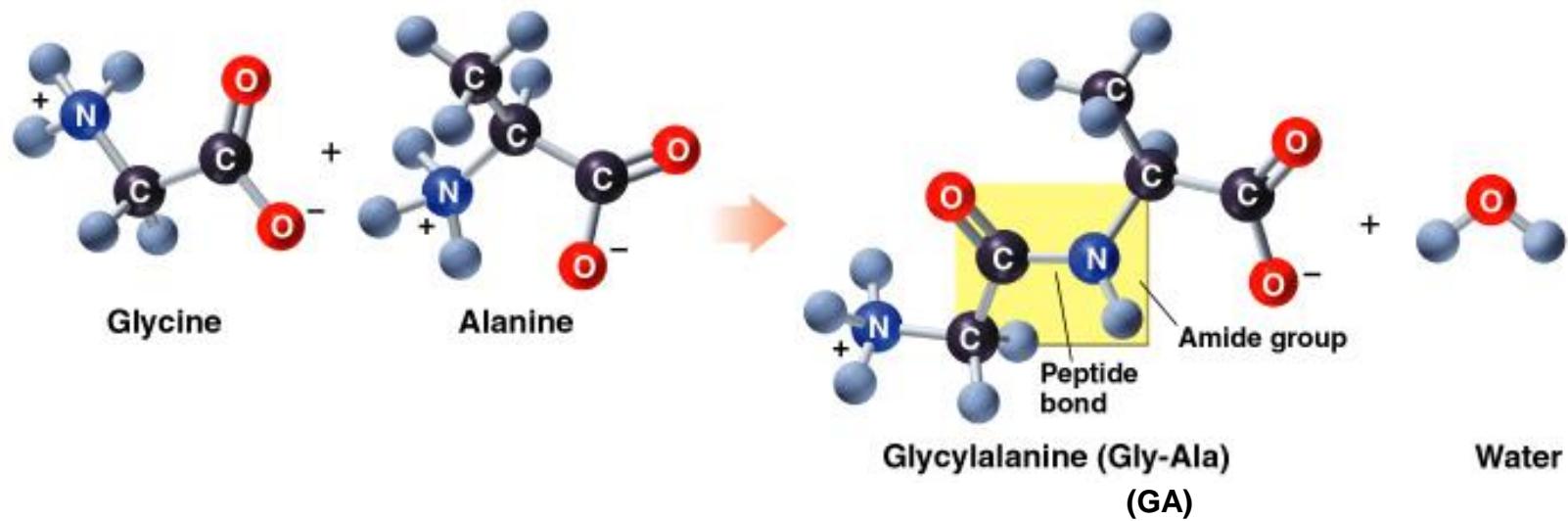
Polypeptides



- Linear polymers (no branches)
- AA monomers linked head to tail
- Terminal residues:
 - Free amino group (N-terminus)
 - Draw on left
 - Free carboxylate group (C-terminus)
 - Draw on right

Naming Peptides

- Name from the free amine (NH_3^+)
- Use *-yl* endings for the names of the amino acids
- The last amino acid with the free carboxyl group (COO^-) uses its amino acid name

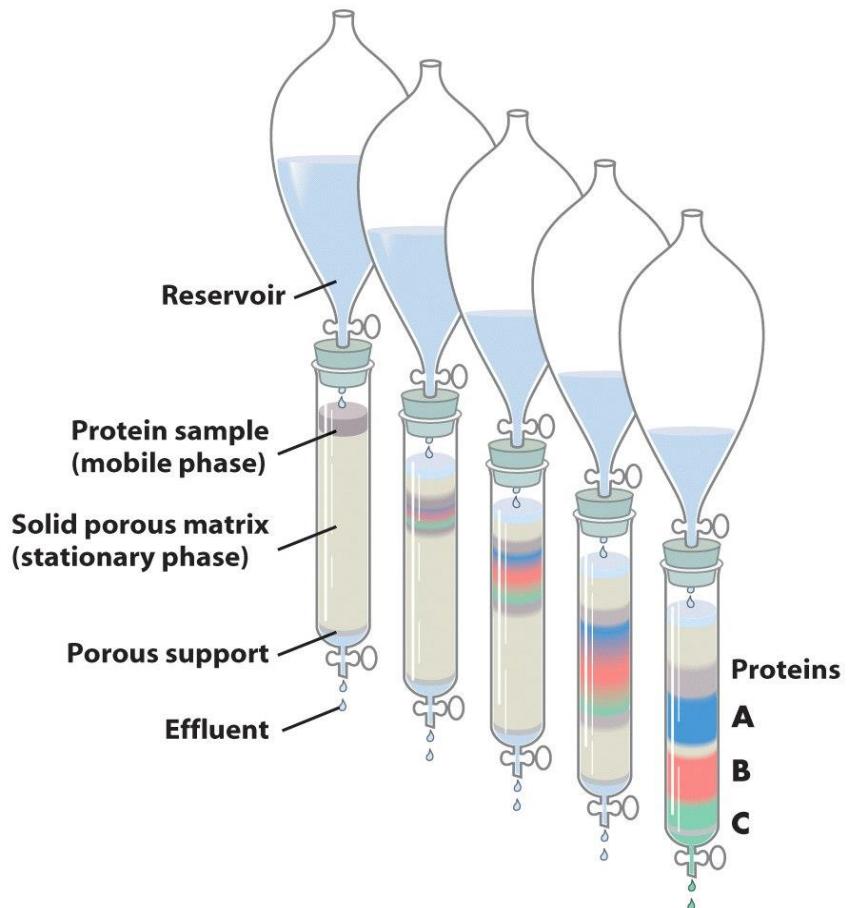


Protein size

- In general, proteins contain > 40 residues
 - Minimum needed to fold into tertiary structure
- Usually 100-1000 residues
- Percent of each AA varies
- Proteins separated based on differences in size and composition
- Proteins must be pure to analyze, determine structure/function

Chromatography

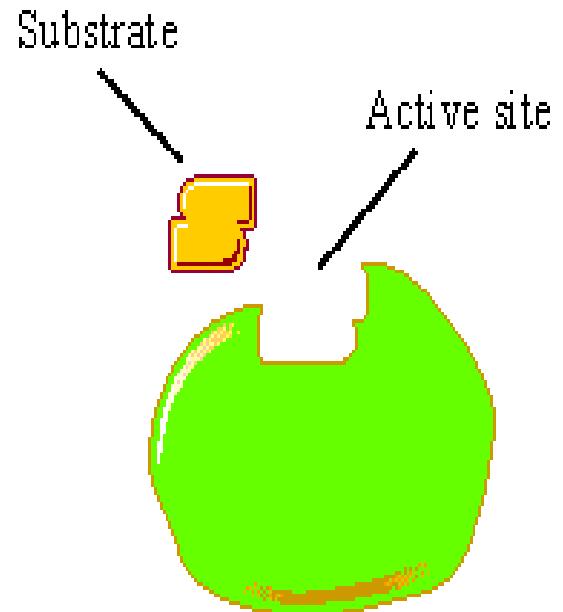
- Mobile phase
 - Mixture dissolved in liquid or solid
- Stationary phase
 - Porous solid matrix
- Components of mixture pass through the column at different rates based on properties



Enzymes

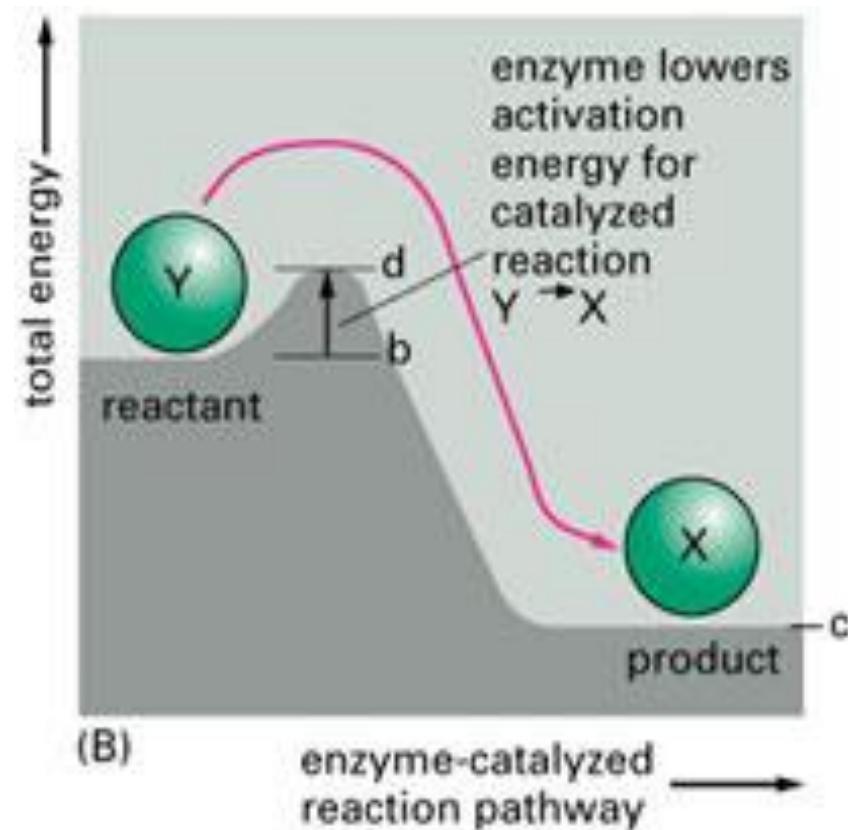
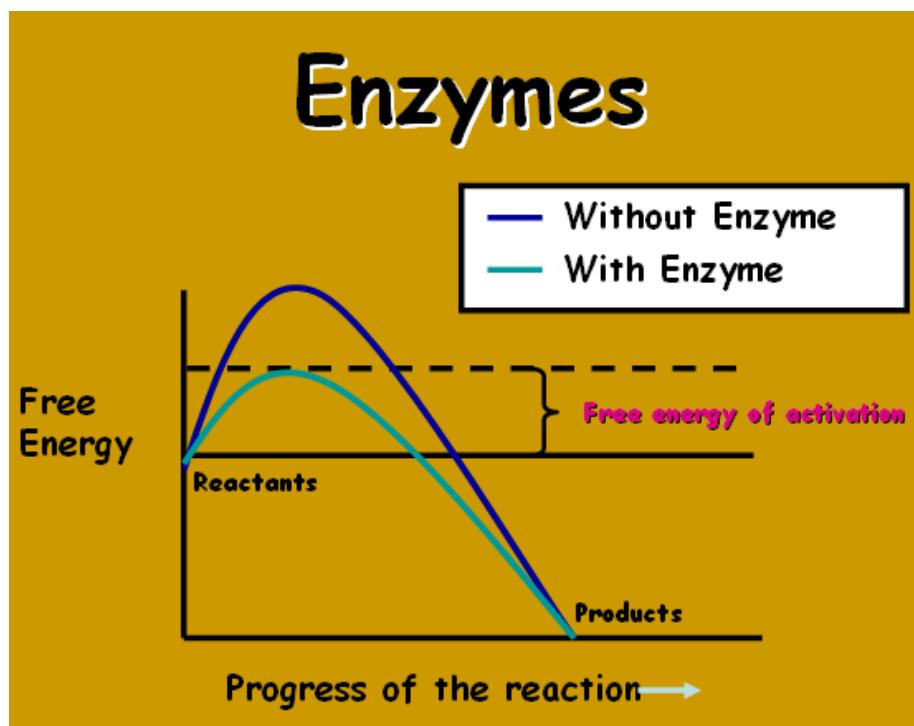
What Are Enzymes?

- Most enzymes are **Proteins** (tertiary and quaternary structures)
- Act as **Catalyst** to accelerates a reaction
- Not permanently changed in the process
- Are specific for what they will **catalyze**
- Are **Reusable**
- End in **-ase**
 - Sucrase***
 - Lactase***
 - Maltase***



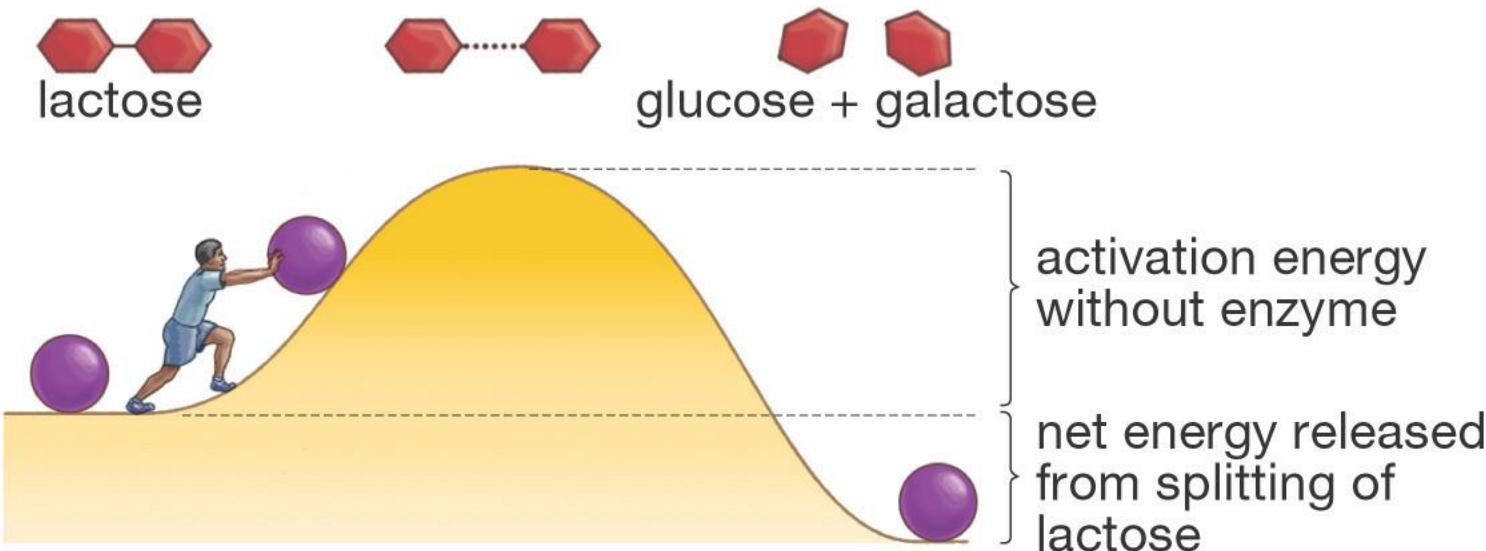
How do enzymes Work?

Enzymes work by weakening bonds which lowers activation energy

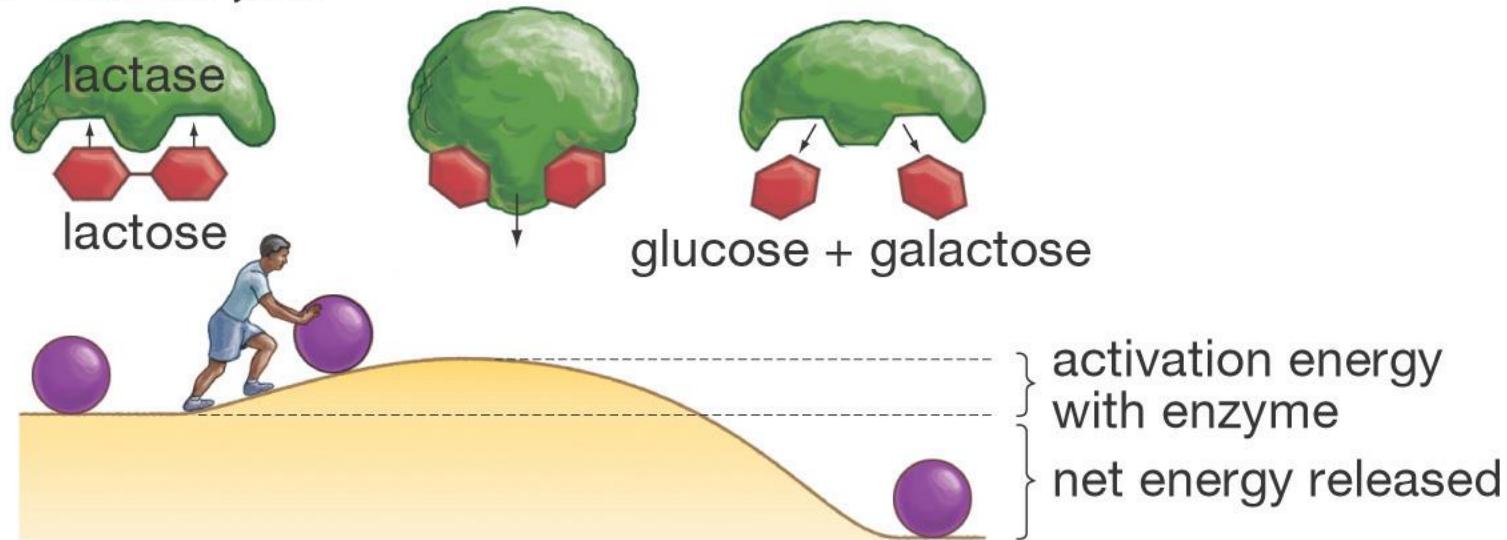


Enzymes Lower a Reaction's Activation Energy

(a) Without enzyme

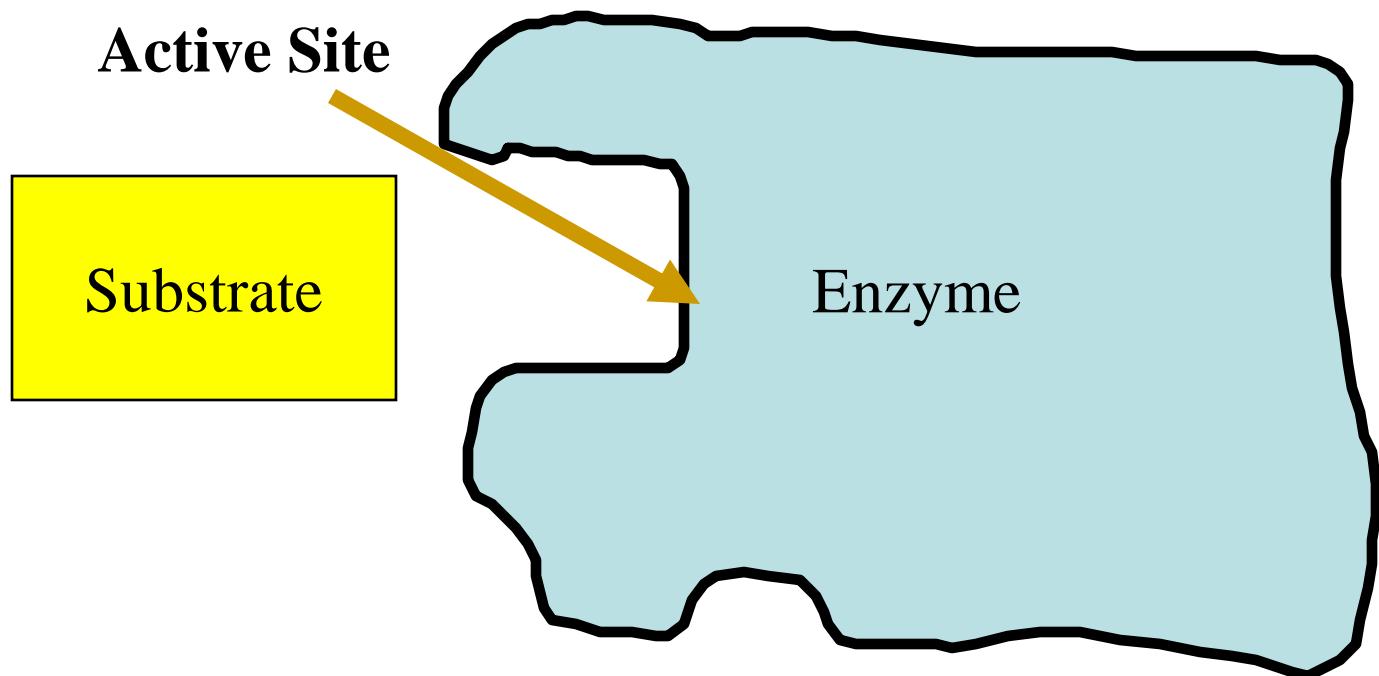


(b) With enzyme



Active Site

- A **restricted region** of an **enzyme** molecule which **binds** to the **substrate**.



What Affects Enzyme Activity?

- Three factors:

1. Environmental Conditions

2. Cofactors and Coenzymes

3. Enzyme Inhibitors

Environmental Conditions

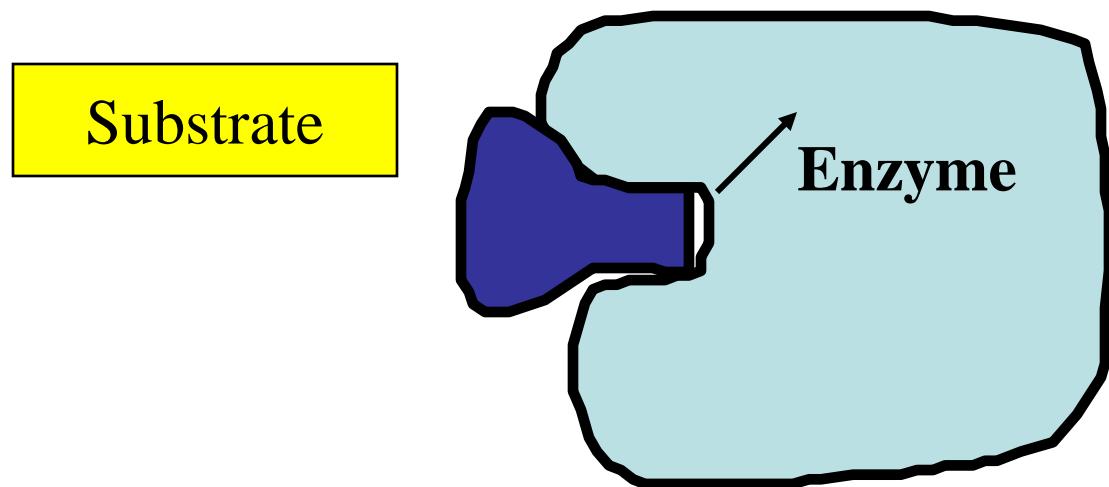
- 1. Extreme Temperature** are the most dangerous
 - **high temp.** may denature (unfold) the enzyme.
- 2. (most like 6 - 8 pH near neutral)**
- 3. Ionic concentration** (salt ions)

2. Cofactors and Coenzymes

- Inorganic substances (**zinc, iron**) and **vitamins** (respectively) are sometimes need for proper enzymatic activity.
- Example:
Iron must be present in the quaternary structure - hemoglobin in order for it to **pick up oxygen**.

Two examples of Enzyme Inhibitors

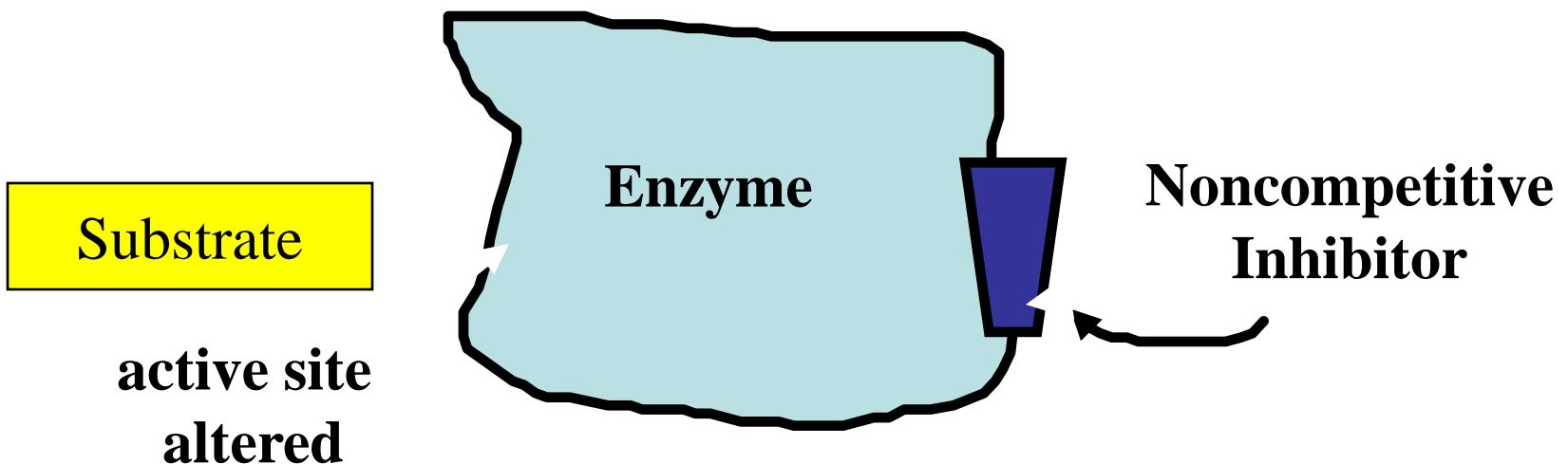
- a. Competitive inhibitors:** are chemicals that resemble an enzyme's normal substrate and compete with it for the active site.



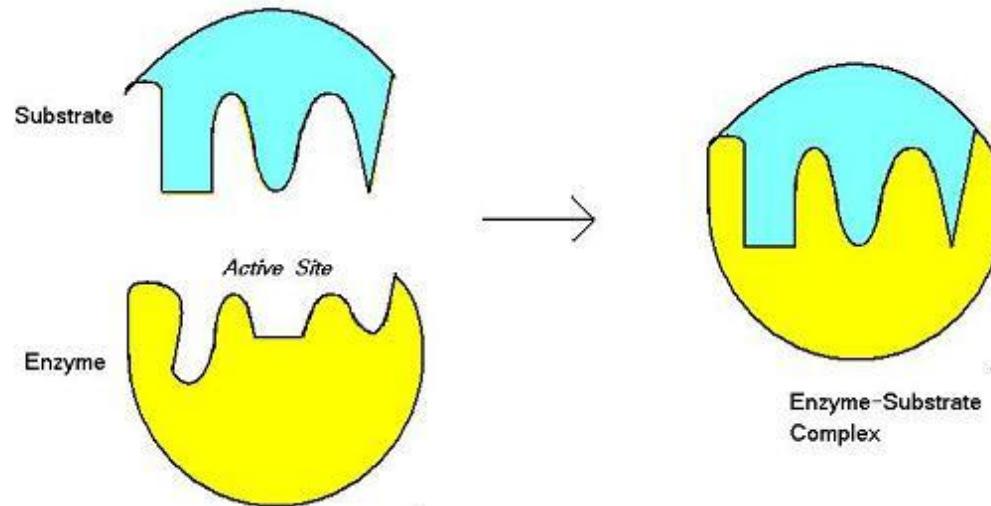
Inhibitors

b. Noncompetitive inhibitors:

Inhibitors that do not enter the active site, but bind to another part of the enzyme causing the enzyme to change its shape, which in turn alters the active site.



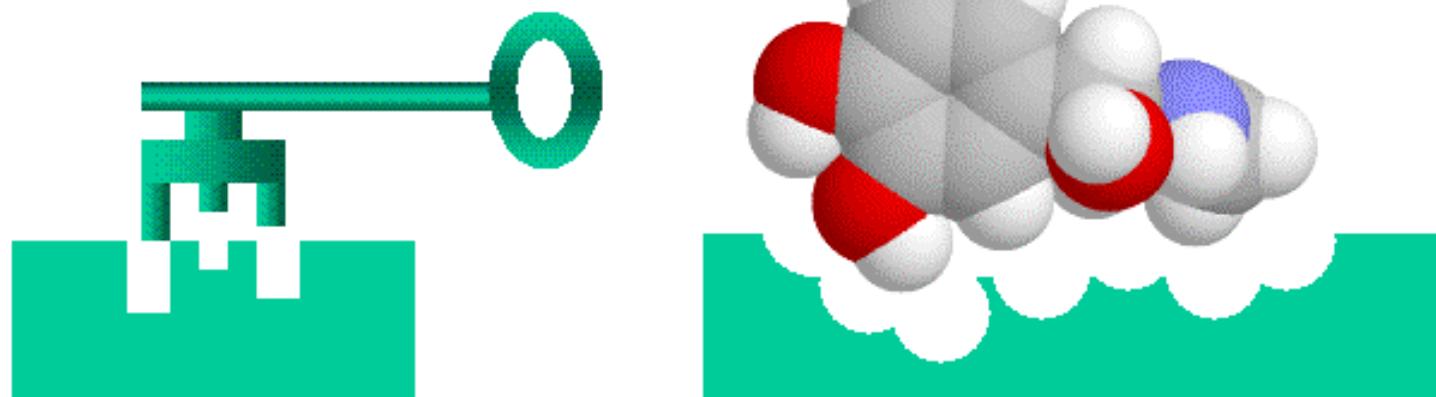
Induced Fit Model



A change in the
shape of an enzyme's
active site
Induced by the
substrate

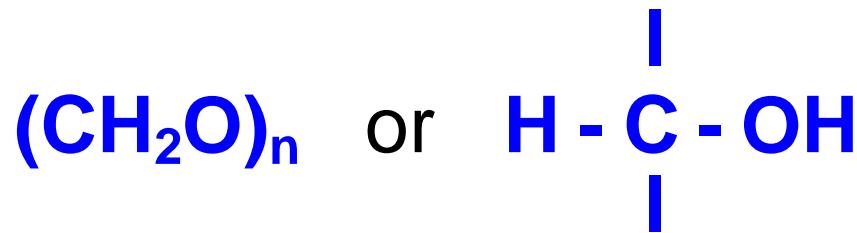
Induced-fit Model. - The enzyme active site forms a complementary shape to the substrate after binding.

Lock and key model



Carbohydrates

Carbohydrates (glycans) have the following basic composition:

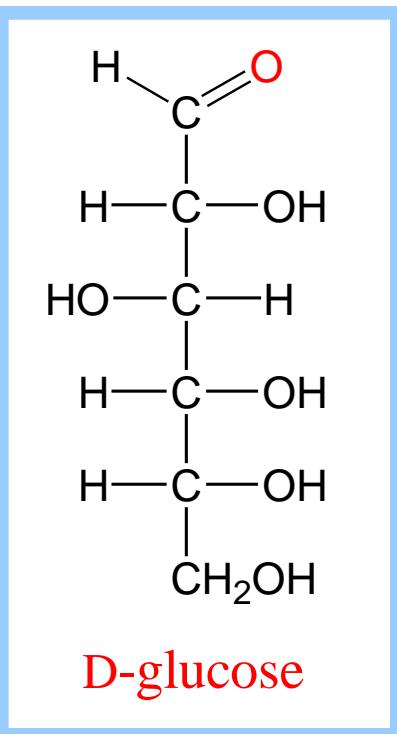


Classification

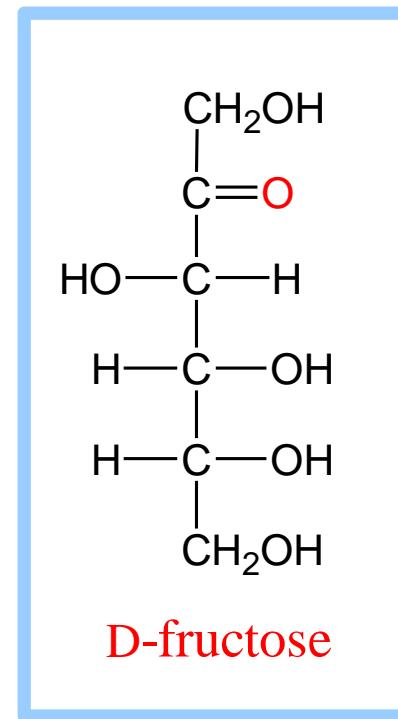
- ◆ **Monosaccharides** - simple sugars with multiple OH groups. Based on number of carbons (3, 4, 5, 6), a monosaccharide is a **triose**, **tetrose**, **pentose** or **hexose**.
- ◆ **Disaccharides** - 2 monosaccharides covalently linked.
- ◆ **Oligosaccharides** - a few monosaccharides covalently linked.
- ◆ **Polysaccharides** - polymers consisting of chains of monosaccharide or disaccharide units.

Monosaccharides

Aldoses (e.g., glucose) have an **aldehyde** group at one end.



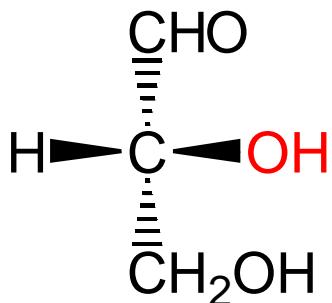
Ketoses (e.g., fructose) have a **keto** group, usually at C2.



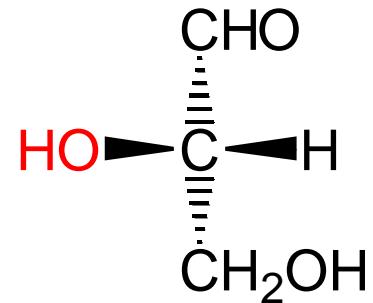
D & L Designation

D & L designations are based on the configuration about the single asymmetric C in glyceraldehyde.

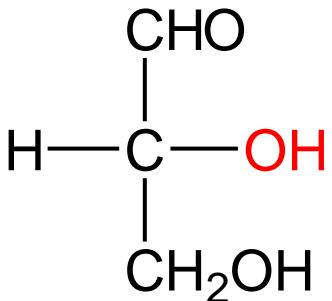
The lower representations are Fischer Projections.



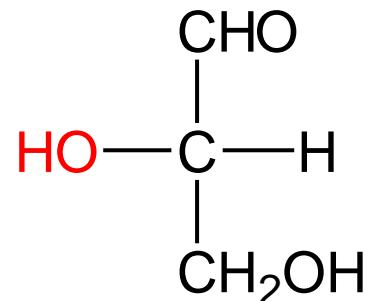
D-glyceraldehyde



L-glyceraldehyde



D-glyceraldehyde

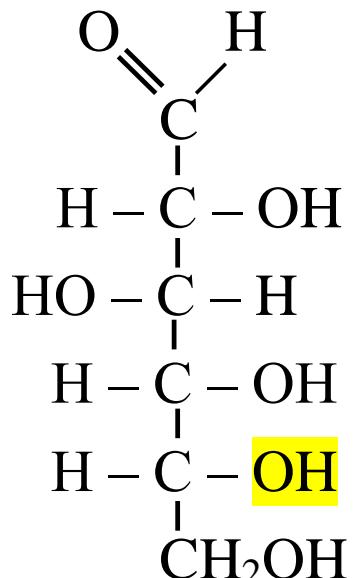


L-glyceraldehyde

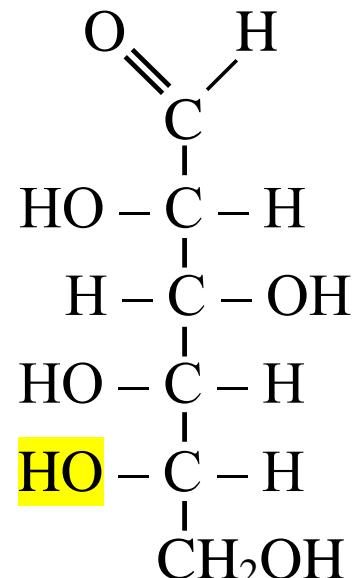
Sugar Nomenclature

For sugars with more than one chiral center, **D** or **L** refers to the asymmetric C farthest from the aldehyde or keto group.

Most naturally occurring sugars are D isomers.



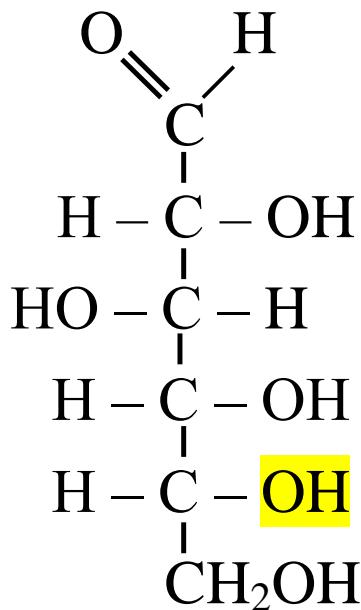
D-glucose



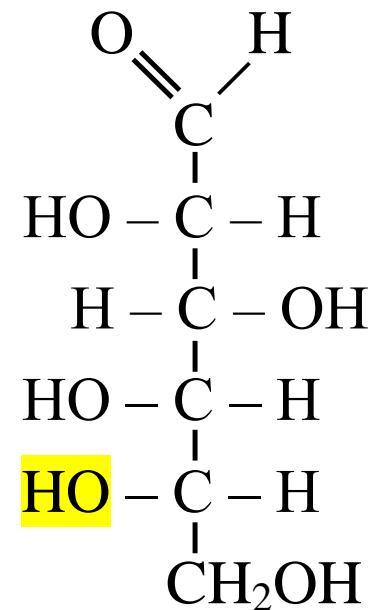
L-glucose

D & L sugars are mirror images of one another.

They have the same name, e.g., D-glucose & L-glucose.



D-glucose



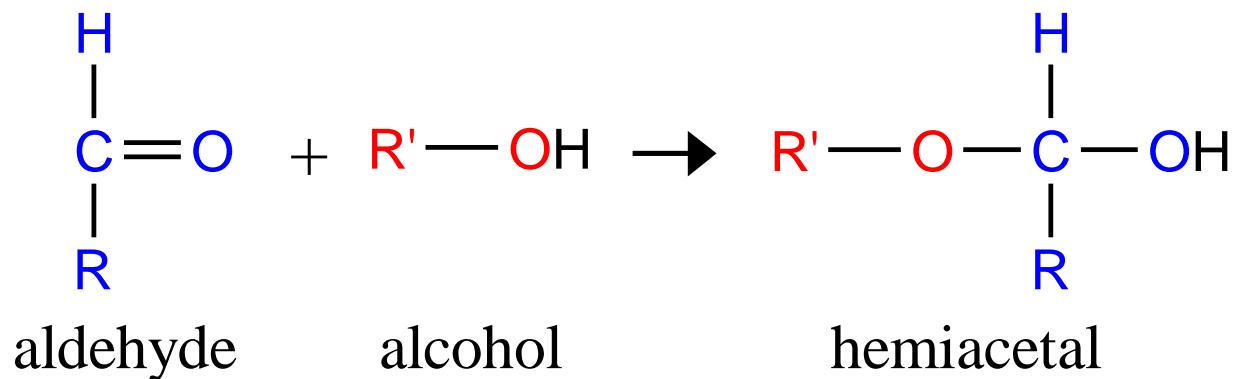
L-glucose

The number of stereoisomers is 2^n , where n is the number of asymmetric centers.

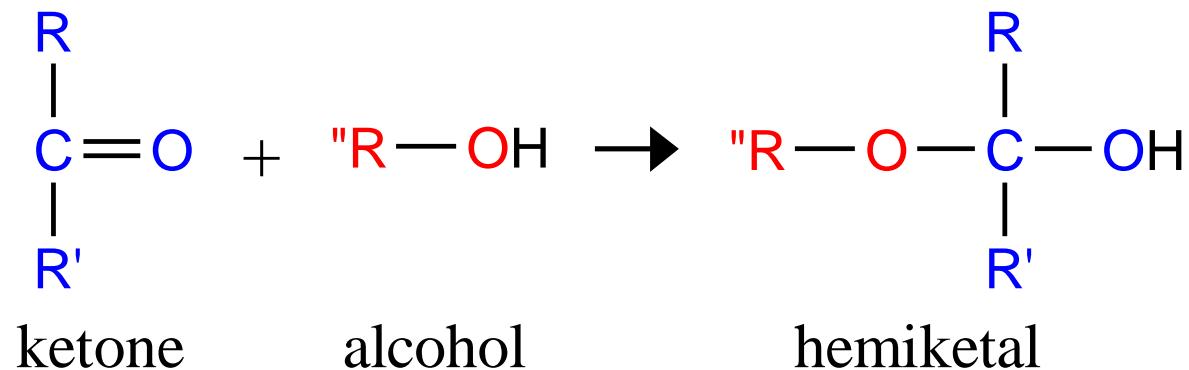
The 6-C aldoses have 4 asymmetric centers. Thus there are 16 stereoisomers (8 D-sugars and 8 L-sugars).

Hemiacetal & hemiketal formation

An aldehyde can react with an alcohol to form a **hemiacetal**.

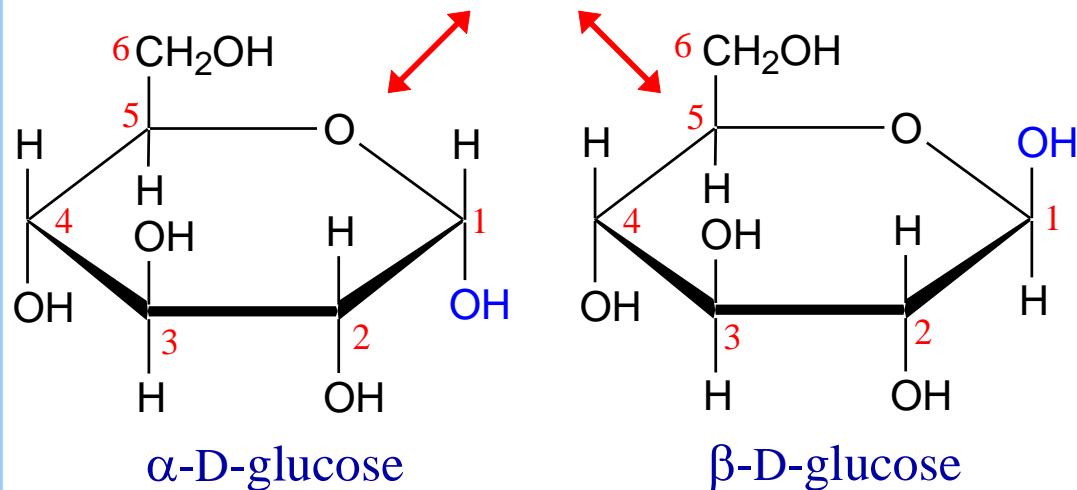
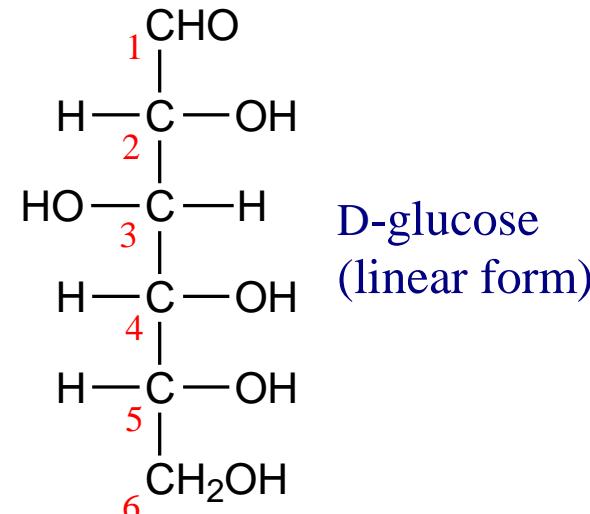


A ketone can react with an alcohol to form a **hemiketal**.

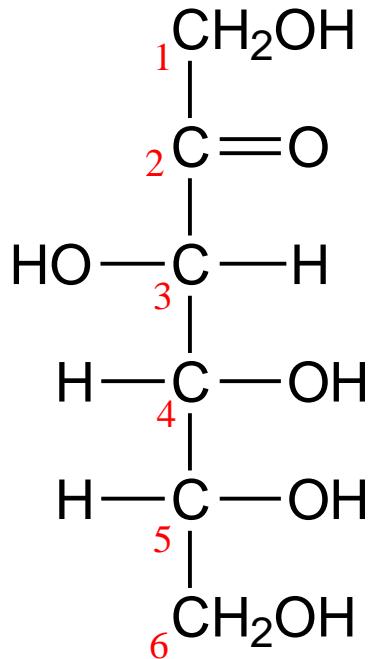


Pentoses and hexoses can cyclize as the ketone or aldehyde reacts with a distal OH.

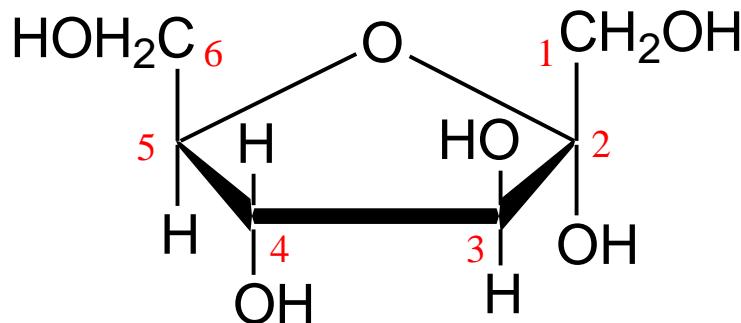
Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.



These representations of the cyclic sugars are called **Haworth** projections.



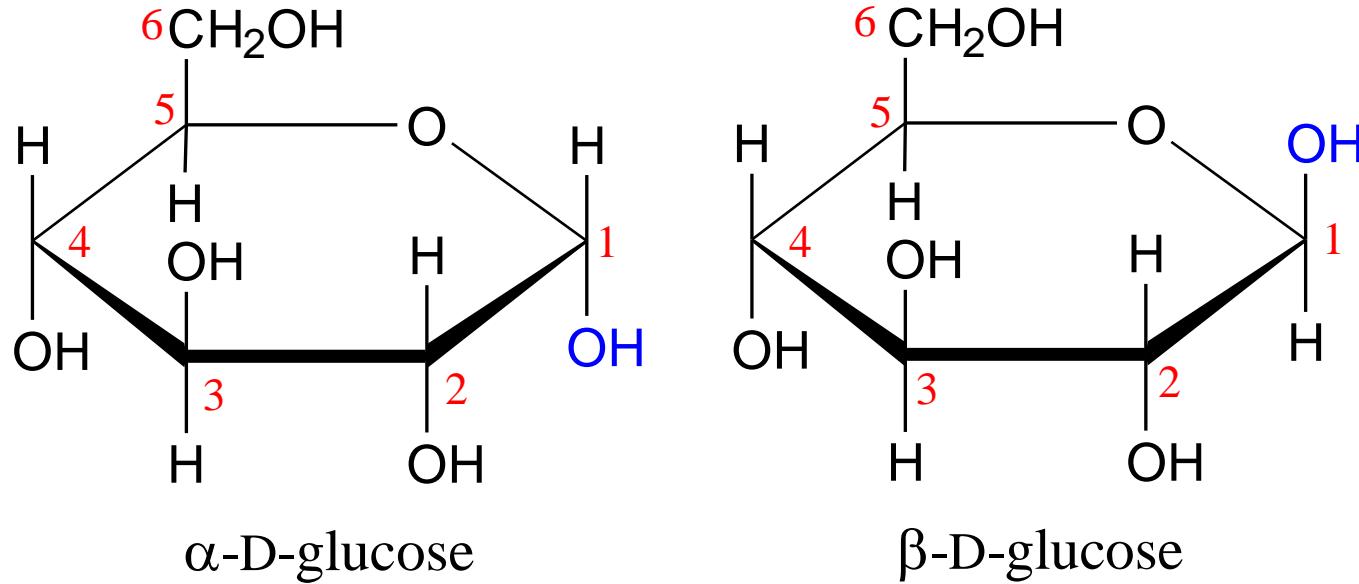
D-fructose (linear)



α -D-fructofuranose

Fructose forms either

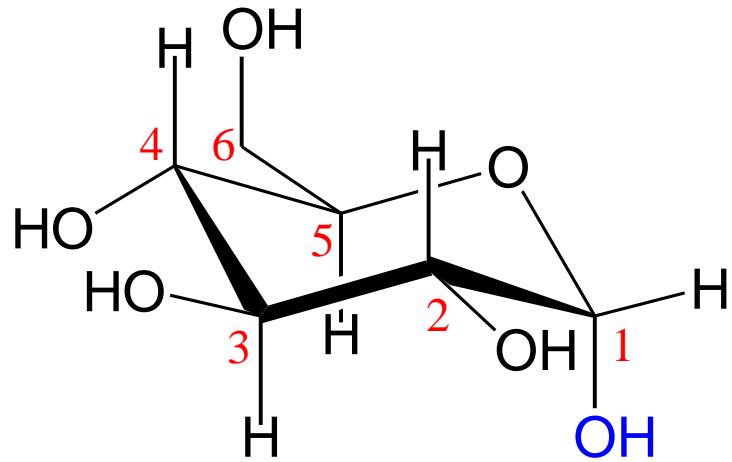
- ◆ a 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or
- ◆ a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.



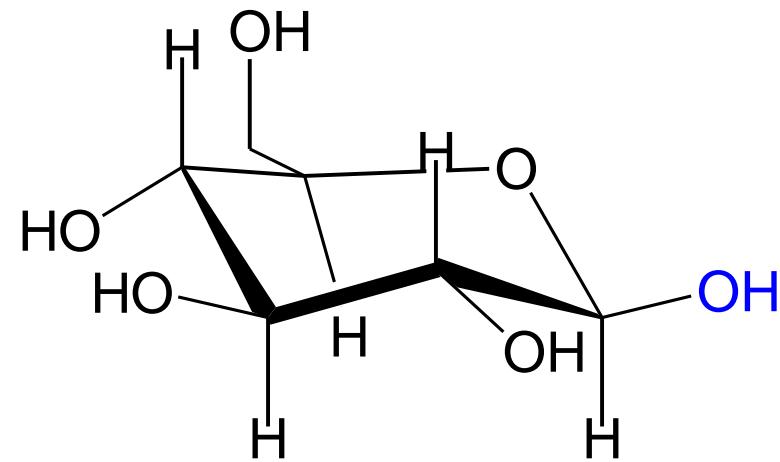
Cyclization of glucose produces a new **asymmetric center** at C1. The 2 stereoisomers are called **anomers**, α & β .

Haworth projections represent the cyclic sugars as having essentially planar rings, with the OH at the anomeric C1:

- ◆ α (OH **below** the ring)
- ◆ β (OH **above** the ring).



α -D-glucopyranose



β -D-glucopyranose

Because of the tetrahedral nature of carbon bonds, pyranose sugars actually assume a "**chair**" or "**boat**" configuration, depending on the sugar.

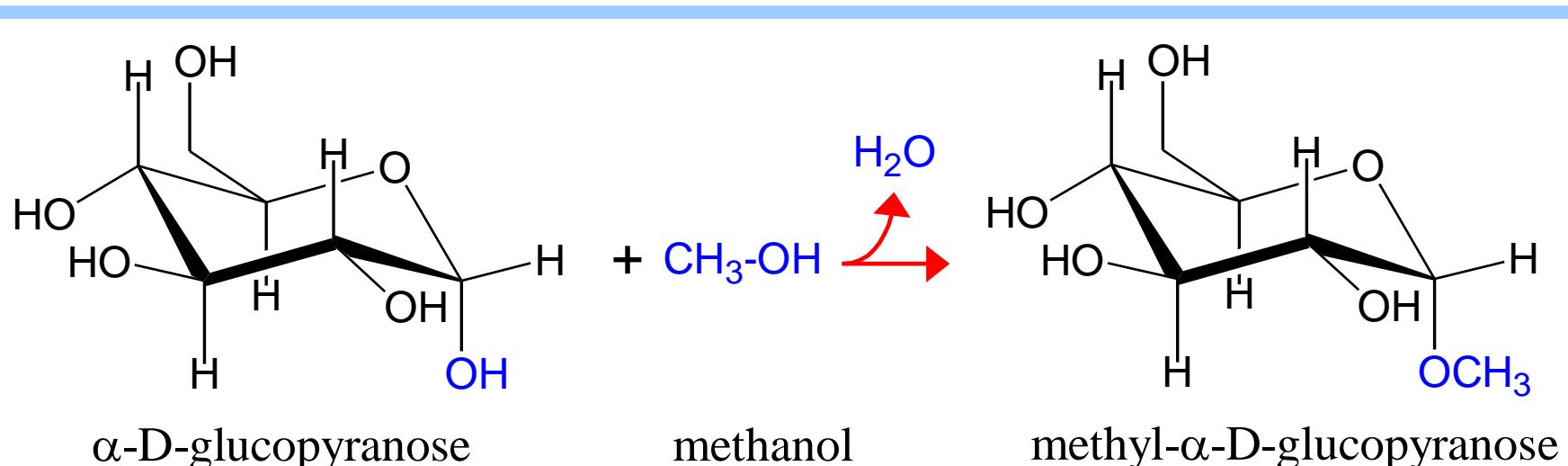
The representation above reflects the chair configuration of the glucopyranose ring more accurately than the Haworth projection.

Glycosidic Bonds

The anomeric hydroxyl and a hydroxyl of another sugar or some other compound can join together, splitting out water to form a **glycosidic bond**:



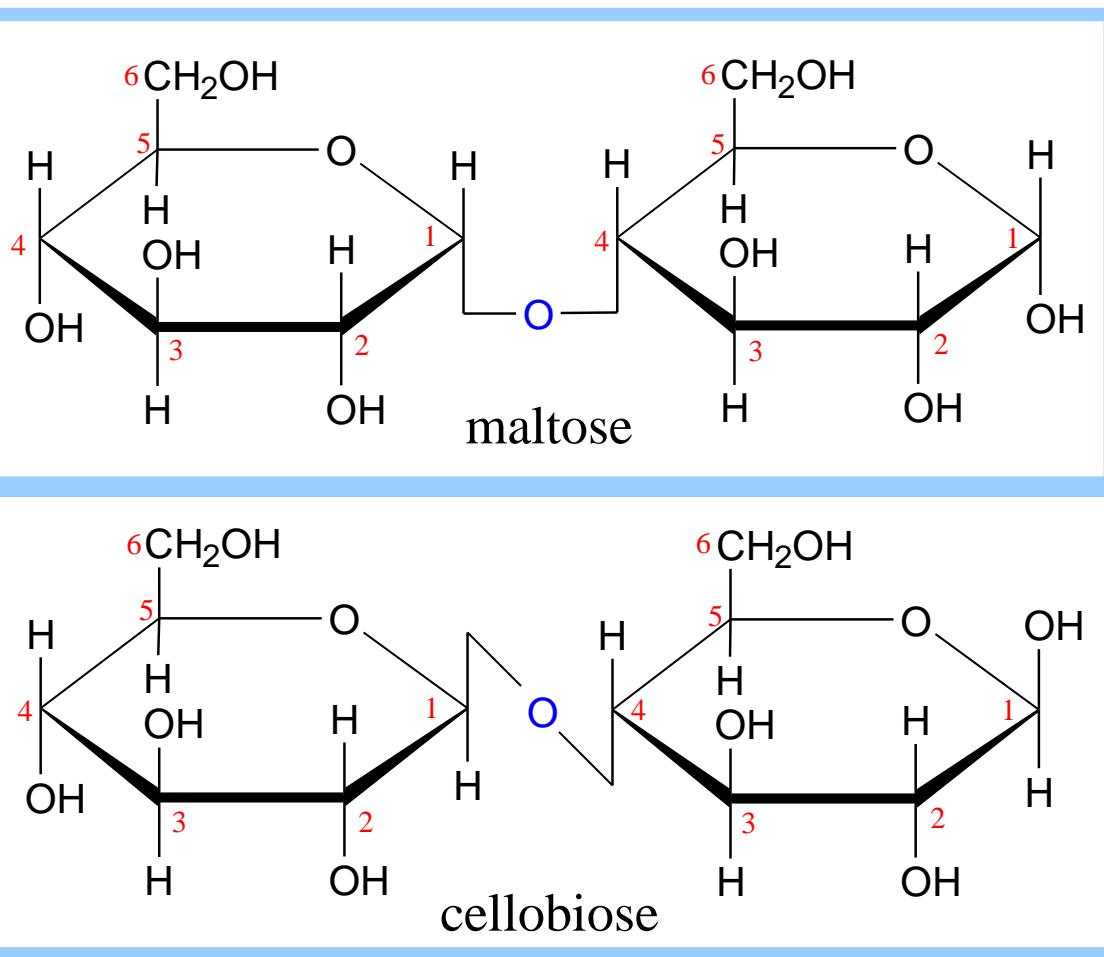
E.g., methanol reacts with the anomeric OH on glucose to form methyl glucoside (methyl-glucopyranose).



Disaccharides:

Maltose, a cleavage product of starch (e.g., amylose), is a disaccharide with an $\alpha(1 \rightarrow 4)$ glycosidic link between C1 - C4 OH of 2 glucose.

It is the α anomer (C1 O points down).



Cellobiose, a product of cellulose breakdown, is the otherwise equivalent β anomer (O on C1 points up).

The $\beta(1 \rightarrow 4)$ glycosidic linkage is represented as a zig-zag, but one glucose is actually **flipped over** relative to the other.

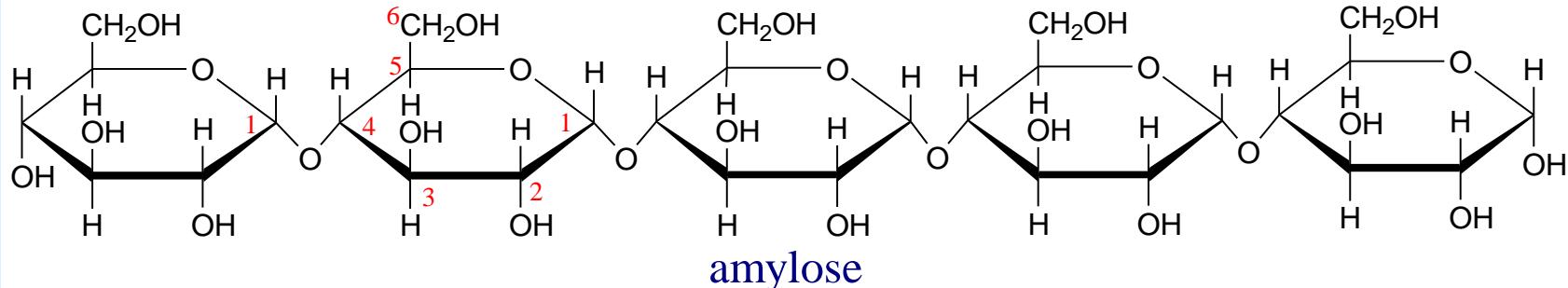
Other **disaccharides** include:

- ◆ **Sucrose**, common table sugar, has a glycosidic bond linking the anomeric hydroxyls of **glucose** & **fructose**.

Because the configuration at the anomeric C of glucose is α (O points down from ring), the linkage is $\alpha(1 \rightarrow 2)$.

The full name of sucrose is α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructopyranose.)

- ◆ **Lactose**, milk sugar, is composed of **galactose** & **glucose**, with $\beta(1 \rightarrow 4)$ linkage from the anomeric OH of galactose. Its full name is β -D-galactopyranosyl-(1 \rightarrow 4)- α -D-glucopyranose



Polysaccharides:

Plants store glucose as **amylose** or **amylopectin**, glucose polymers collectively called starch.

Amylose is a glucose polymer with $\alpha(1 \rightarrow 4)$ linkages.

The end of the polysaccharide with an anomeric C1 not involved in a glycosidic bond is called the **reducing end**.

Fatty Acids and Lipids

Lipids are non-polar (hydrophobic) compounds, soluble in organic solvents.

Most membrane lipids are **amphipathic**, having a **non-polar** end and a **polar** end.

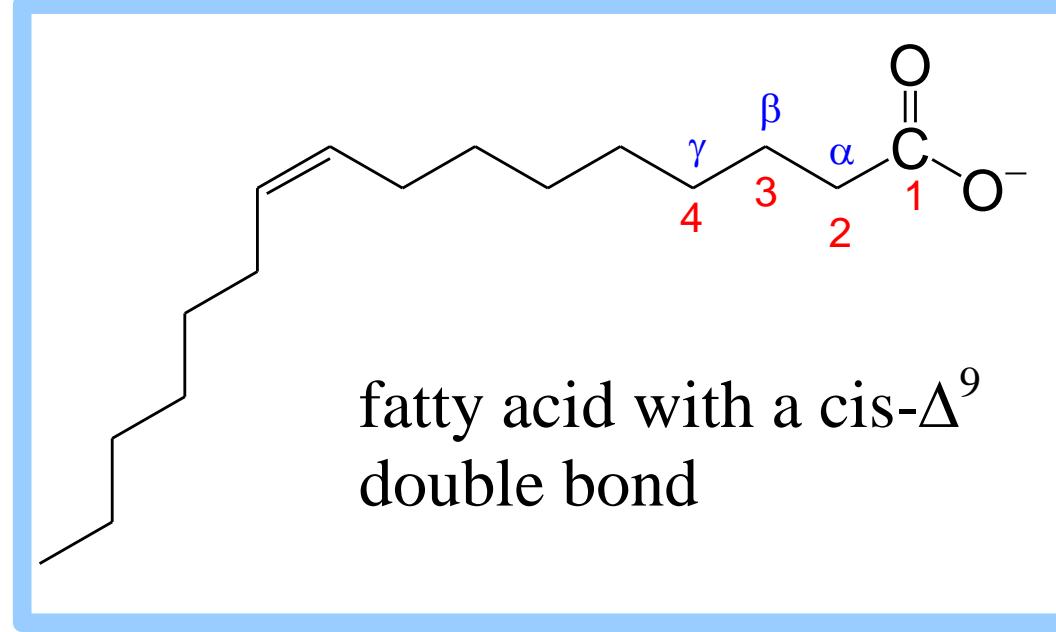
Fatty acids consist of a hydrocarbon chain with a carboxylic acid at one end.



A 16-C fatty acid with one cis double bond between C atoms 9-10 may be represented as **16:1 cis Δ⁹**.

Double bonds in fatty acids usually have the **cis** configuration.

Most naturally occurring fatty acids have an **even number** of carbon atoms.



fatty acid with a $\text{cis-}\Delta^9$ double bond

Some fatty acids and their common names:

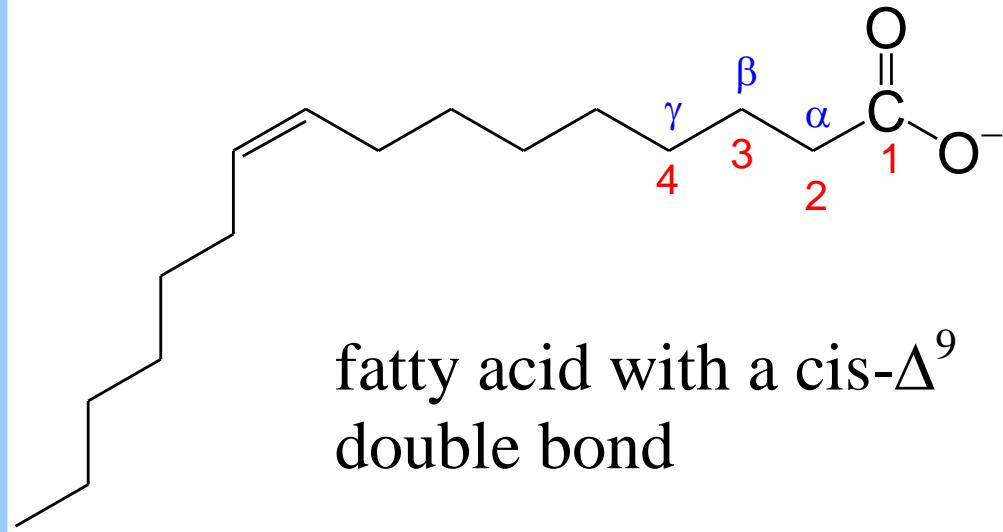
14:0 myristic acid; 16:0 palmitic acid; 18:0 stearic acid;
18:1 $\text{cis}\Delta^9$ oleic acid

18:2 $\text{cis}\Delta^{9,12}$ linoleic acid

18:3 $\text{cis}\Delta^{9,12,15}$ α -linonenic acid

20:4 $\text{cis}\Delta^{5,8,11,14}$ arachidonic acid

20:5 $\text{cis}\Delta^{5,8,11,14,17}$ eicosapentaenoic acid (an omega-3)



There is free rotation about **C-C** bonds in the fatty acid hydrocarbon, except where there is a double bond.

Each *cis* double bond causes a **kink** in the chain.

Rotation about other **C-C** bonds would permit a more linear structure than shown, but there would be a kink.

Glycerophospholipids

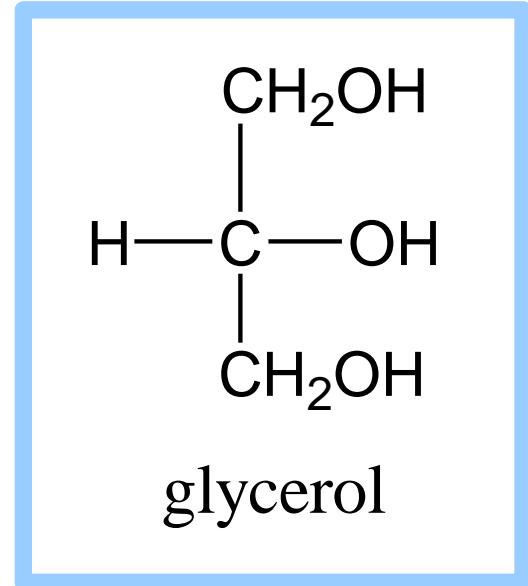
Glycerophospholipids

(phosphoglycerides), are common constituents of cellular membranes.

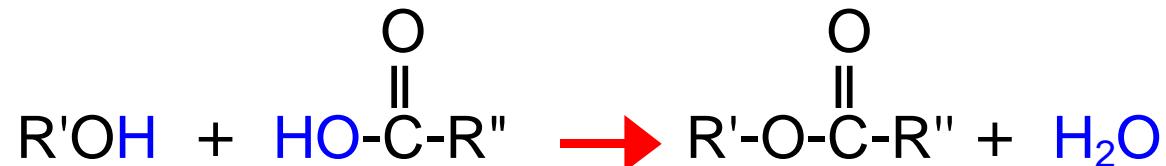
They have a **glycerol** backbone.

Hydroxyls at **C1 & C2** are esterified to **fatty acids**.

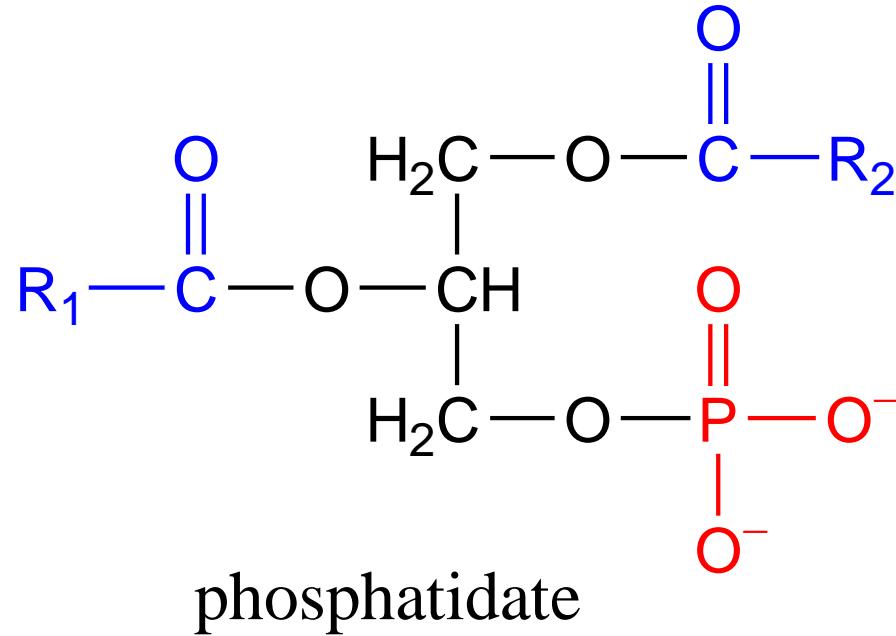
An **ester** forms when a hydroxyl reacts with a carboxylic acid, with loss of H_2O .



Formation of an ester:

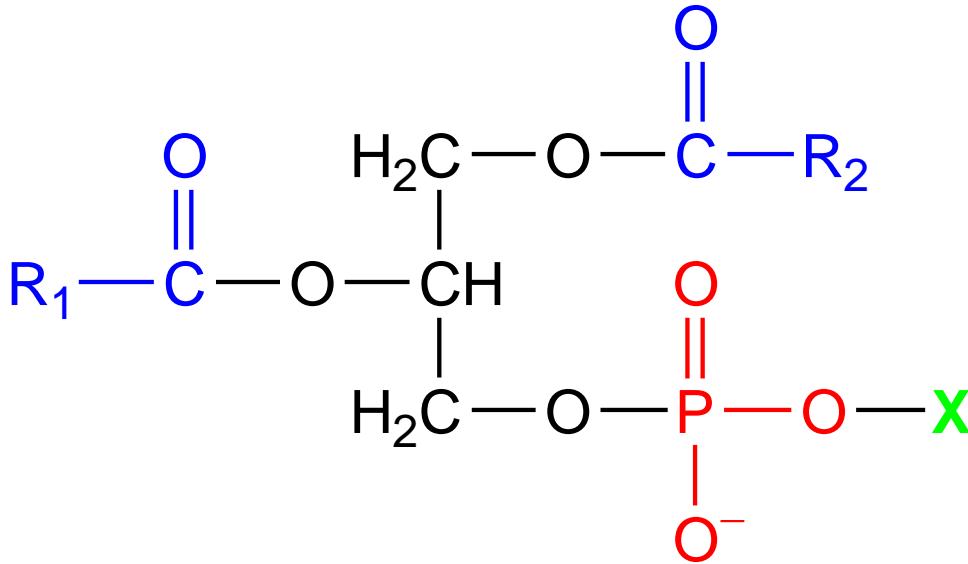


Phosphatidate



In **phosphatidate**:

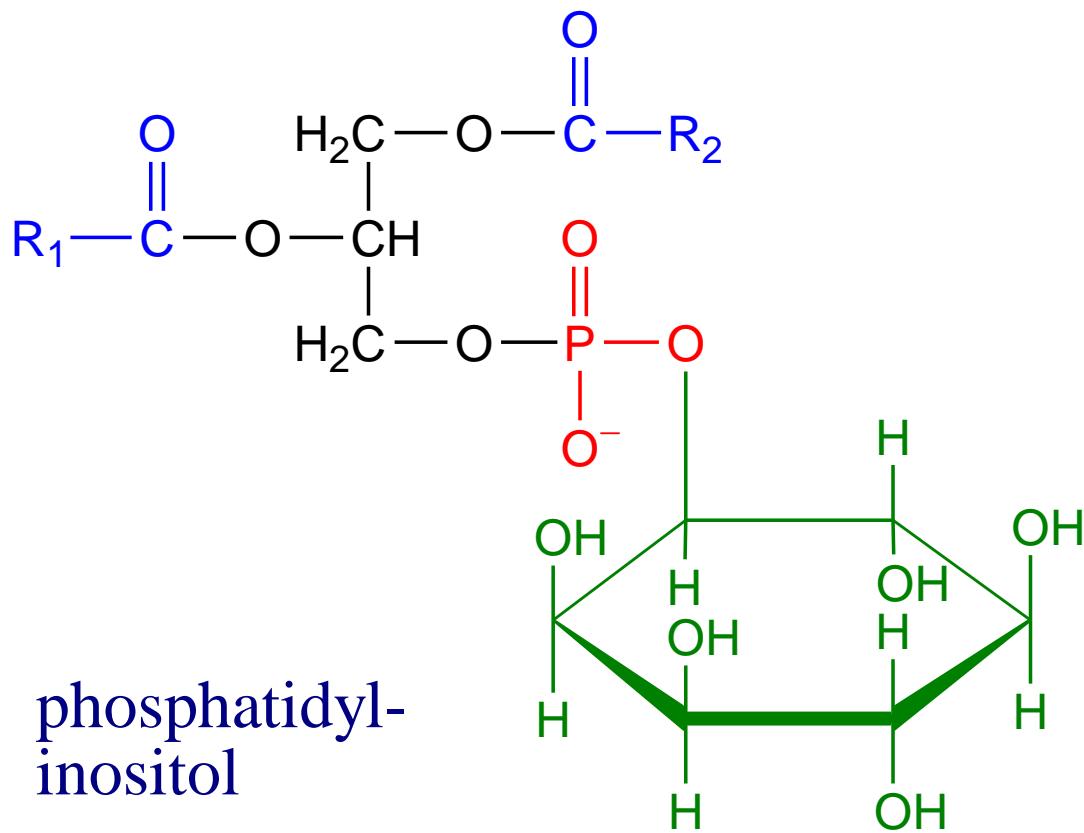
- ◆ **fatty acids** are esterified to hydroxyls on **C1 & C2**
- ◆ the **C3** hydroxyl is esterified to **P_i**.



glycerophospholipid

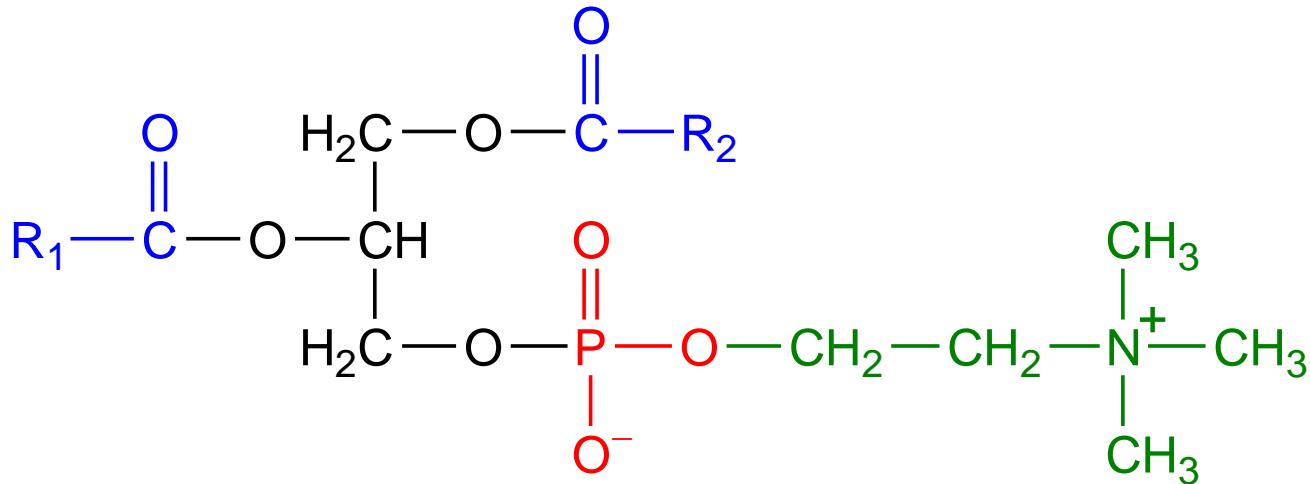
In most **glycerophospholipids** (phosphoglycerides), **P_i** is in turn esterified to **OH** of a **polar head group** (**X**): e.g., **serine, ethanolamine, glycerol etc.**

The 2 fatty acids tend to be non-identical. They may differ in length and/or the presence/absence of double bonds.



Phosphatidylinositol, with inositol as polar head group, is one glycerophospholipid.

In addition to being a membrane lipid, phosphatidylinositol has roles in cell signaling.



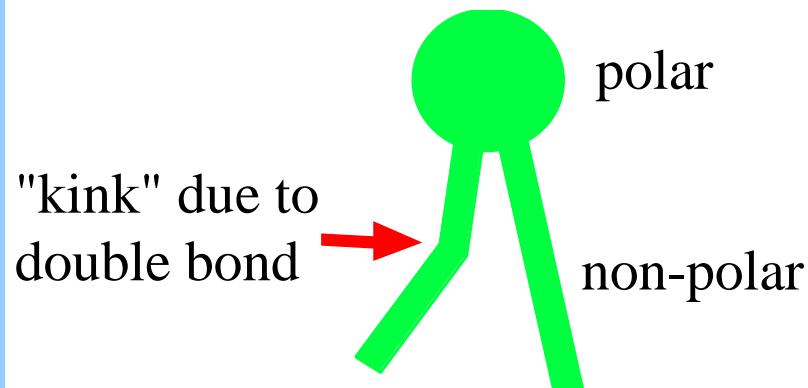
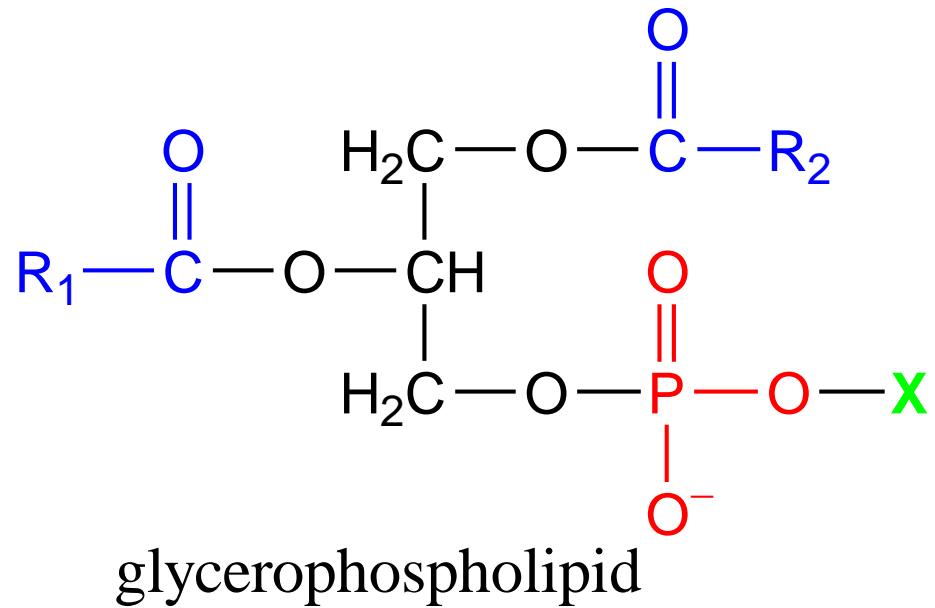
phosphatidylcholine

Phosphatidylcholine, with choline as polar head group, is another glycerophospholipid.

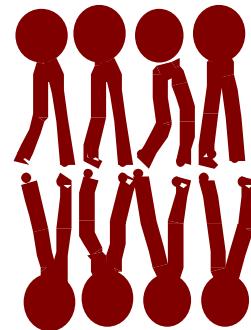
It is a common membrane lipid.

Each glycerophospholipid includes

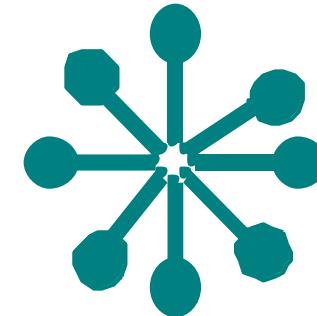
- ◆ a **polar** region:
glycerol, carbonyl O
of fatty acids, **P_i**, & the
polar head group (**X**)
- ◆ **non-polar** hydrocarbon
tails of fatty acids (**R₁, R₂**).



Amphipathic lipids in association with water form complexes in which polar regions are in contact with water and hydrophobic regions away from water.



Bilayer



Spherical Micelle

Depending on the lipid, possible molecular arrangements:

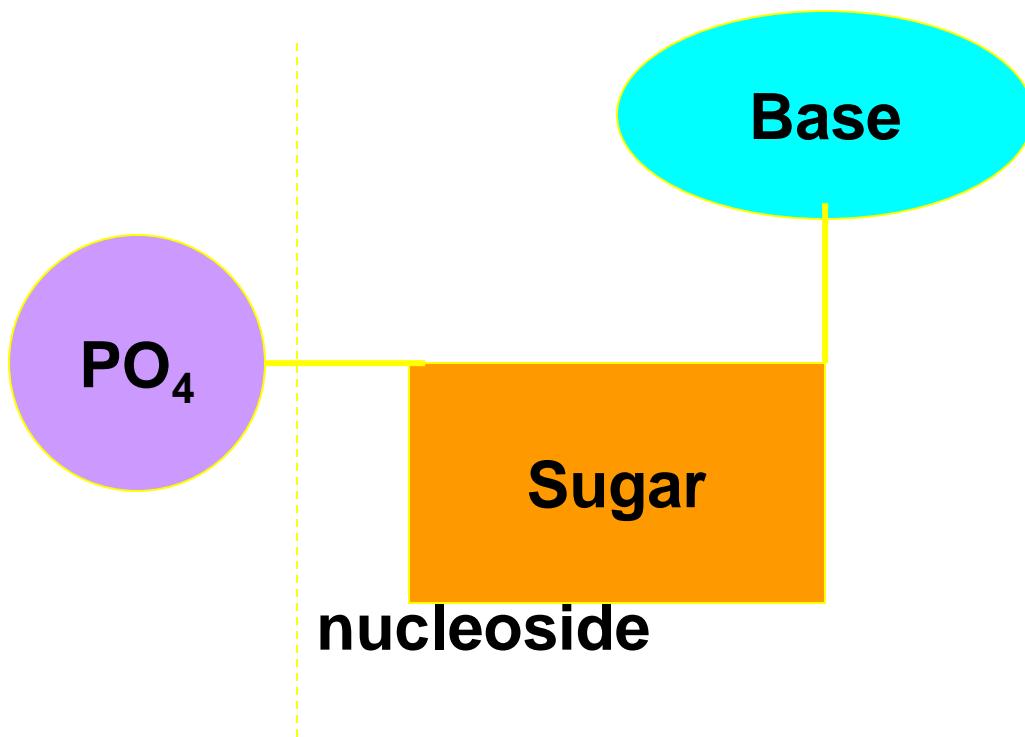
- ◆ Various **micelle** structures. E.g., a spherical micelle is a stable configuration for amphipathic lipids with a **conical** shape, such as **fatty acids**.
- ◆ A **bilayer**. This is the most stable configuration for amphipathic lipids with a **cylindrical** shape, such as **phospholipids**.

BIOORGANIC CHEMISTRY

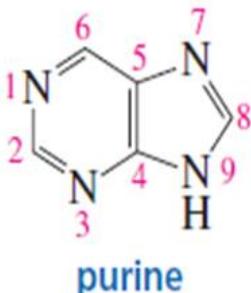
Nucleic Acids
Structures of Nucleic Acids
DNA and RNA

Nucleotides

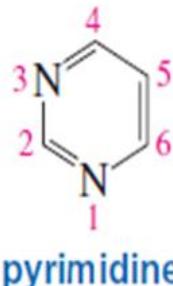
Nucleic acids consist of nucleotides that have a sugar, nitrogen base, and phosphate



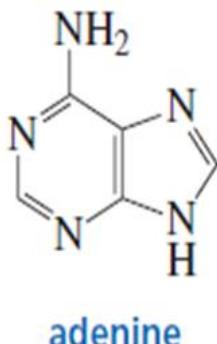
Nitrogen-Containing Bases



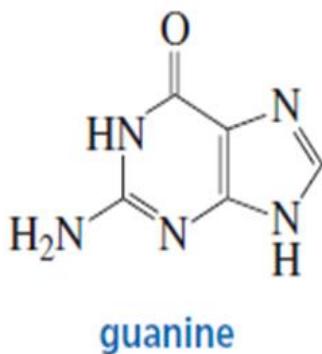
purine



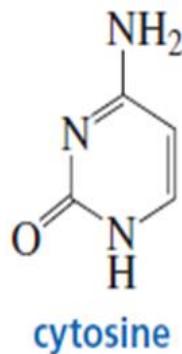
pyrimidine



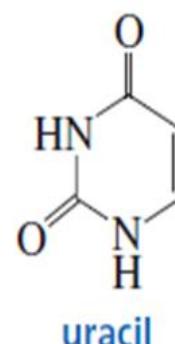
adenine



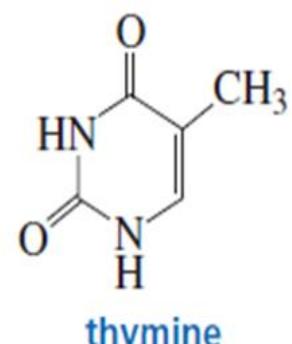
guanine



cytosine

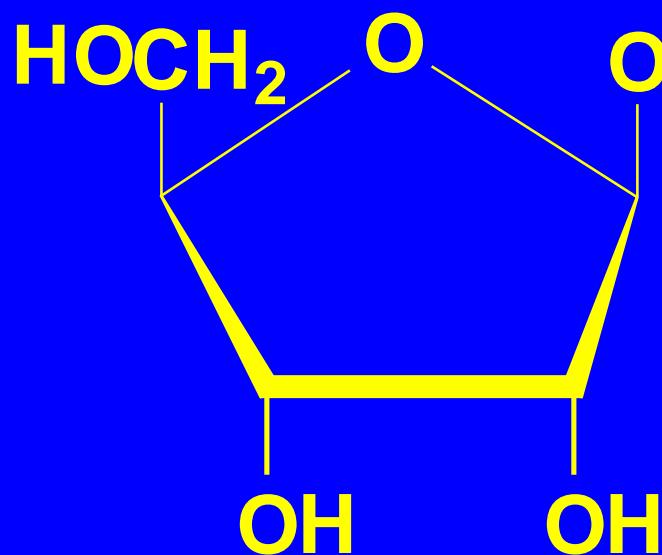


uracil

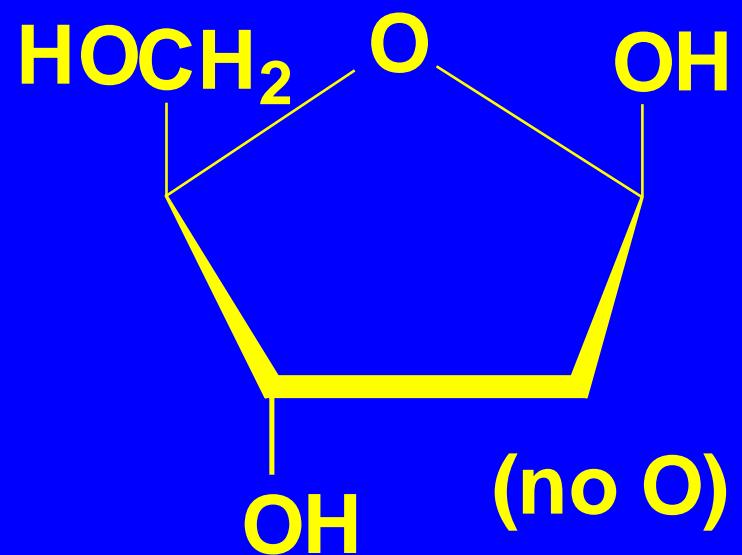


thymine

Sugars



ribose



deoxyribose

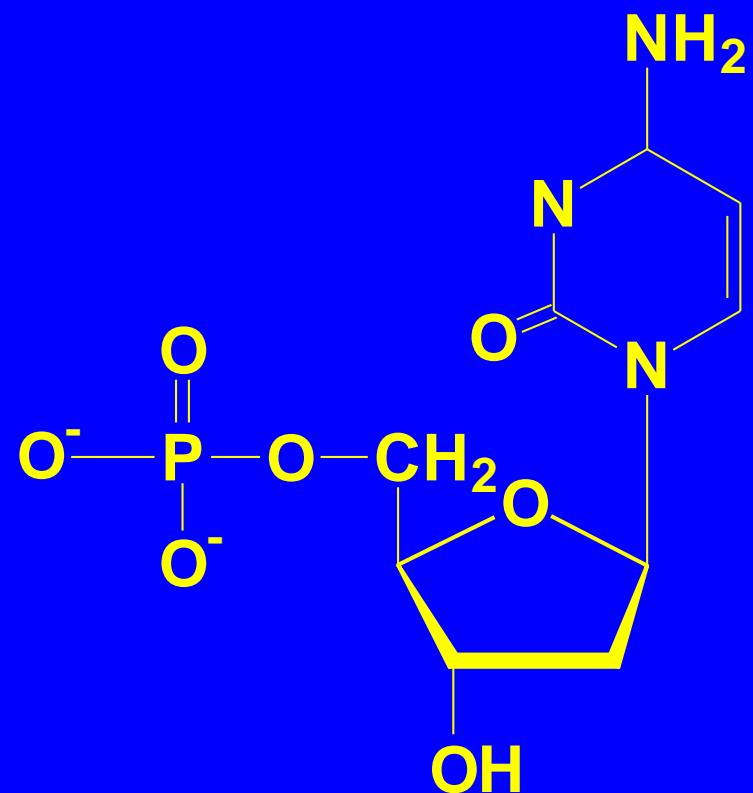
Nucleosides in DNA and RNA

<u>Base</u>	<u>Sugar</u>	<u>Nucleoside</u>
Adenine (A)	Deoxyribose	Adenosine
Guanine (G)	Deoxyribose	Guanosine
Cytosine (C)	Deoxyribose	Cytidine
Thymine (T)	Deoxyribose	Thymidine

RNA

<u>Base</u>	<u>Sugar</u>	<u>Nucleoside</u>
Adenine (A)	ribose	Adenosine
Guanine (G)	ribose	Guanosine
Cytosine (C)	ribose	Cytidine
Uracil (U)	ribose	Uridine

Example of a Nucleoside



deoxyctyidine monophosphate (dCMP)

Nucleotides in DNA and RNA

DNA

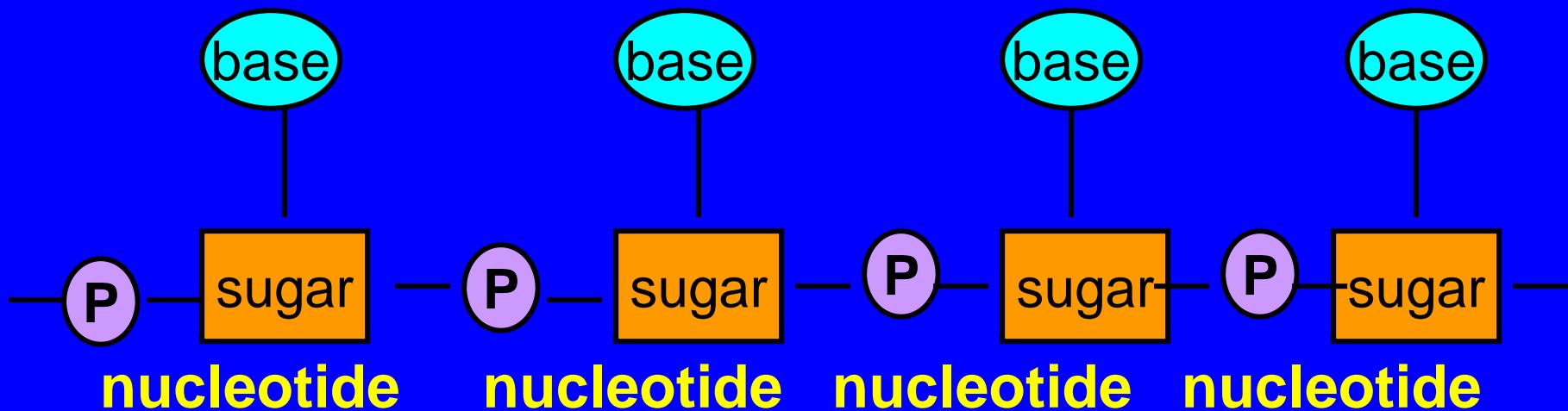
dAMP	Deoxyadenosine monophosphate
dGMP	Deoxyguanosine monophosphate
dCMP	Deoxycytidine monophosphate
dTMP	Deoxythymidine monophosphate

RNA

AMP	adenosine monophosphate
GMP	guanosine monophosphate
CMP	cytidine monophosphate
UMP	uridine monophosphate

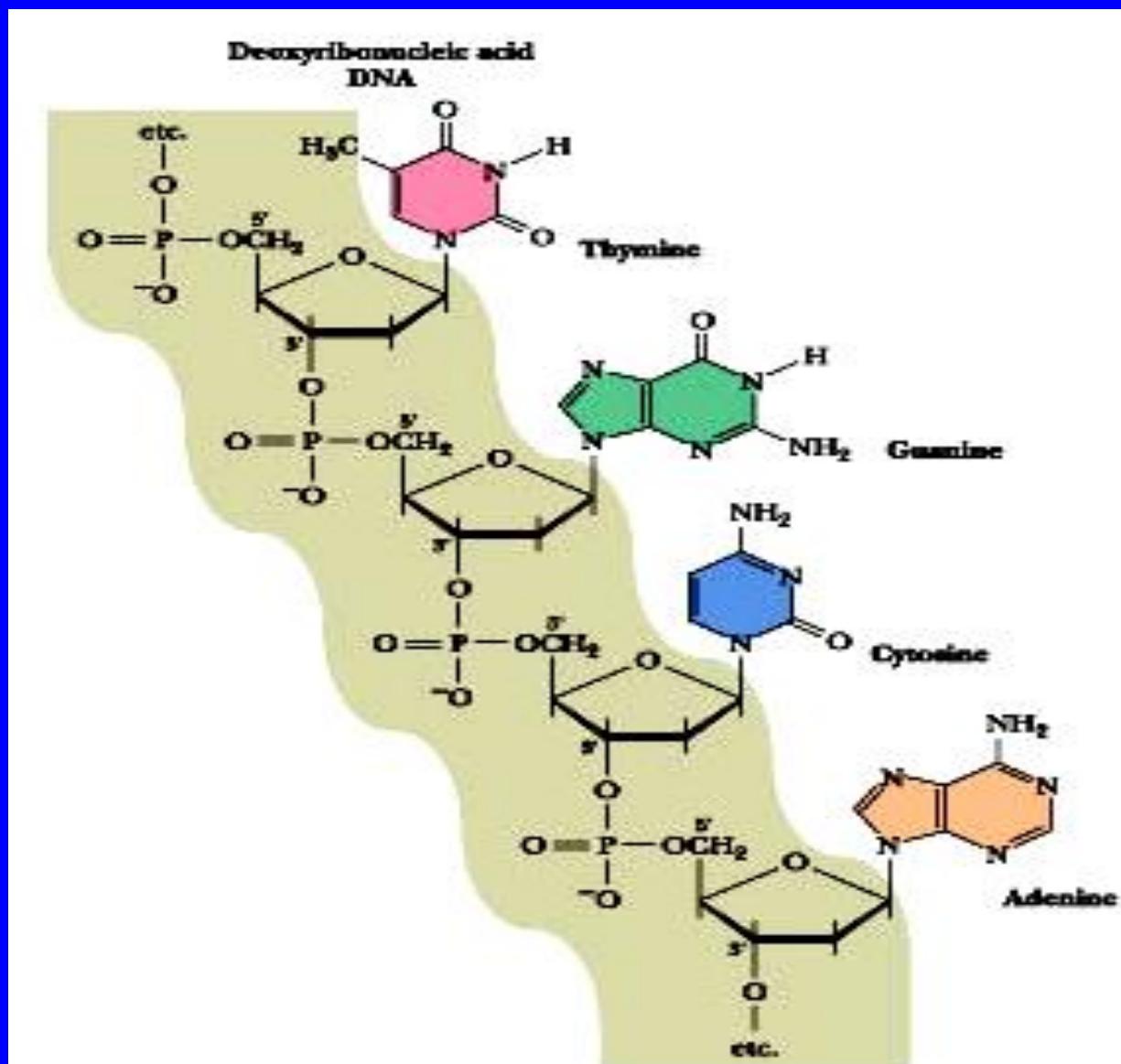
Structure of Nucleic Acids

- Polymers of four nucleotides
- Linked by alternating sugar-phosphate bonds
- RNA: ribose and A, G, C, U
- DNA: deoxyribose and A,G,C,T



Nucleic Acid Structure

3,5-phosphodiester
bond

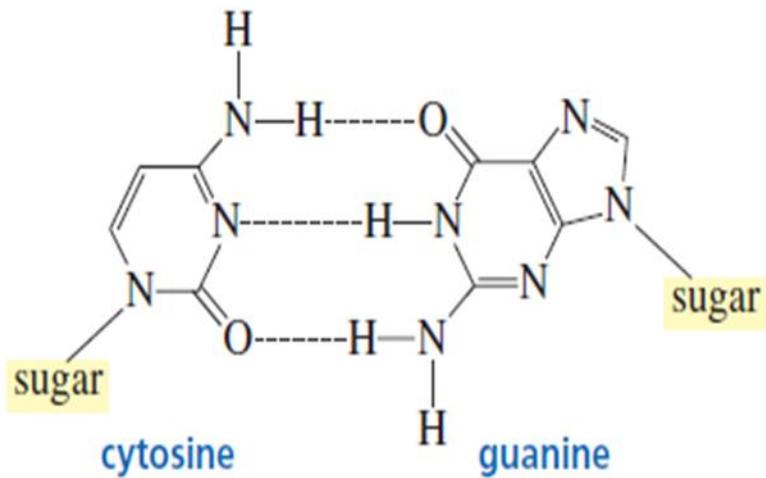
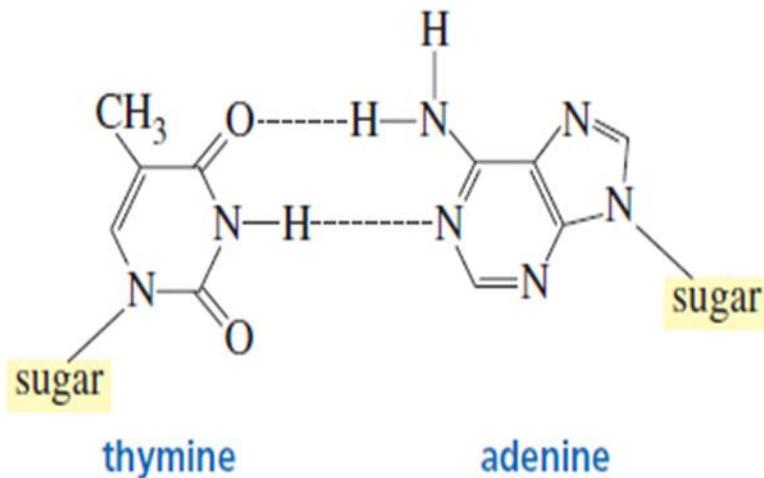


Double Helix of DNA

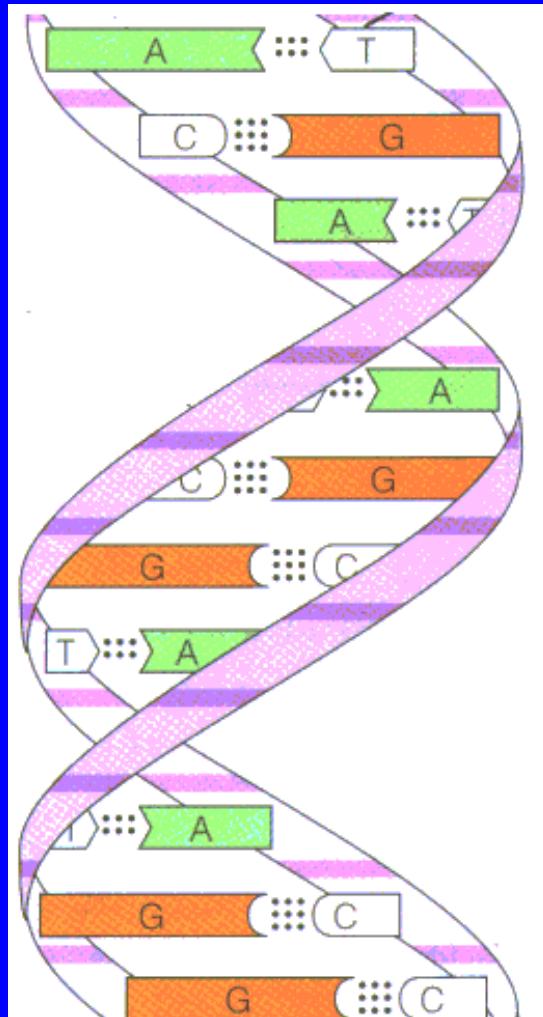
- DNA contains two strands of nucleotides
- H bonds hold the two strands in a double-helix structure
- A helix structure is like a spiral stair case
- Bases are always paired as A-T and G-C
- Thus the bases along one strand complement the bases along the other

Complementary Base Pairs

- Two H bonds for A-T
- Three H bonds for G-C



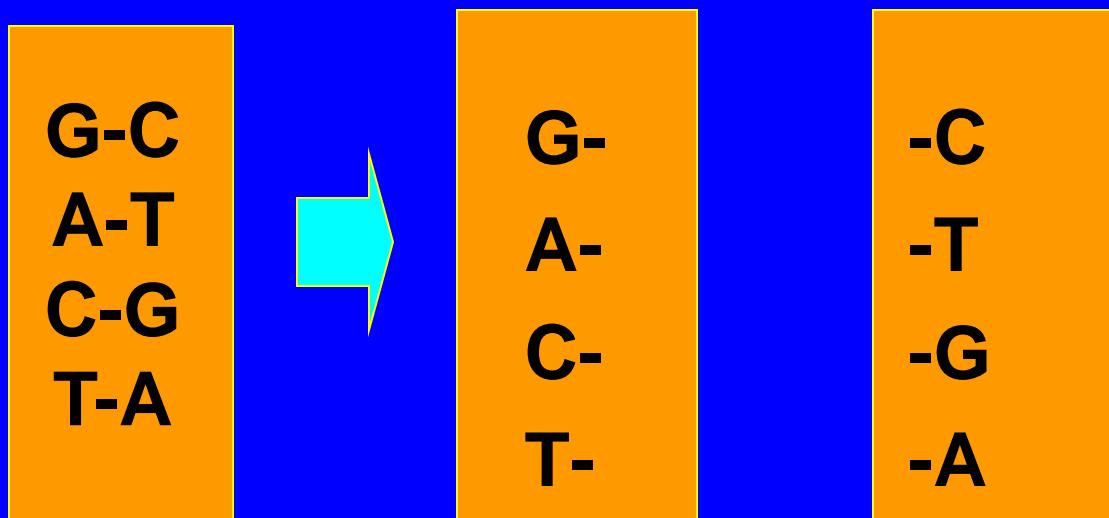
Double Helix of DNA



DNA Replication

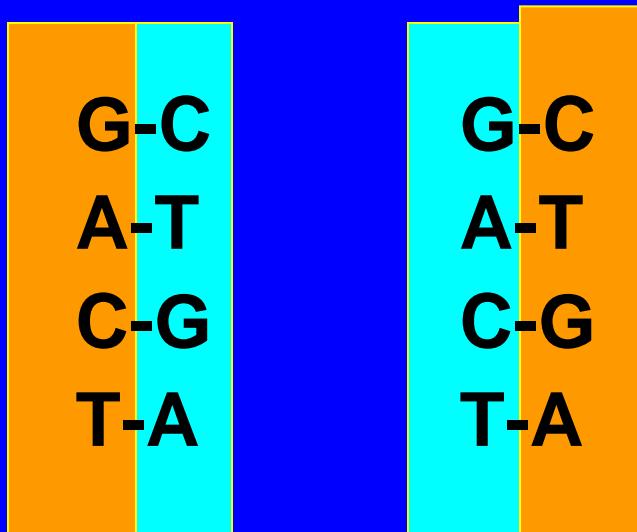
- DNA in the chromosomes replicates itself every cell division
- Maintains correct genetic information
- Two strands of DNA unwind
- Each strand acts like a template
- New bases pair with their complementary base
- Two double helixes form that are copies of original DNA

DNA Unwinds

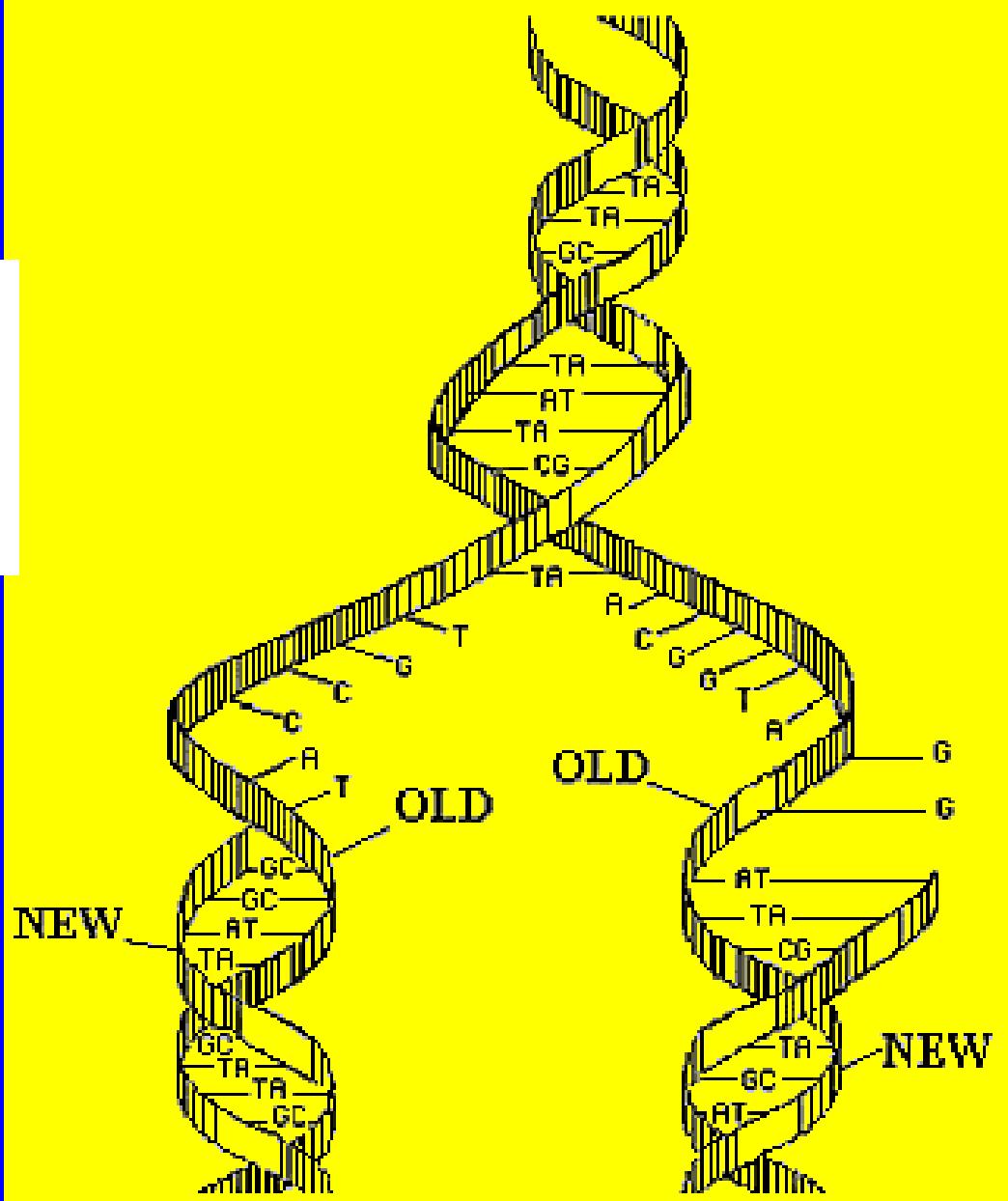


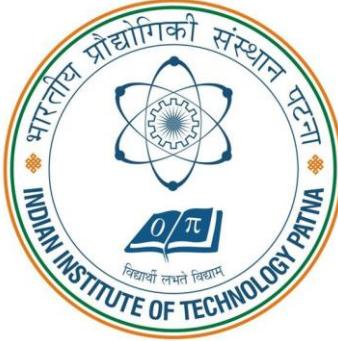
DNA Copied with Base Pairs

Two copies of original DNA strand



DNA unwinding
During homologous
Recombination –
a DNA replication method





INDIAN INSTITUTE OF TECHNOLOGY PATNA

DEPARTMENT OF CHEMISTRY

CH 103

Instructor: Dr. Neeladri Das
Email: neeladri@iitp.ac.in

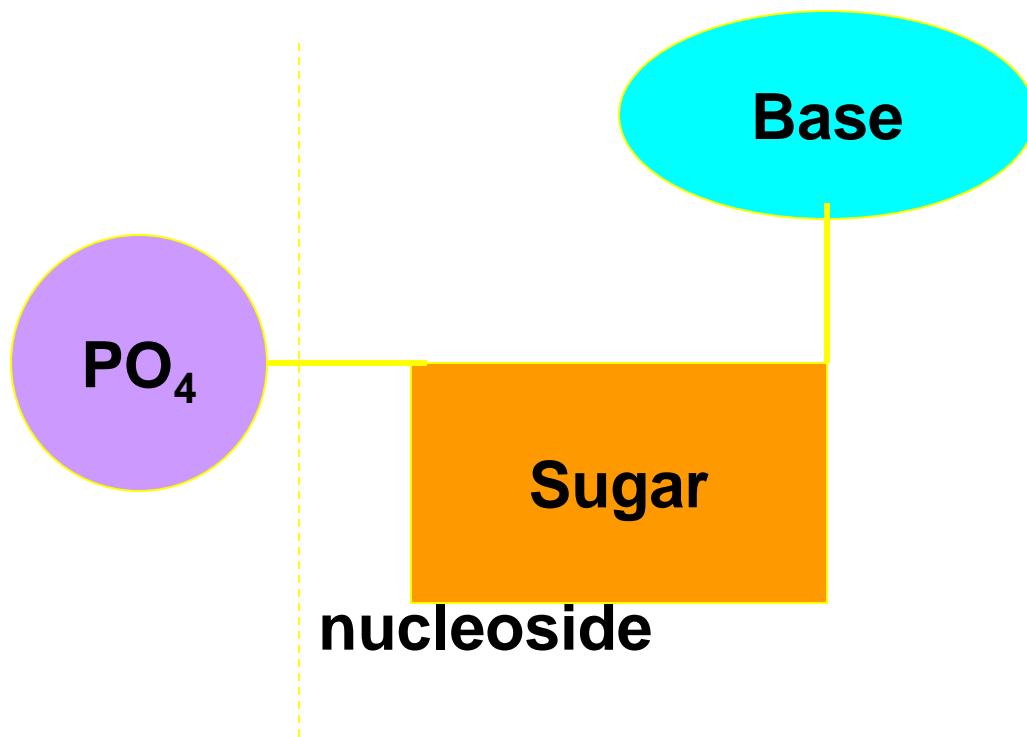
Associate Professor, Chemistry Dept., IIT Patna
Rm-215, Block-IV
Chemistry department
IIT Patna

BIOORGANIC CHEMISTRY

Nucleic Acids
Structures of Nucleic Acids
DNA and RNA

Nucleotides

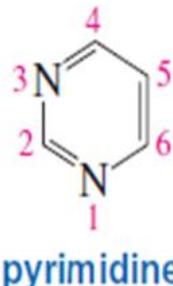
Nucleic acids consist of nucleotides that have a sugar, nitrogen base, and phosphate



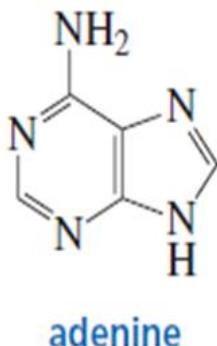
Nitrogen-Containing Bases



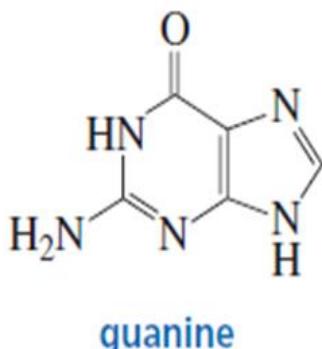
purine



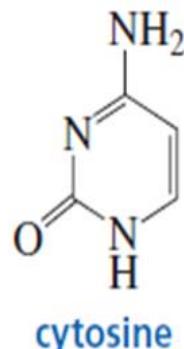
pyrimidine



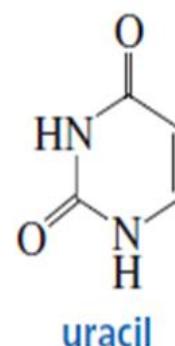
adenine



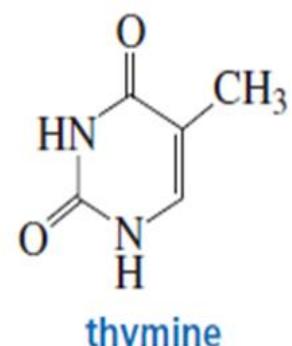
guanine



cytosine

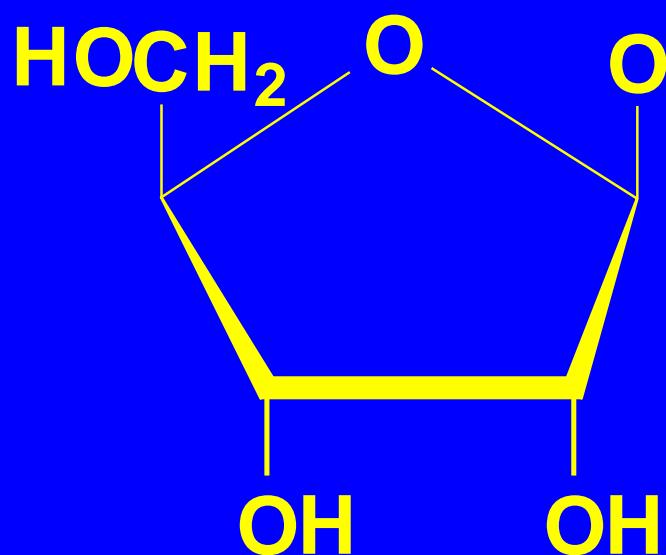


uracil

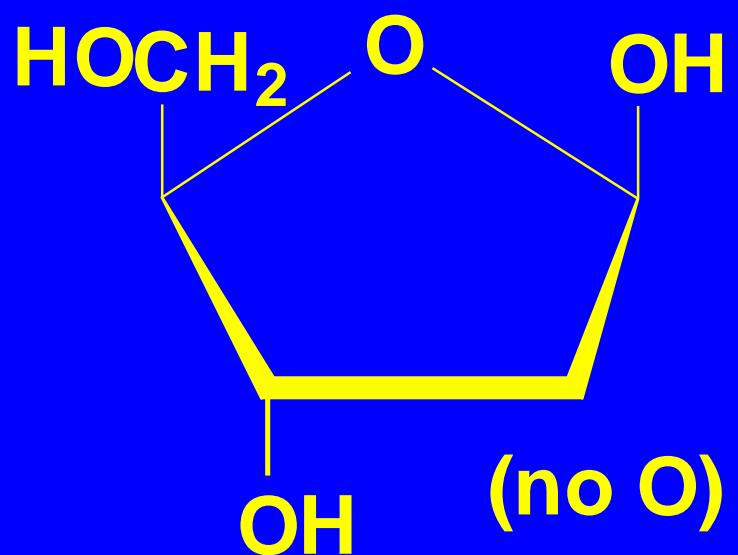


thymine

Sugars



ribose



deoxyribose

Nucleosides in DNA and RNA

<u>Base</u>	<u>Sugar</u>	<u>Nucleoside</u>
Adenine (A)	Deoxyribose	Adenosine
Guanine (G)	Deoxyribose	Guanosine
Cytosine (C)	Deoxyribose	Cytidine
Thymine (T)	Deoxyribose	Thymidine

RNA

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Guanine (G)	ribose	Guanosine
Cytosine (C)	ribose	Cytidine
Uracil (U)	ribose	Uridine

Nucleotides in DNA and RNA

DNA

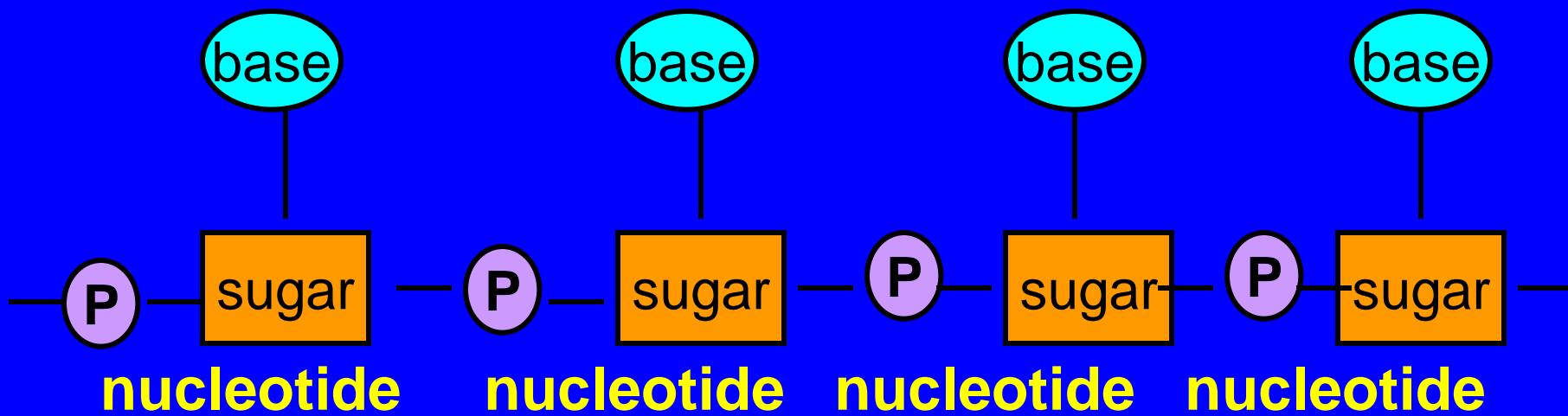
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dCMP	Deoxycytidine monophosphate
dTMP	Deoxythymidine monophosphate

RNA

AMP	adenosine monophosphate
GMP	guanosine monophosphate
CMP	cytidine monophosphate
UMP	uridine monophosphate

Structure of Nucleic Acids

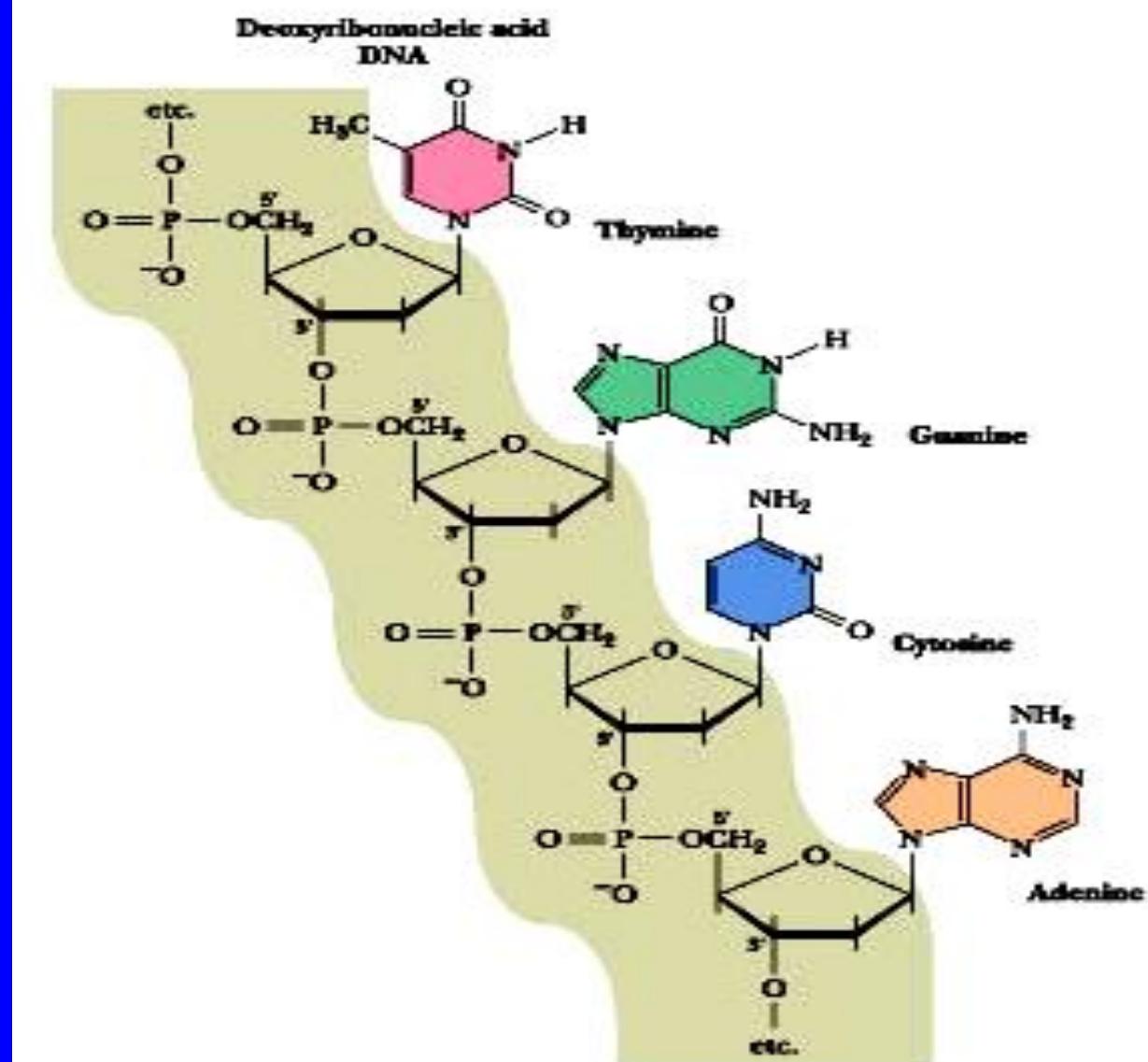
- Polymers of four nucleotides
- Linked by alternating sugar-phosphate bonds
- RNA: ribose and A, G, C, U
- DNA: deoxyribose and A,G,C,T



Nucleic Acid Structure

Generating the
nucleic acid
structure

Using
3,5-phosphodiester
bond



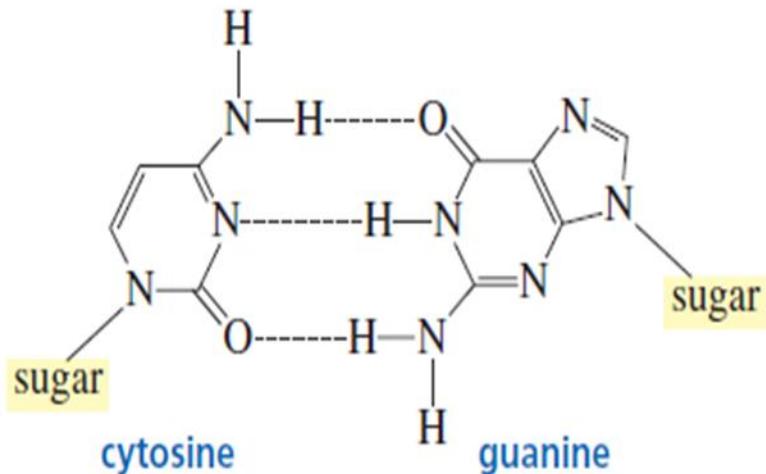
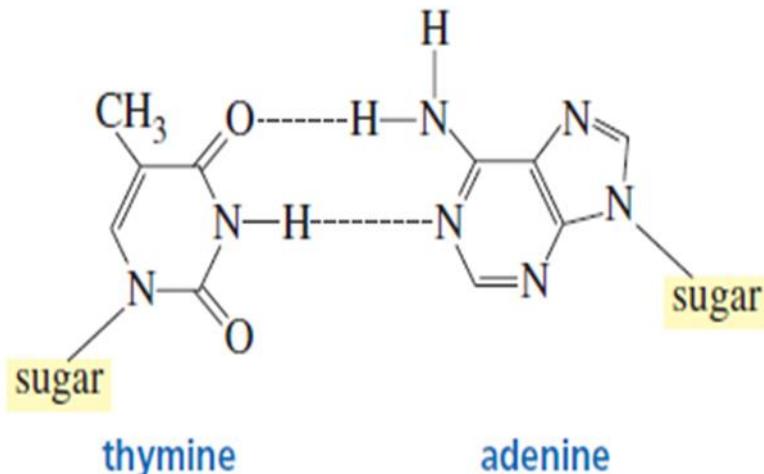
Double Helix of DNA

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- A helix structure is like a spiral staircase
- Bases are always paired as A-T and G-C
- Thus the bases along one strand complement the bases along the other

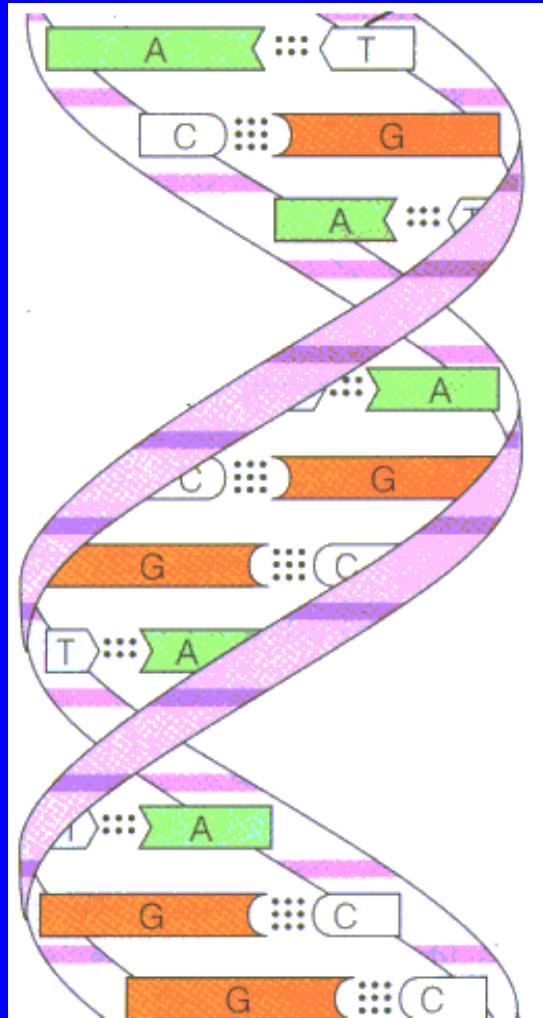


Complementary Base Pairs

- Two H bonds for A-T
- Three H bonds for G-C



Double Helix of DNA



Modern Techniques for Structure Elucidation of compounds

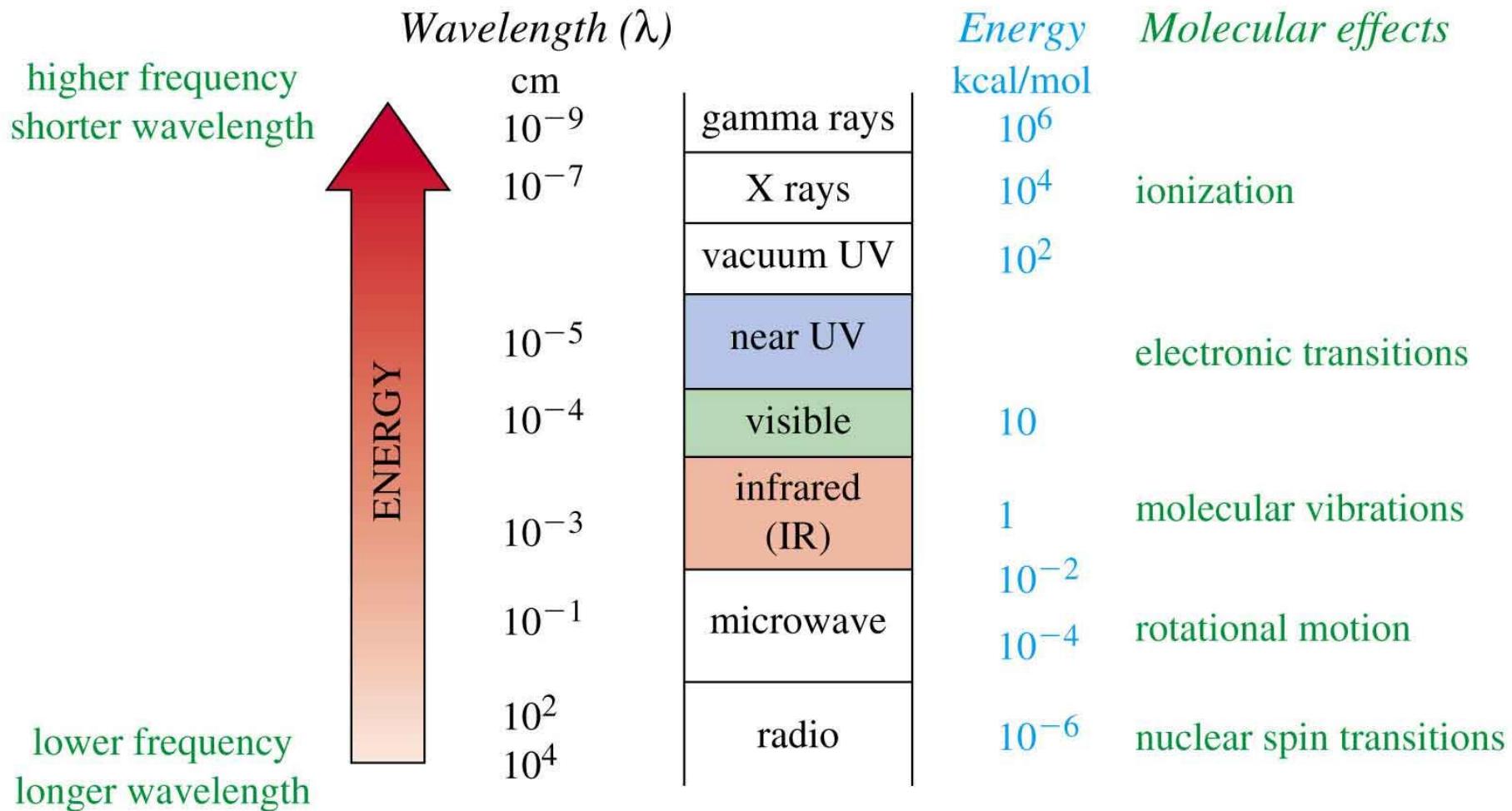
*Electromagnetic waves interacting
with matter as an analytical tool*

UV-Vis, IR and NMR

Spectroscopic Techniques and Chemistry they Probe

UV-Vis Spectroscopy	UV-vis region	bonding electrons
Atomic Absorption	UV-vis region	atomic transitions (val. e-)
FT-IR	IR/Microwave	vibrations, rotations
Raman	IR/UV	vibrations
FT-NMR	Radio waves	nuclear spin states
X-Ray Spectroscopy	X-rays	inner electrons, elemental
X-ray Crystallography	X-rays	3-D structure

The Spectrum and Molecular Effects



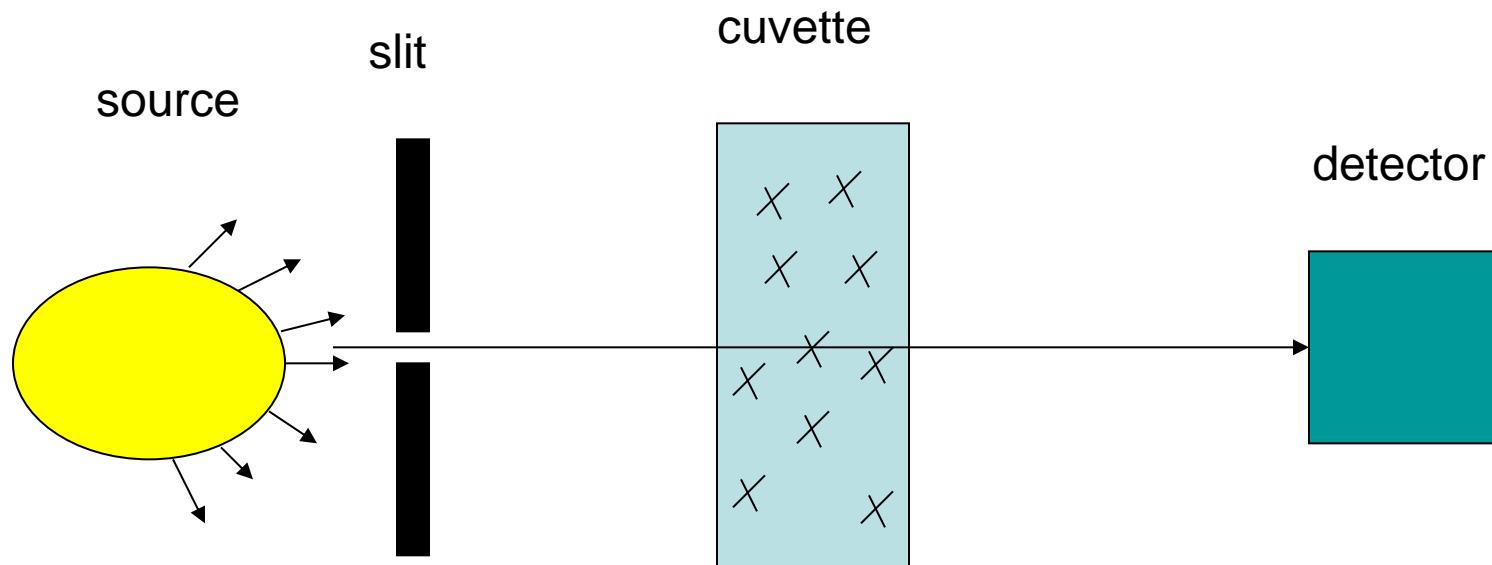
Spectroscopic Techniques and Common Uses		
UV-Vis Spectroscopy	UV-vis region	Quantitative analysis/Beer's Law
Atomic Absorption	UV-vis region	Quantitative analysis Beer's Law
FT-IR	IR/Microwave	Functional Group Analysis
Raman	IR/UV	Functional Group Analysis
FT-NMR	Radio waves	Structure determination
X-Ray Spectroscopy	X-rays	Elemental Analysis
X-ray Crystallography	X-rays	3-D structure Analysis

UV-Vis Spectroscopy

- Lambert - Beer's Law $A = e \cdot l \cdot c$

e = molar absorptivity (unique for a compound)

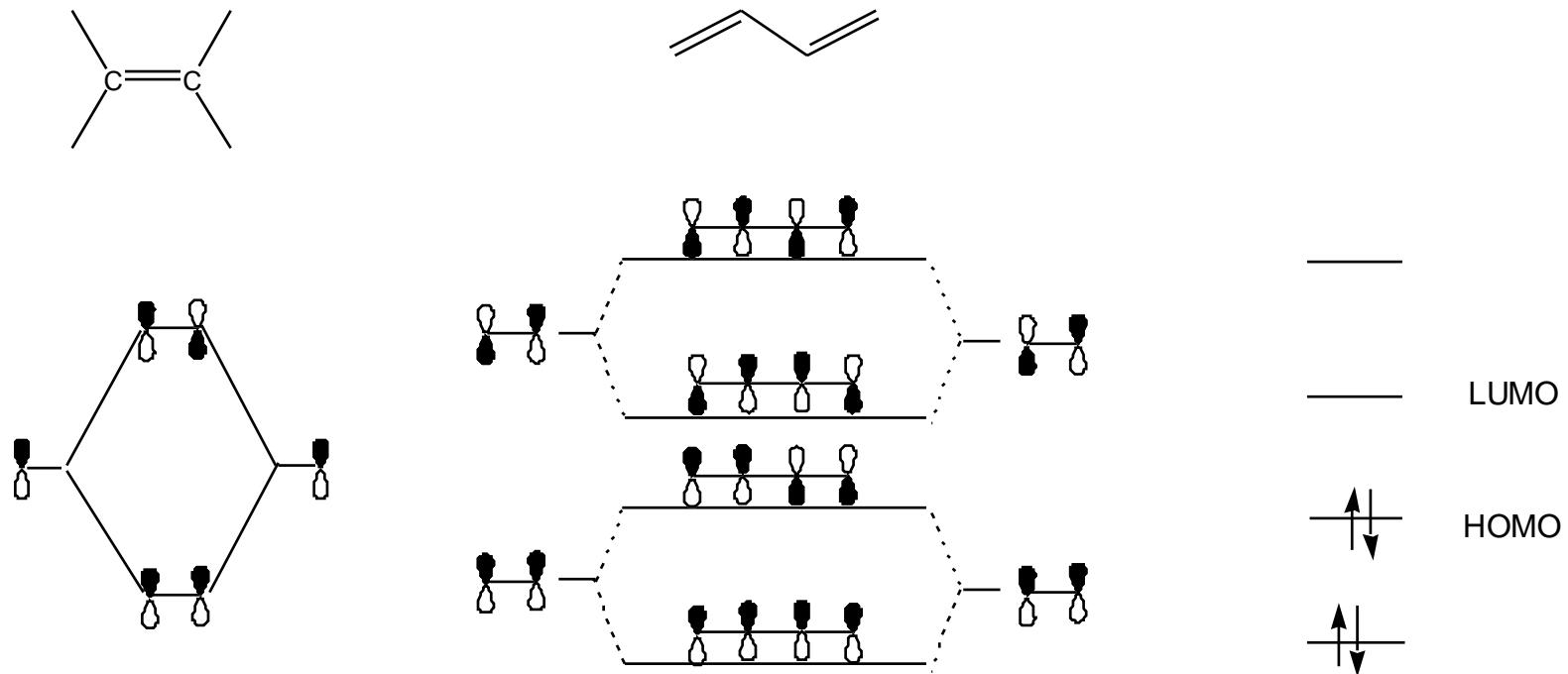
l = path length c = concentration



UV-Vis Spectroscopy

- UV- organic molecules
 - Outer electron bonding transitions
 - conjugation
- Visible – metal/ligands in solution
 - d-orbital transitions

Conjugated systems:



Preferred transition is between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

Note: Additional conjugation (double bonds) lowers the HOMO-LUMO energy gap:

Example:

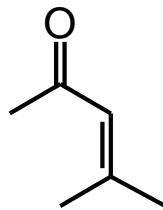
1,3 butadiene:

$\lambda_{\max} = 217 \text{ nm ; } \epsilon = 21,000$

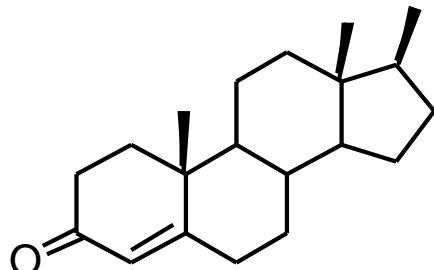
1,3,5-hexatriene

$\lambda_{\max} = 258 \text{ nm ; } \epsilon = 35,000$

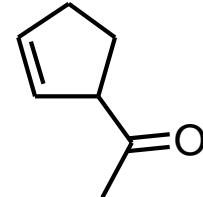
Similar structures have similar UV spectra:



$\lambda_{\max} = 238, 305 \text{ nm}$

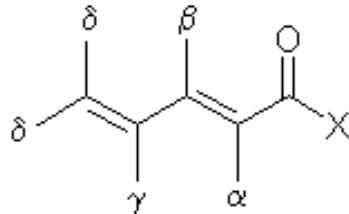
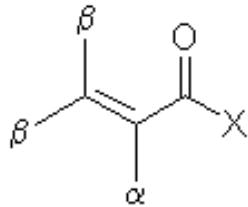


$\lambda_{\max} = 240, 311 \text{ nm}$



$\lambda_{\max} = 173, 192 \text{ nm}$
Not conjugated

Woodward's Rules for Conjugated Carbonyl Compounds



Base values:

$X = R$

Six-membered ring or acyclic parent enone $\lambda = 215 \text{ nm}$

Five-membered ring parent enone $\lambda = 202 \text{ nm}$

$X = H$ $\lambda = 208 \text{ nm}$

$X = OH, OR$ $\lambda = 195 \text{ nm}$

Increments for:

Double bond extending conjugation 30

Exocyclic double bond 5

Endocyclic double bond in a 5- or 7-membered ring for $X = OH, OR$ 5

Homocyclic diene component 39

Alkyl substituent or ring residue α 10

β 12

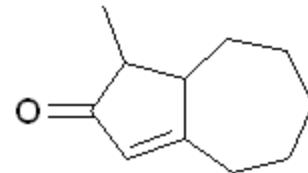
γ or higher 18

Polar groupings: α 35

-OH β 30

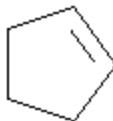
An example

Considering C = O
Bond as an exocyclic
bond

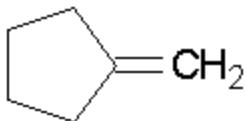


Five-membered ring parent enone:	202 nm
β -Alkyl groups or ring residues:	$2 \times 12 =$ 24 nm
Exocyclic double bond:	<u>5 nm</u>
Calculated:	231 nm
Observed:	226 nm

Cyclopentene is an example of an **endocyclic** double bond.



Methylenecyclopentane is an example of an **exocyclic** double bond.

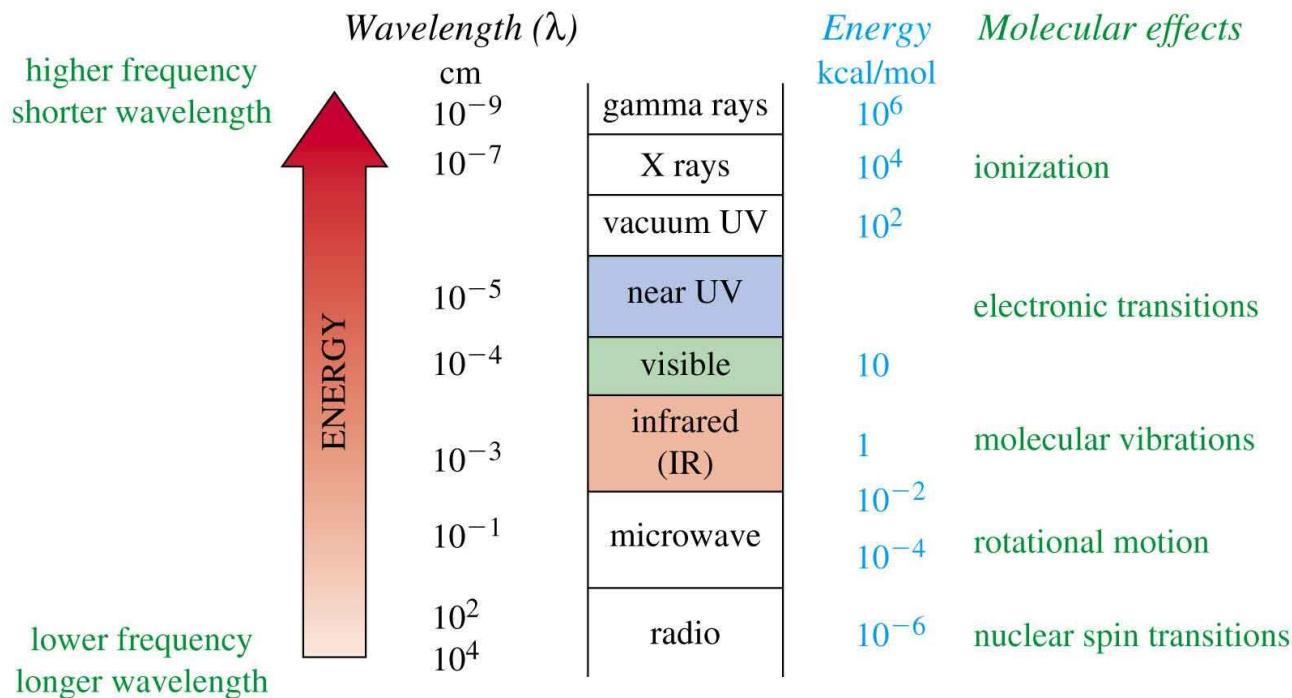


Woodward-Fieser Rules for Dienes

<http://www.chemistry.ccsu.edu/glagovich/teaching/316/uvvis/uvvis.html>

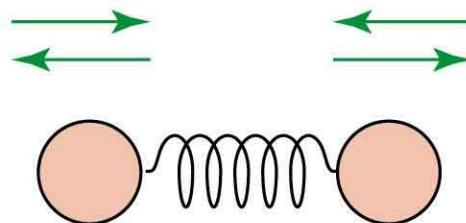
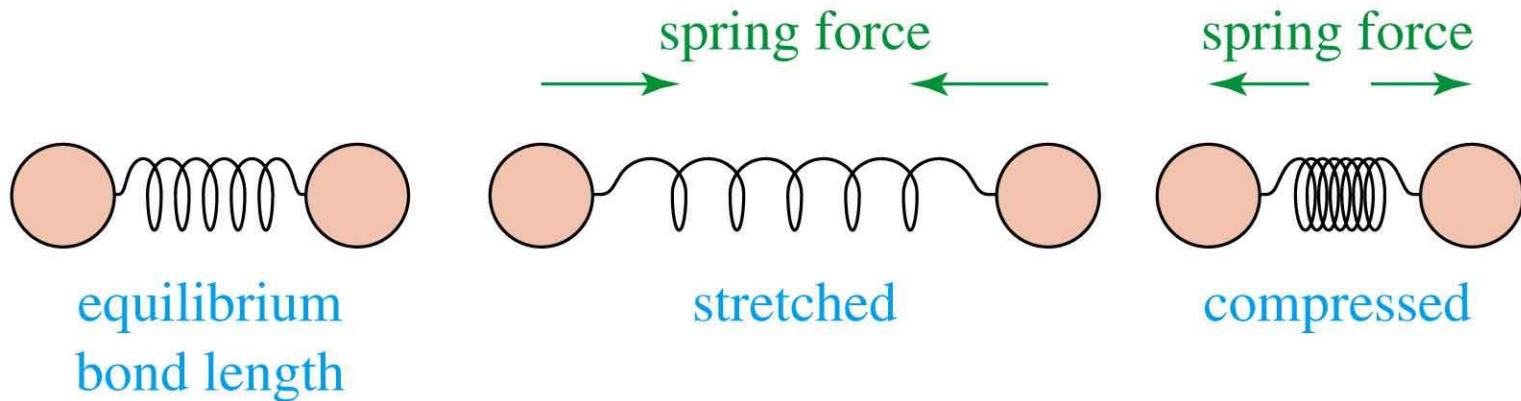
Infrared Spectroscopy

- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.



Molecular Vibrations

Covalent bonds vibrate at only certain allowable frequencies.



Stretching Frequencies

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C ↓ heavier atoms	83 (350)	1200
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611) ↓ stronger bond	1660
C≡C	200 (840) ↓	2200

- Frequency decreases with increasing atomic weight.
- Frequency increases with increasing bond energy.

cm⁻¹ is a commonly used unit in spectroscopy,
denotes **wavenumber** and is proportional to frequency



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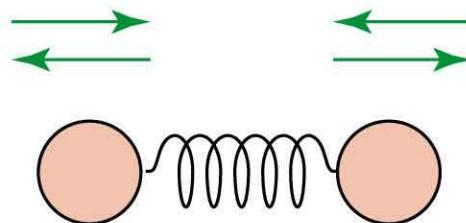
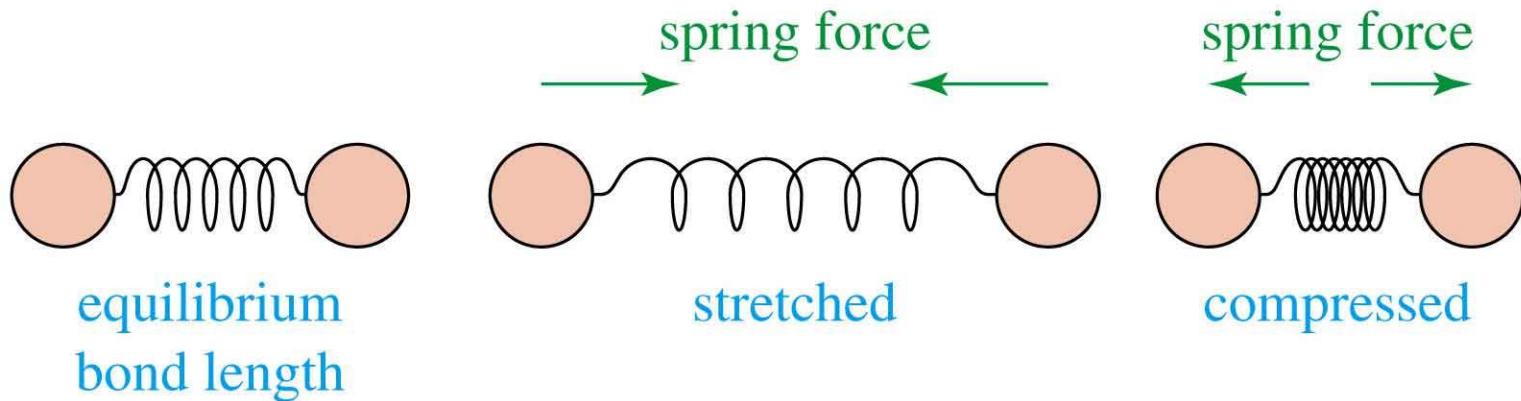
CH 103

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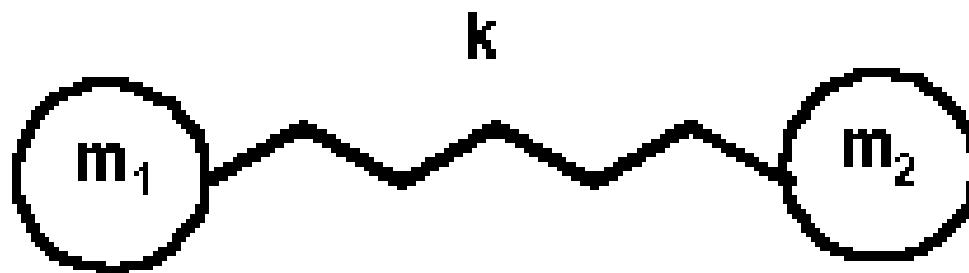
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Chemistry department
IIT Patna

Molecular Vibrations

Covalent bonds vibrate at only certain allowable frequencies.



Hooke's Law



$$\bar{v} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

\bar{v} = frequency

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

μ = reduced mass

Stretching Frequencies

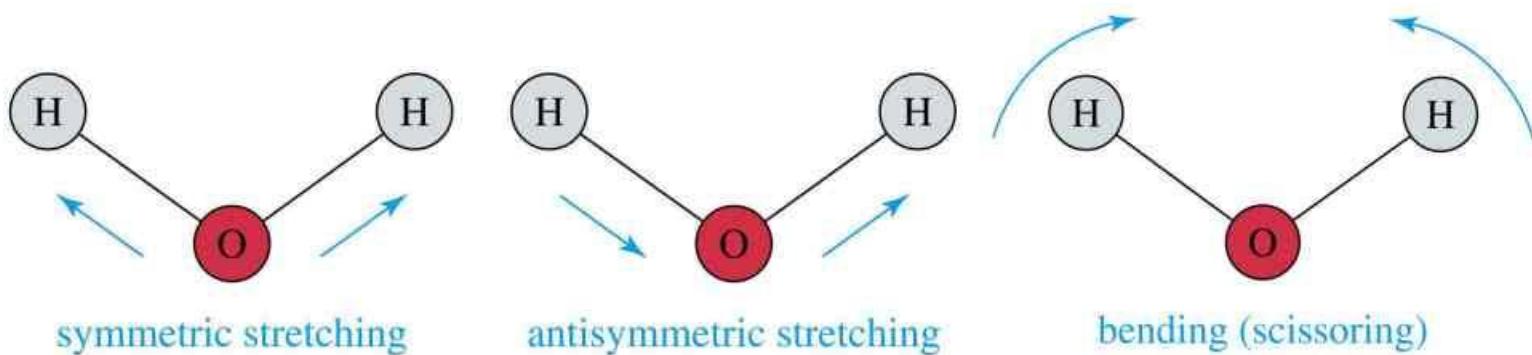
Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C ↓ heavier atoms	83 (350)	1200
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611) ↓ stronger bond	1660
C≡C	200 (840) ↓	2200

- Frequency decreases with increasing atomic weight.
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cm⁻¹ is a commonly used unit in spectroscopy,
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Vibrational Modes

Nonlinear molecule with n atoms usually has $3n - 6$ fundamental vibrational modes.



Fingerprint of Molecule

- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Most useful vibrations: $1600\text{-}3500\text{ cm}^{-1}$.
- Other vibrations: $600\text{-}1400\text{ cm}^{-1}$, called the “fingerprint region.”
 - Often unique for a given molecule

IR-Active and Inactive

- A polar bond is usually IR-active.
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.

Carbon dioxide is IR Inactive (very weak)

Water is IR Active

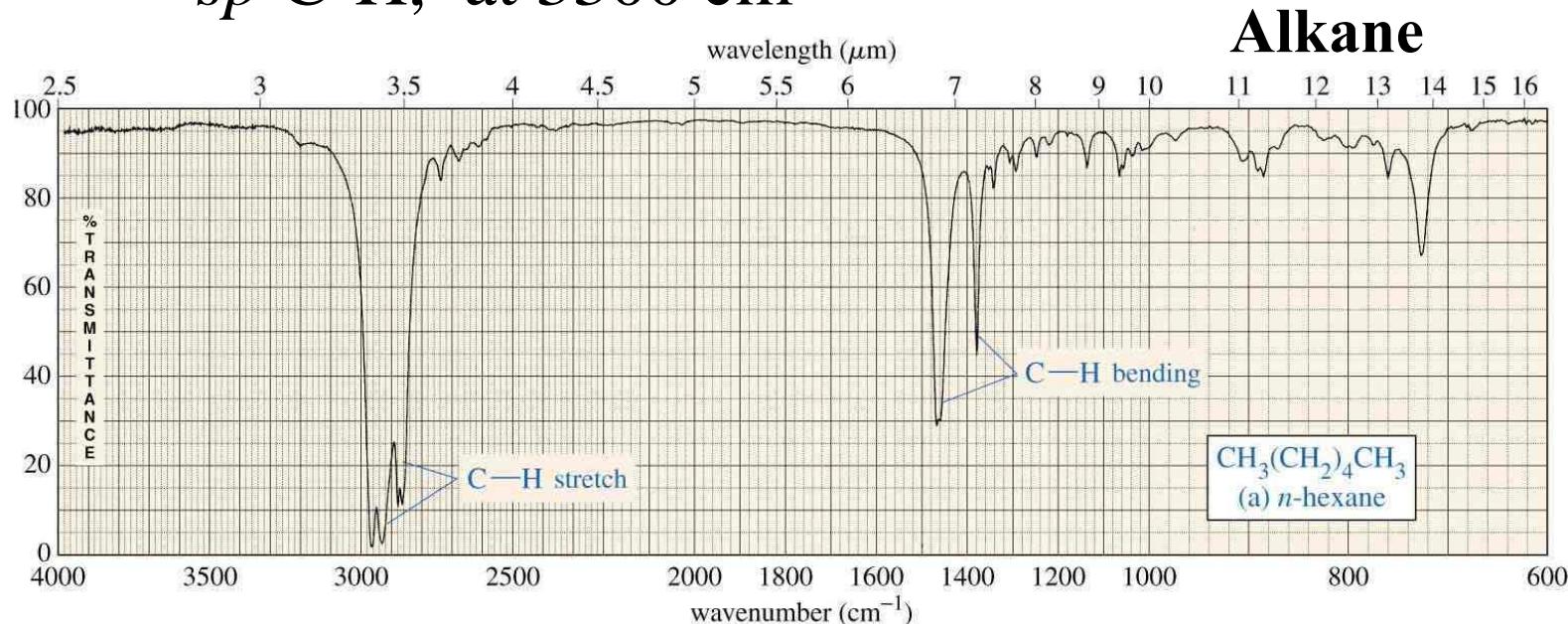
Carbon-Carbon Bond Stretching

- Stronger bonds absorb at higher frequencies:
 - C-C 1200 cm^{-1}
 - C=C 1660 cm^{-1}
 - C≡C 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
 - isolated C=C $1640\text{-}1680\text{ cm}^{-1}$
 - conjugated C=C $1620\text{-}1640\text{ cm}^{-1}$
 - aromatic C=C approx. 1600 cm^{-1}

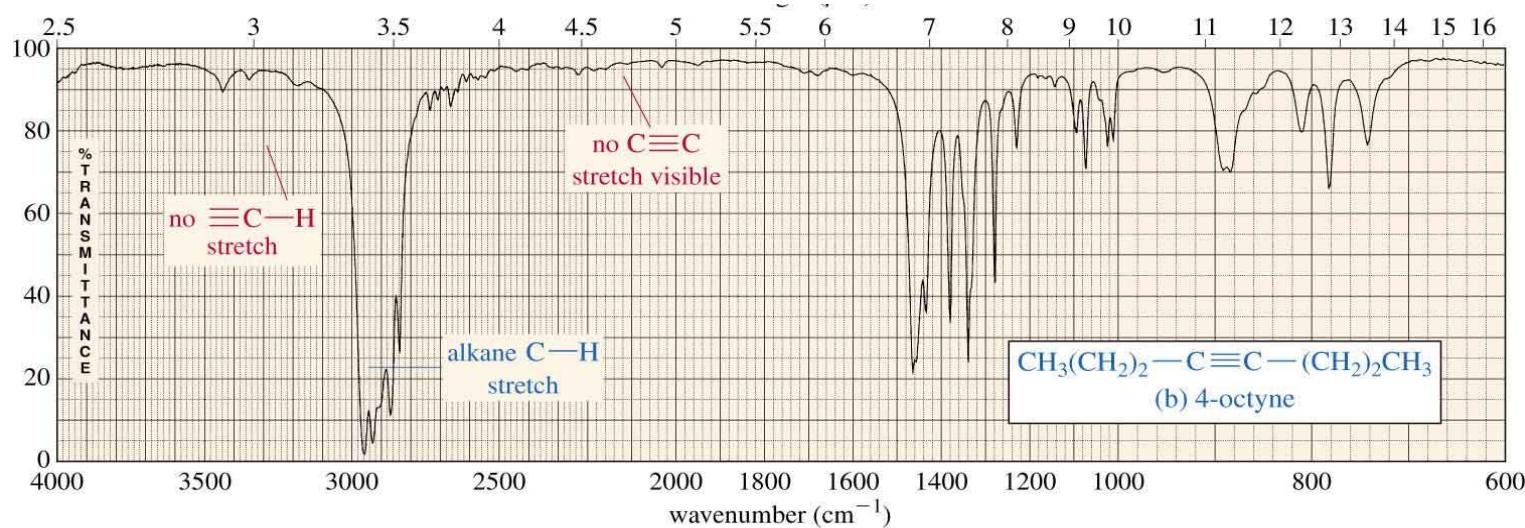
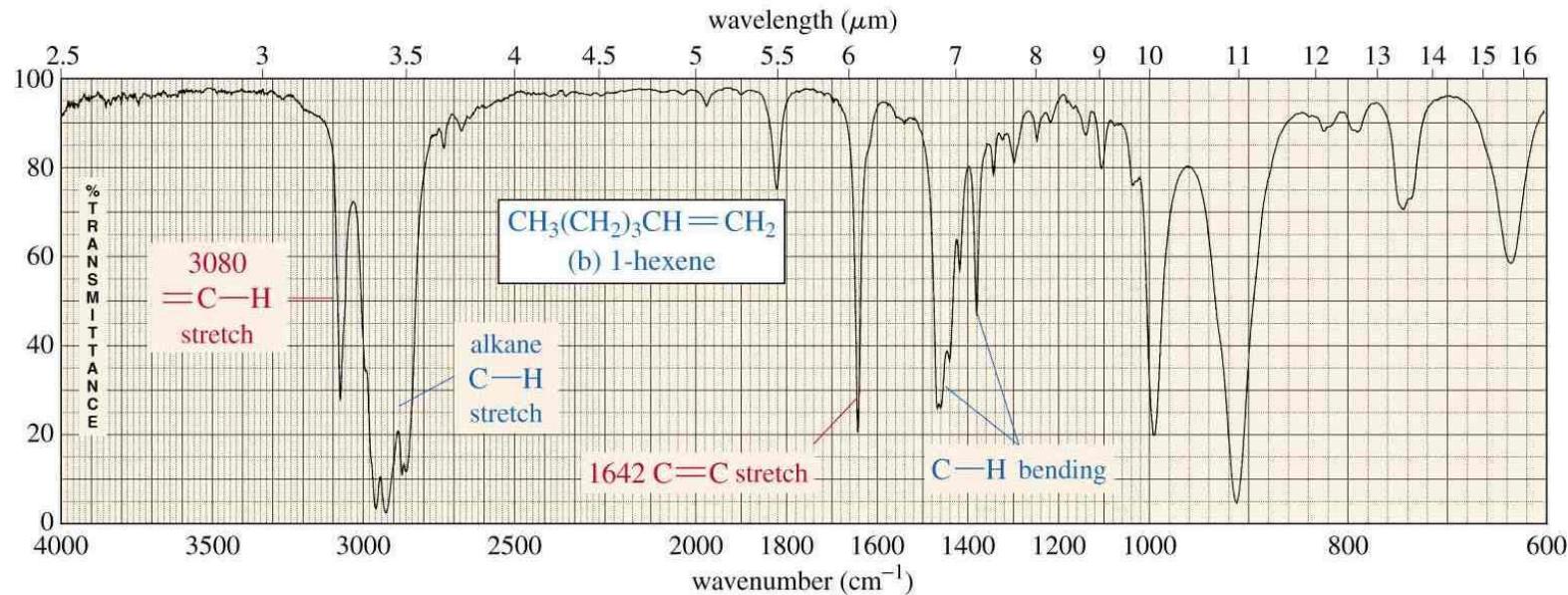
Carbon-Hydrogen Stretching

Bonds with more *s* character absorb at a higher frequency.

- sp^3 C-H, just below 3000 cm^{-1} (to the right)
- sp^2 C-H, just above 3000 cm^{-1} (to the left)
- sp C-H, at 3300 cm^{-1}

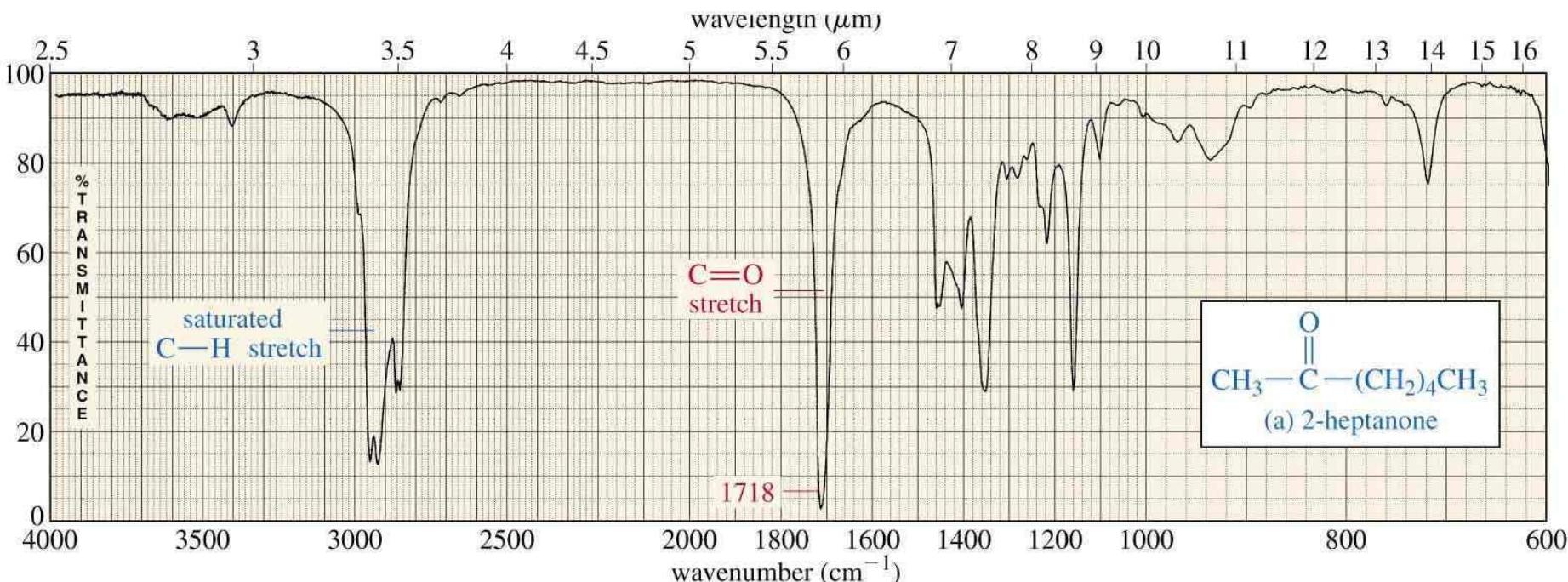


Alkene & Alkyne IR Spectrum

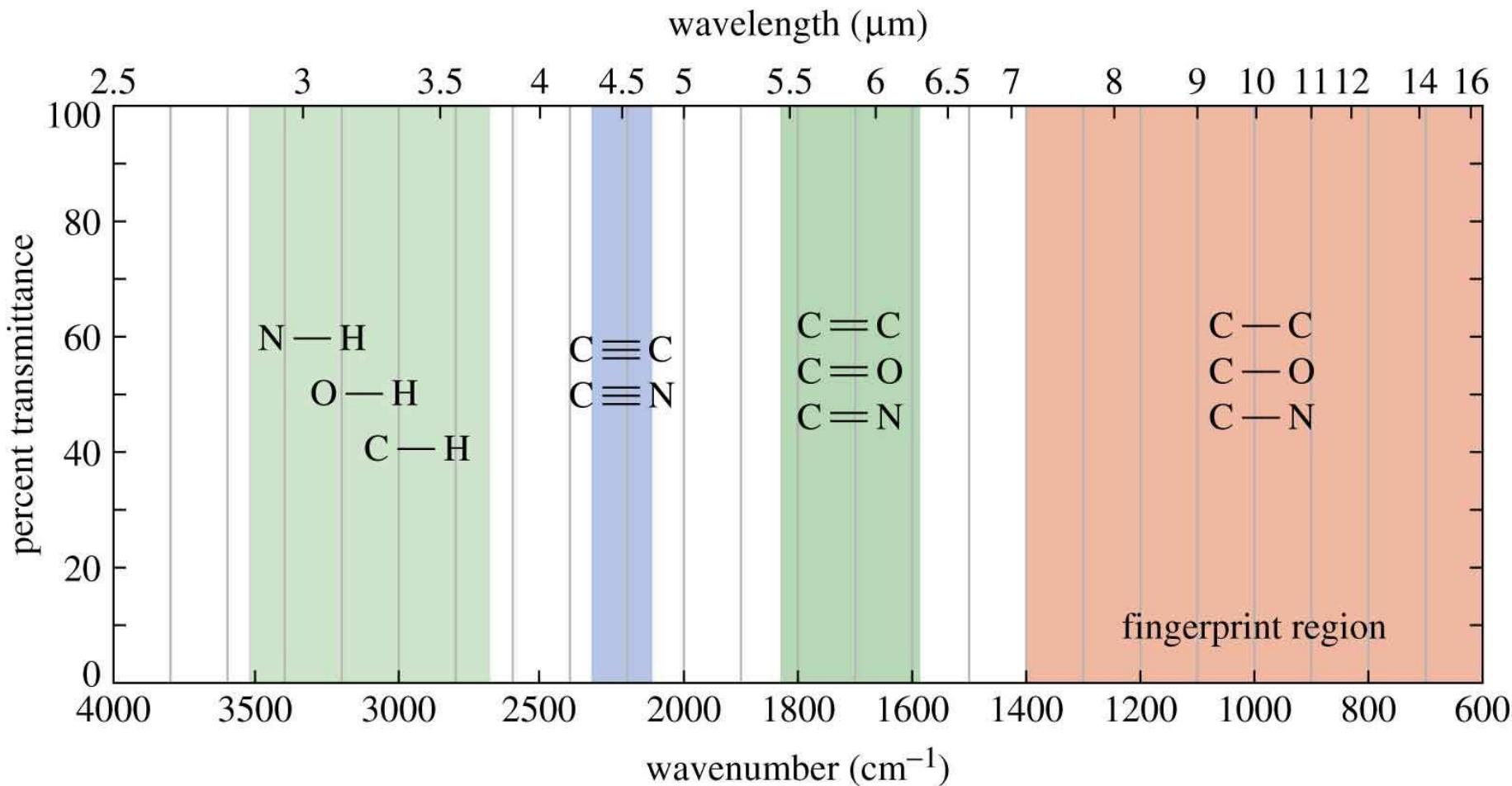


Carbonyl Stretching

- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1} .
- Usually, it's the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1} .



Summary of IR Absorptions



Alcohol and amine peaks are broad at around 3300-3500

Strengths and Limitations

- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

Nuclear Magnetic Resonance Spectroscopy

- NMR is one of the most powerful tool available for organic structure determination.
- It is used to study a wide variety of nuclei:
 - ^1H
 - ^{13}C
 - ^{15}N
 - ^{19}F
 - ^{31}P

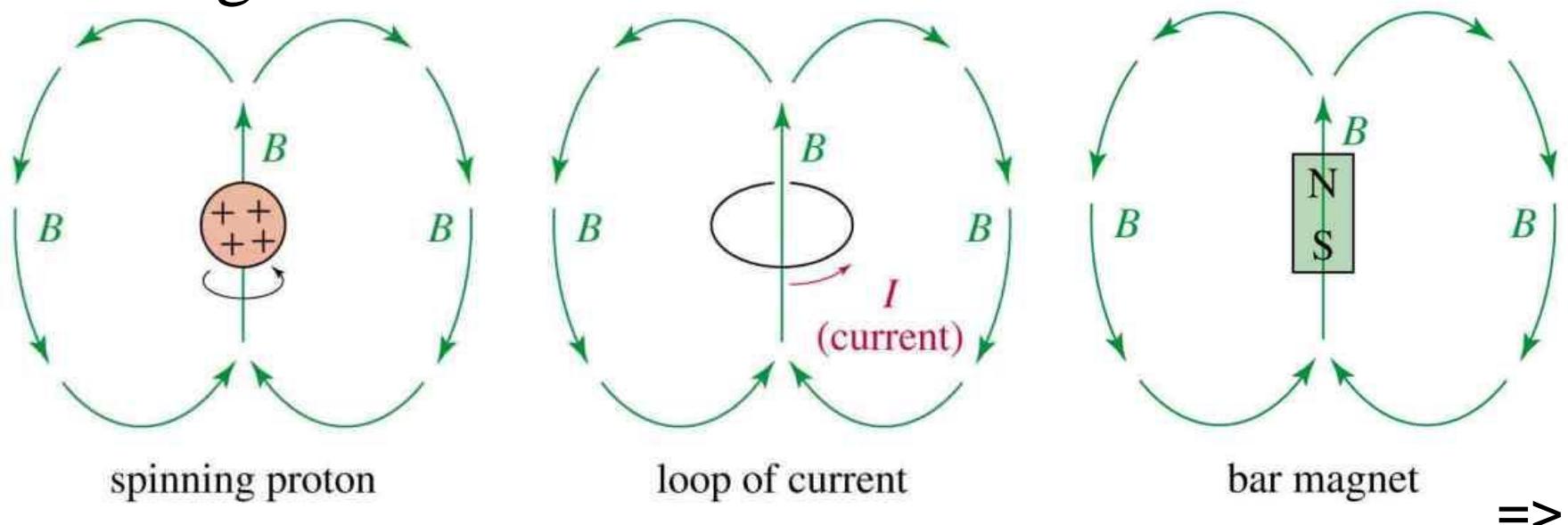


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Magnetic shielding of nucleus by surrounding electron cloud

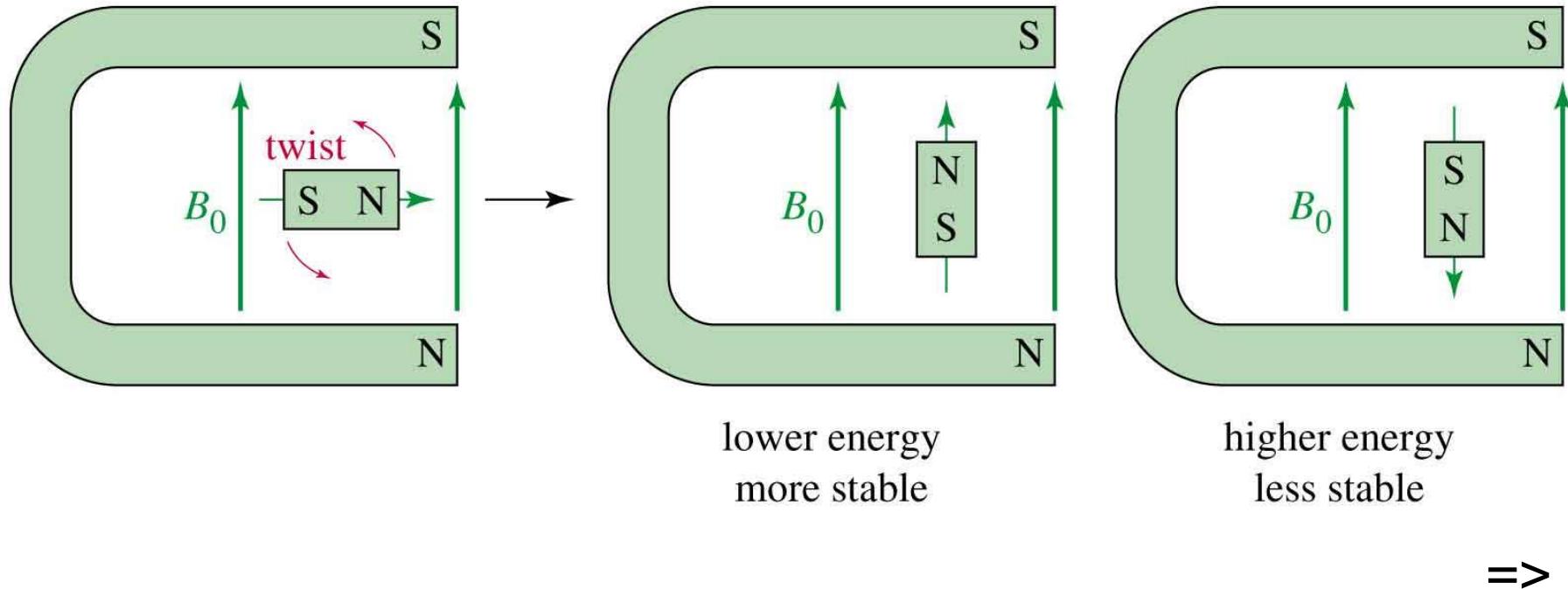
Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.



External Magnetic Field

When placed in an external field, spinning protons act like bar magnets.

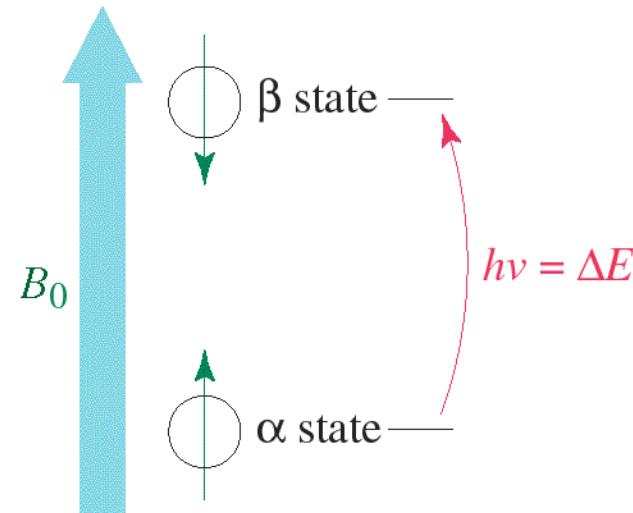


Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.

- Energy difference is proportional to the magnetic field strength.
- $\Delta E \propto B_0$

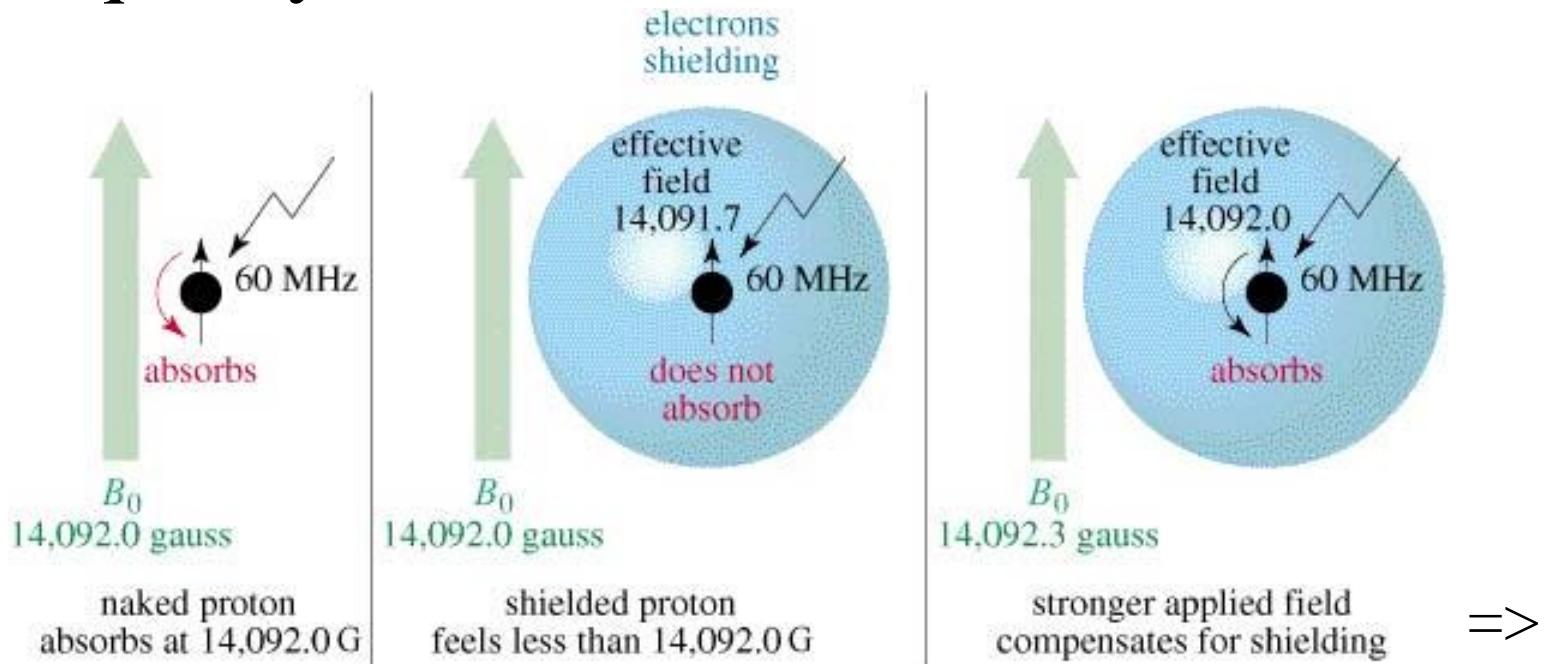


Magnetic Shielding

- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.

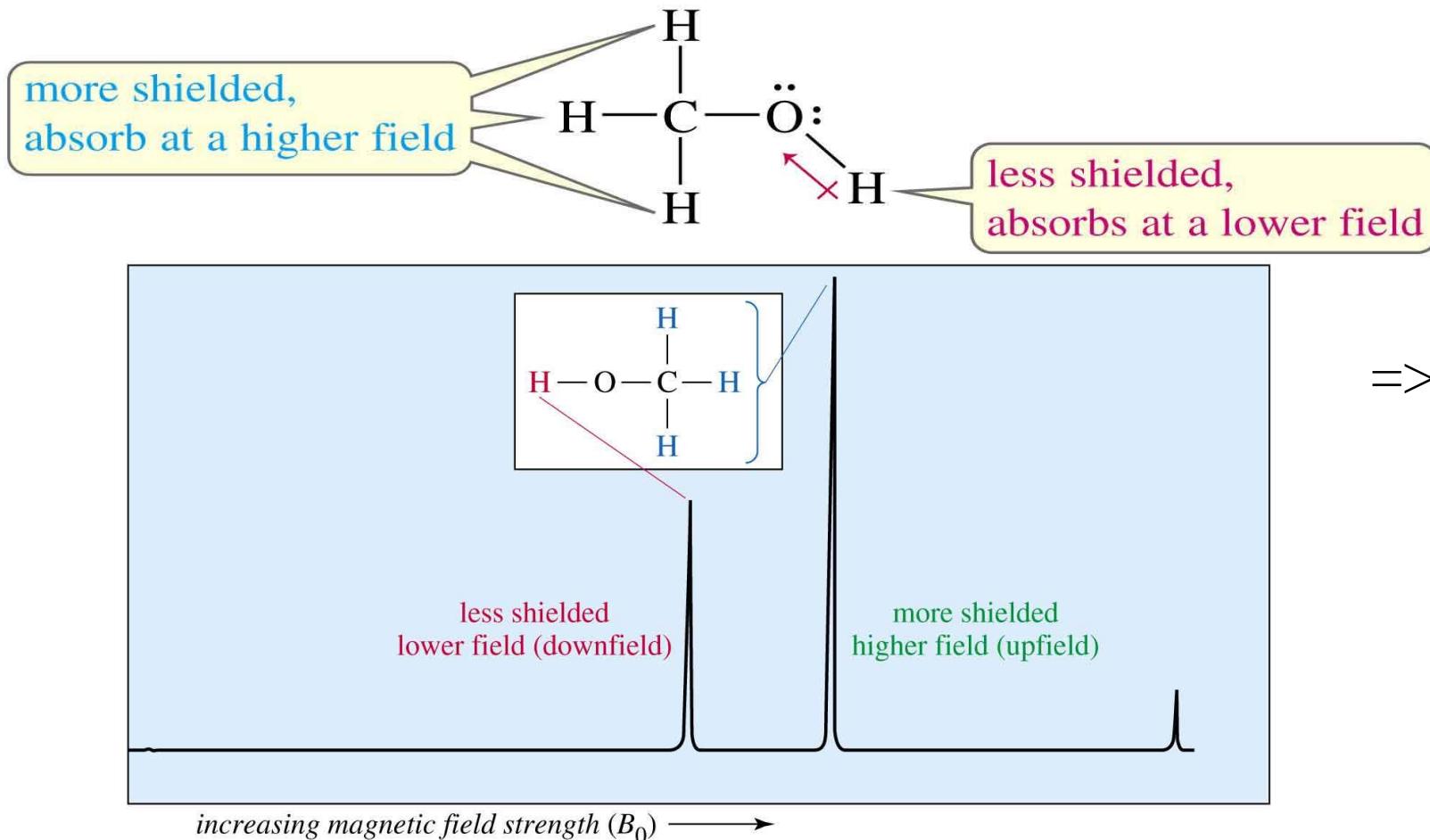
Shielded Protons

Magnetic field strength must be increased for a shielded proton to flip at the same frequency.



Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.





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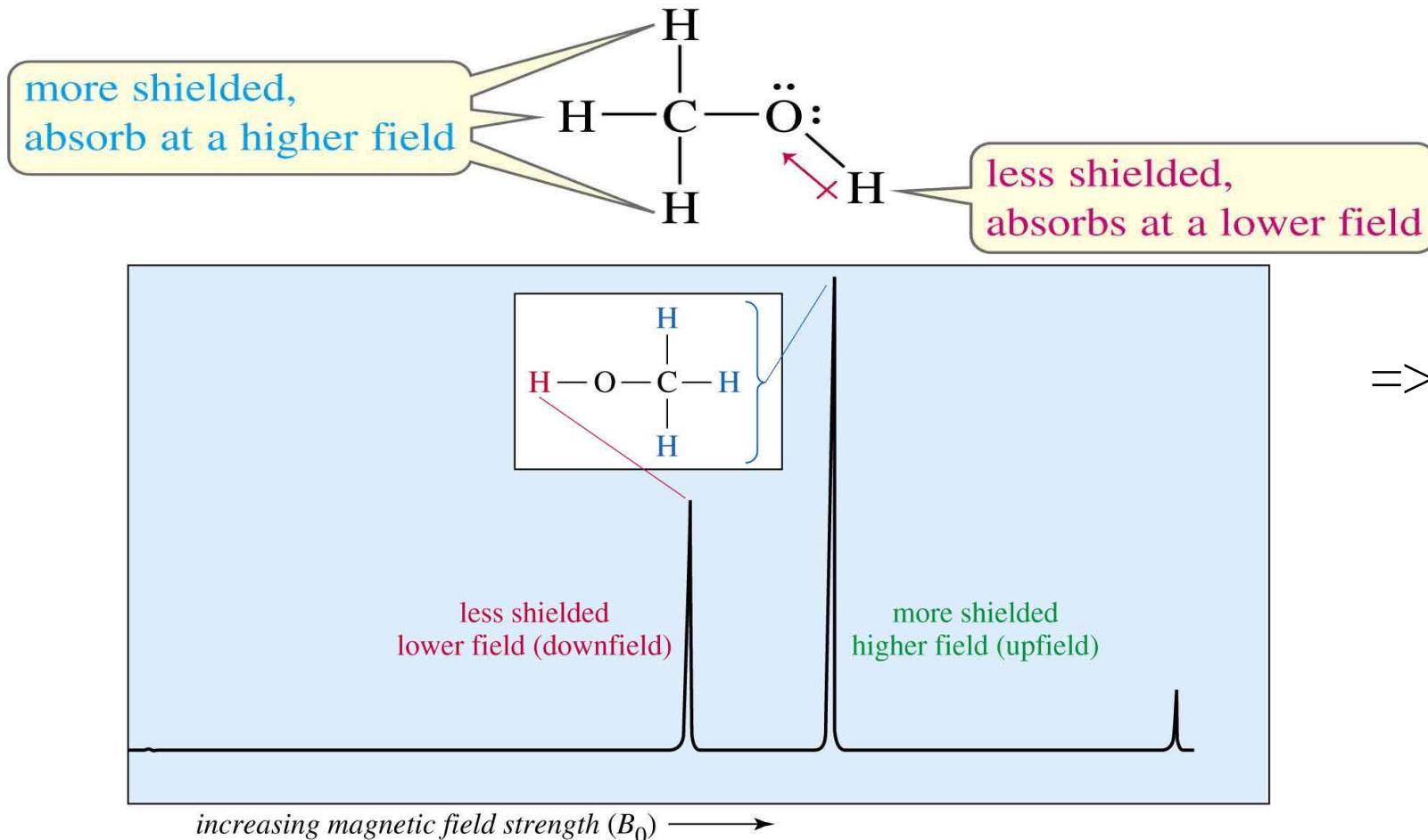
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Protons in a Molecule

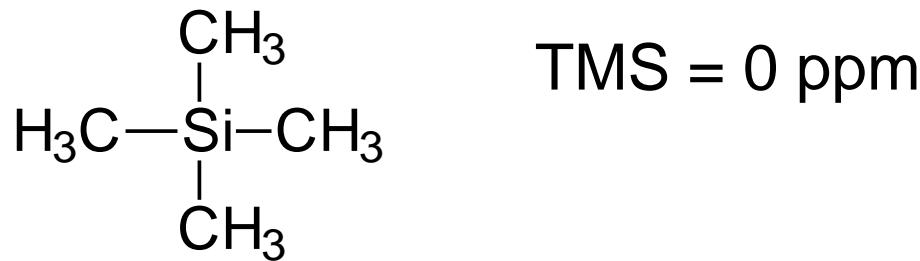
Depending on their chemical environment, protons in a molecule are shielded by different amounts.



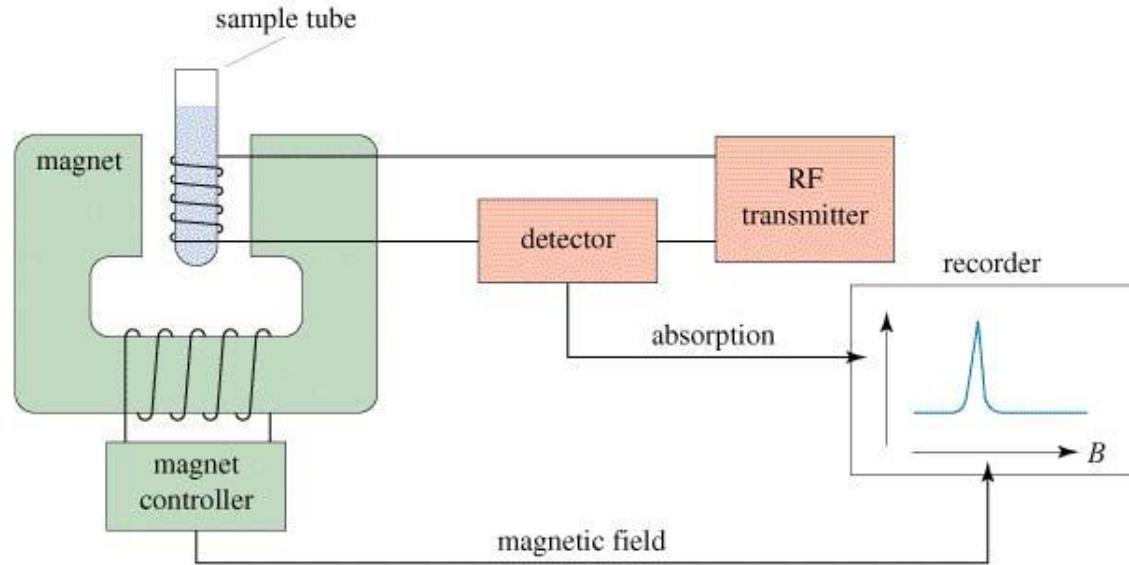
NMR Signals

- The *number* of signals shows how many different kinds of protons are present.
- The *location* of the signals shows how shielded or deshielded the proton is.
- The *intensity* of the signal shows the number of protons of that type.
- Signal *splitting* shows the number of protons on adjacent atoms.

Organic protons absorb downfield (to the left) of the TMS signal.



The NMR Spectrometer



Chemical Shift: Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz).

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Location of Signals

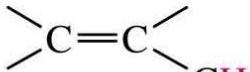
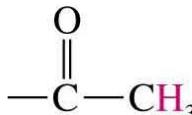
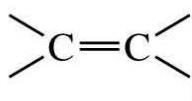
Compound	Chemical Shift	Difference
CH_3H	$\delta 0.2$	
CH_2Cl	$\delta 3.0$	2.8 ppm
CHCl_2	$\delta 5.3$	2.3 ppm
CCl_3	$\delta 7.2$	1.9 ppm

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- More electronegative atoms deshield more and give larger shift values.
- Effect decreases with distance.
- Additional electronegative atoms cause increase in chemical shift.

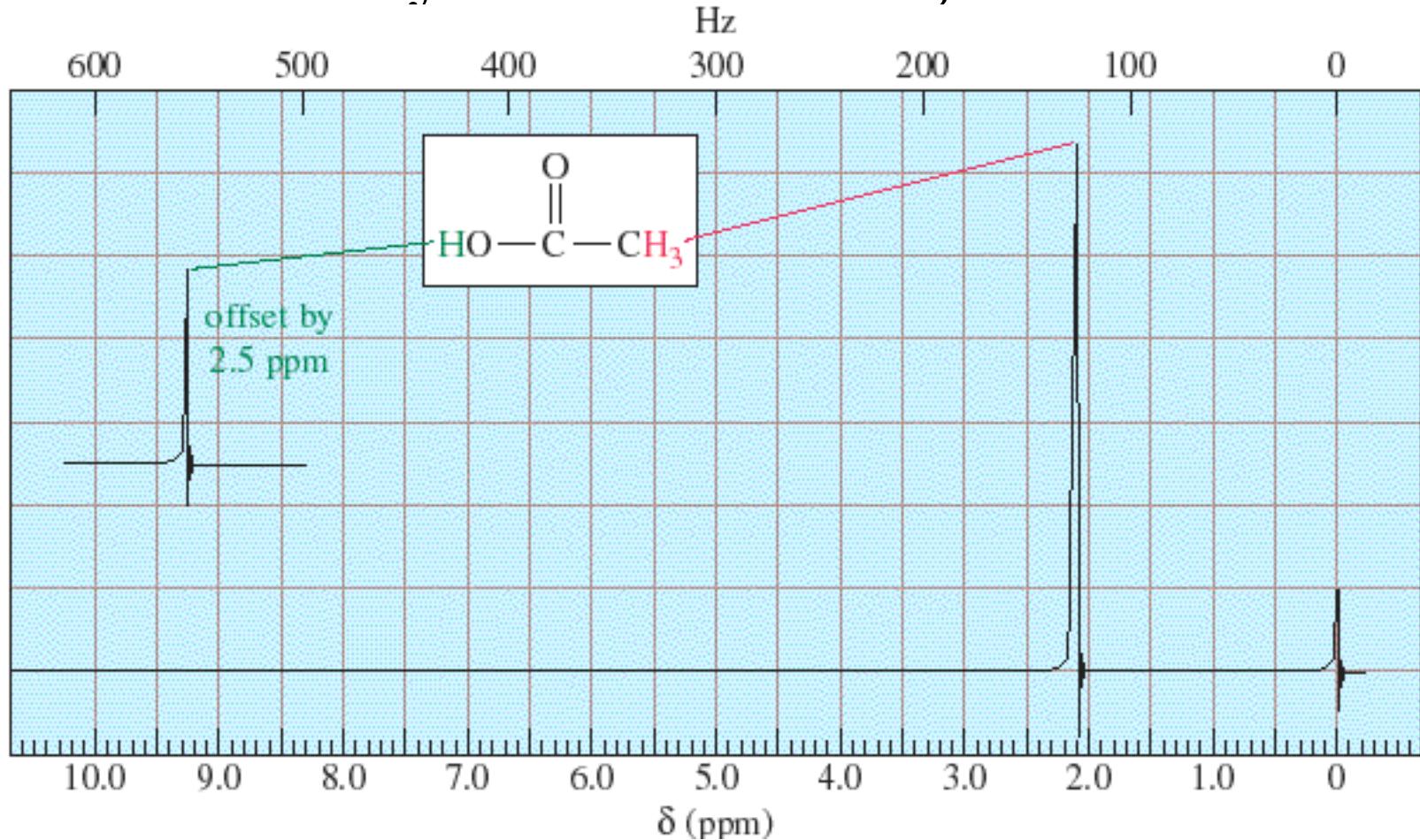
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Typical Values

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-\text{CH}_3$)	0.9		1.7
alkane ($-\text{CH}_2-$)	1.3	$\text{Ph}-\text{H}$	7.2
alkane ($-\overset{\text{H}}{\underset{ }{\text{C}}}-$)	1.4	$\text{Ph}-\text{CH}_3$	2.3
	2.1	$\text{R}-\text{CHO}$	9–10
$-\text{C}\equiv\text{C}-\text{H}$	2.5	$\text{R}-\text{COOH}$	10–12
$\text{R}-\text{CH}_2-\text{X}$ (X = halogen, O)	3–4	$\text{R}-\text{OH}$	variable, about 2–5
	5–6	$\text{Ar}-\text{OH}$	variable, about 4–7
		$\text{R}-\text{NH}_2$	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

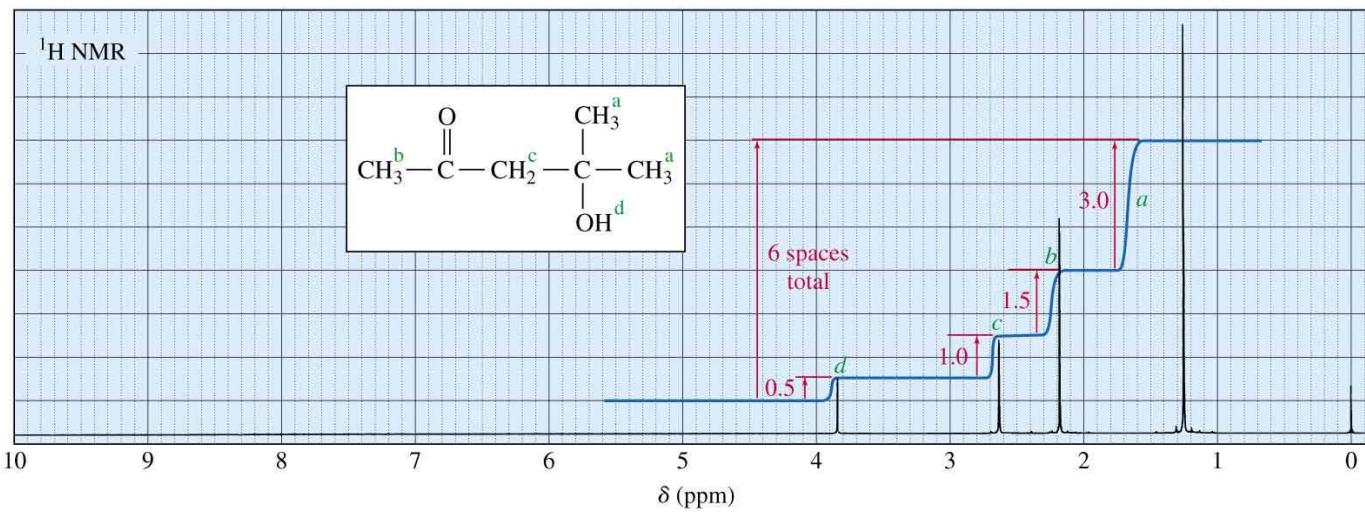
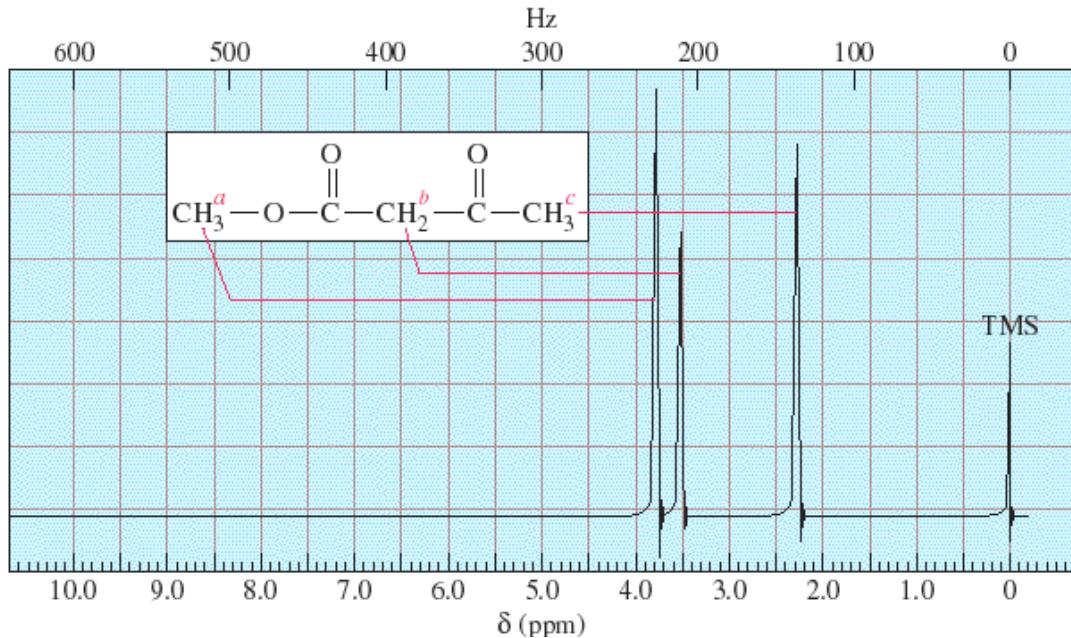
Carboxylic Acid Proton, δ 10+



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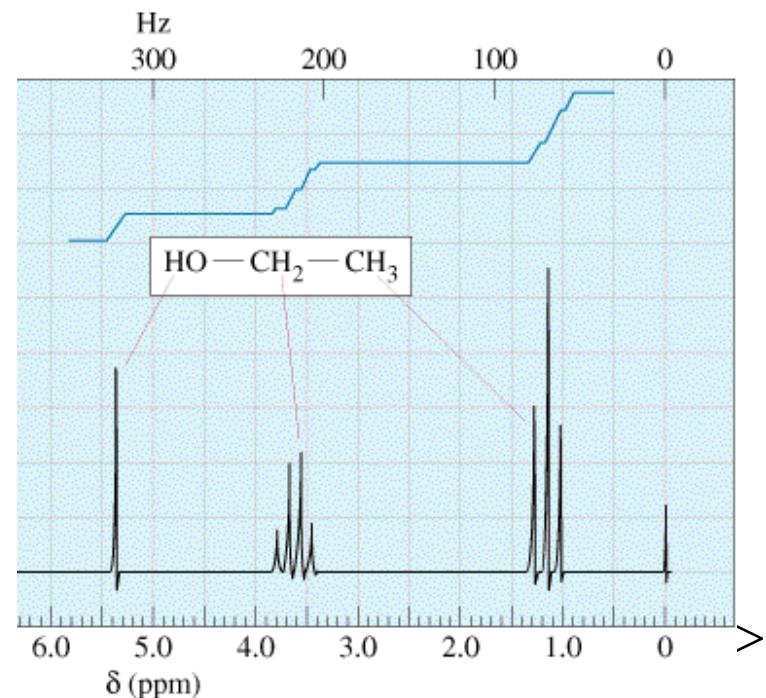
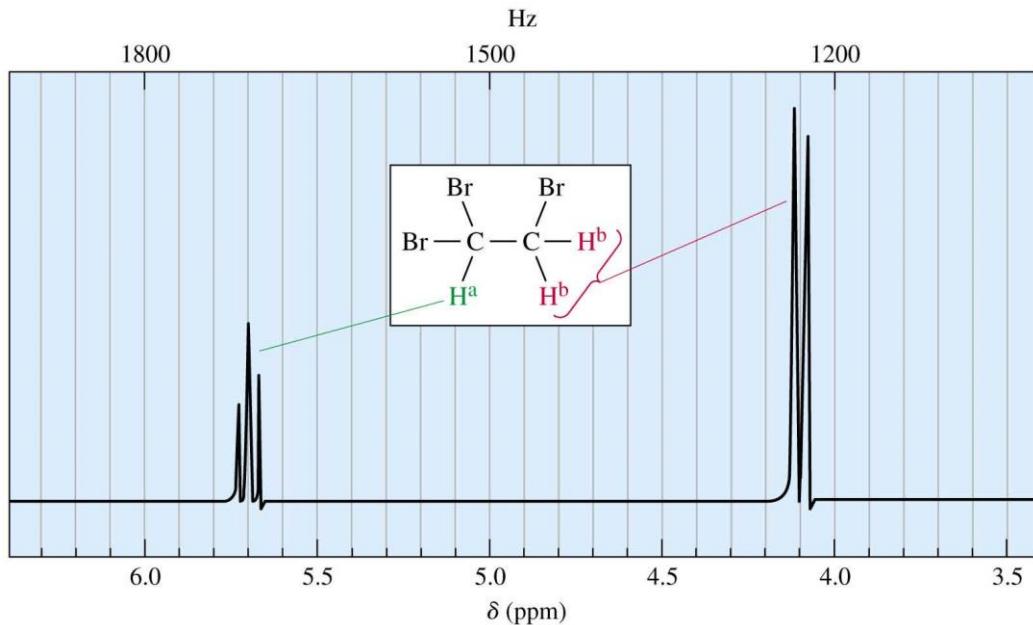
Number of Signals

Equivalent hydrogens have the same chemical shift.



1,1,2-Tribromoethane

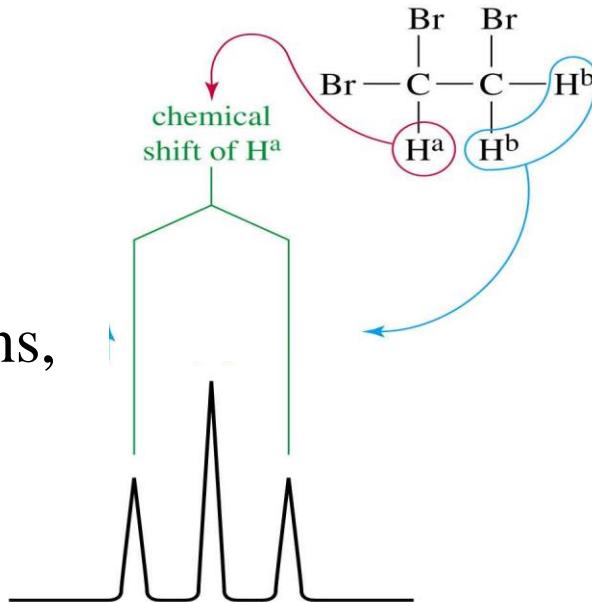
Nonequivalent protons on adjacent carbons.



Ethanol

The $N + 1$ Rule

If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.



Relative Peak Intensities of Symmetric Multiplets

<i>Number of Equivalent Protons Causing Splitting</i>	<i>Number of Peaks (multiplicity)</i>	<i>Area Ratios (Pascal's triangle)</i>
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

Green Chemical Processes

Sustainability: **GOAL**

Meeting the needs of the present generation without
compromising the needs of future generations

Green Chemistry: is the means

Technologies that are energy efficient,minimise or preferably
eliminate the formation of waste,avoid the use of toxic and/or
hazardous solvents and reagents and, where possible,utilise
renewable raw materials.

GREEN CHEMISTRY IS ABOUT

- Waste Minimisation at Source
- Use of Catalysts in place of Reagents
- Using Non-Toxic Reagents
- Use of Renewable Resources
- Improved Atom Efficiency
- Use of Solvent Free or Recyclable Environmentally Benign Solvent systems



The E Factor

Is the **actual** amount of waste formed in the process, including solvent losses, acids and bases used in work-up,process aids, and,in principle,waste from energy production

$$E = [\text{raw materials}-\text{product}]/\text{product}$$

Amount of waste/kg product:

	Product tonnage	E Factor
– Bulk Chemicals	10^4 - 10^6	<1 - 5
– Fine chemical Industry	10^2 - 10^4	5 - >50
– Pharmaceutical Industry	10 - 10^3	25 - >100