INDIAN INSTITUTE OF TECHNOLOGY PATNA DEPARTMENT OF CHEMISTRY

CH 103

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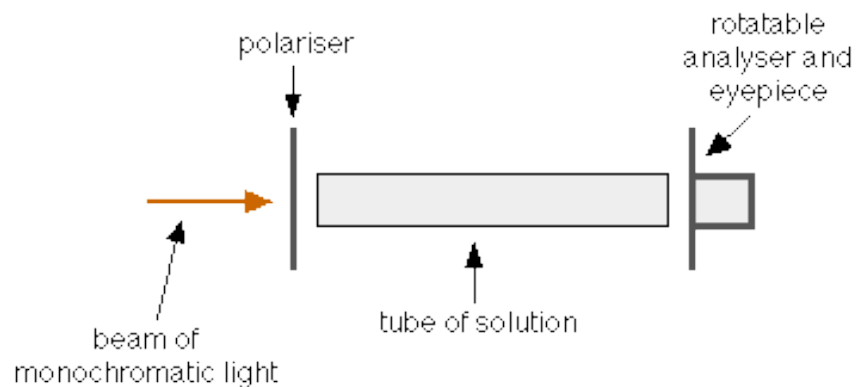**Email: neeladri@iitp.ac.in**

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

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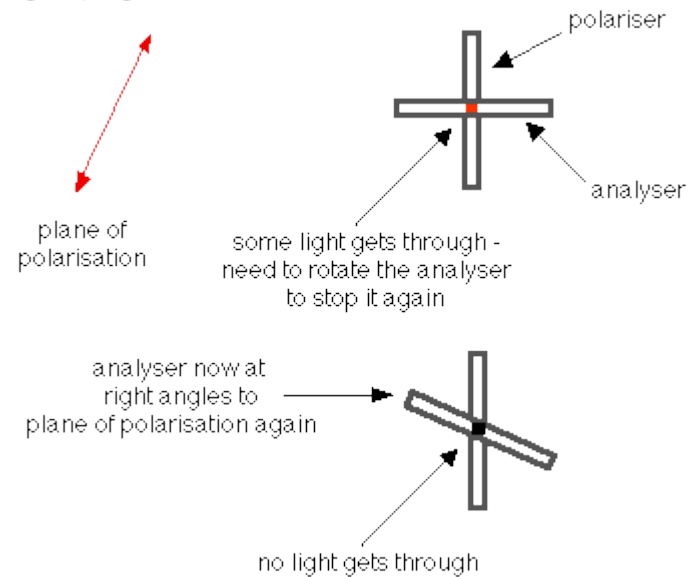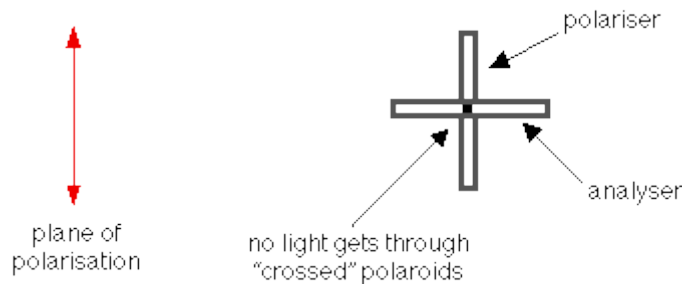
- **Use a polarimeter**

- 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".**

plane of polarisation

no light gets through "crossed" polaroids

polariser

analyser

plane of polarisation

some light gets through - need to rotate the analyser to stop it again

polariser

analyser

analyser now at right angles to plane of polarisation again
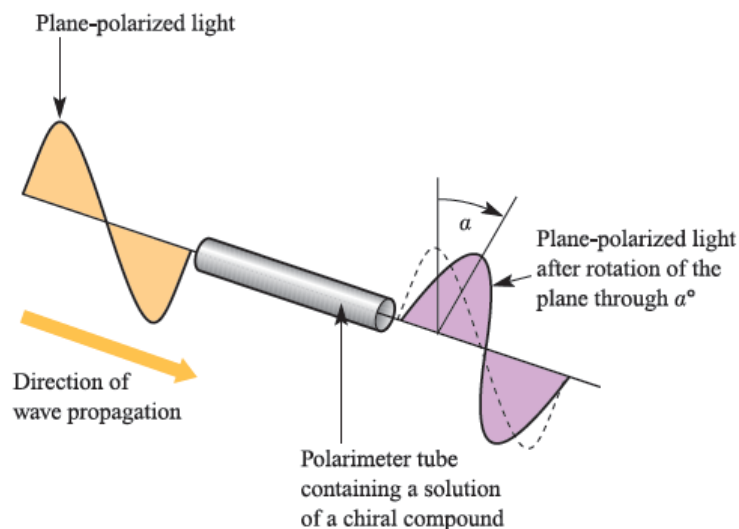
no light gets through

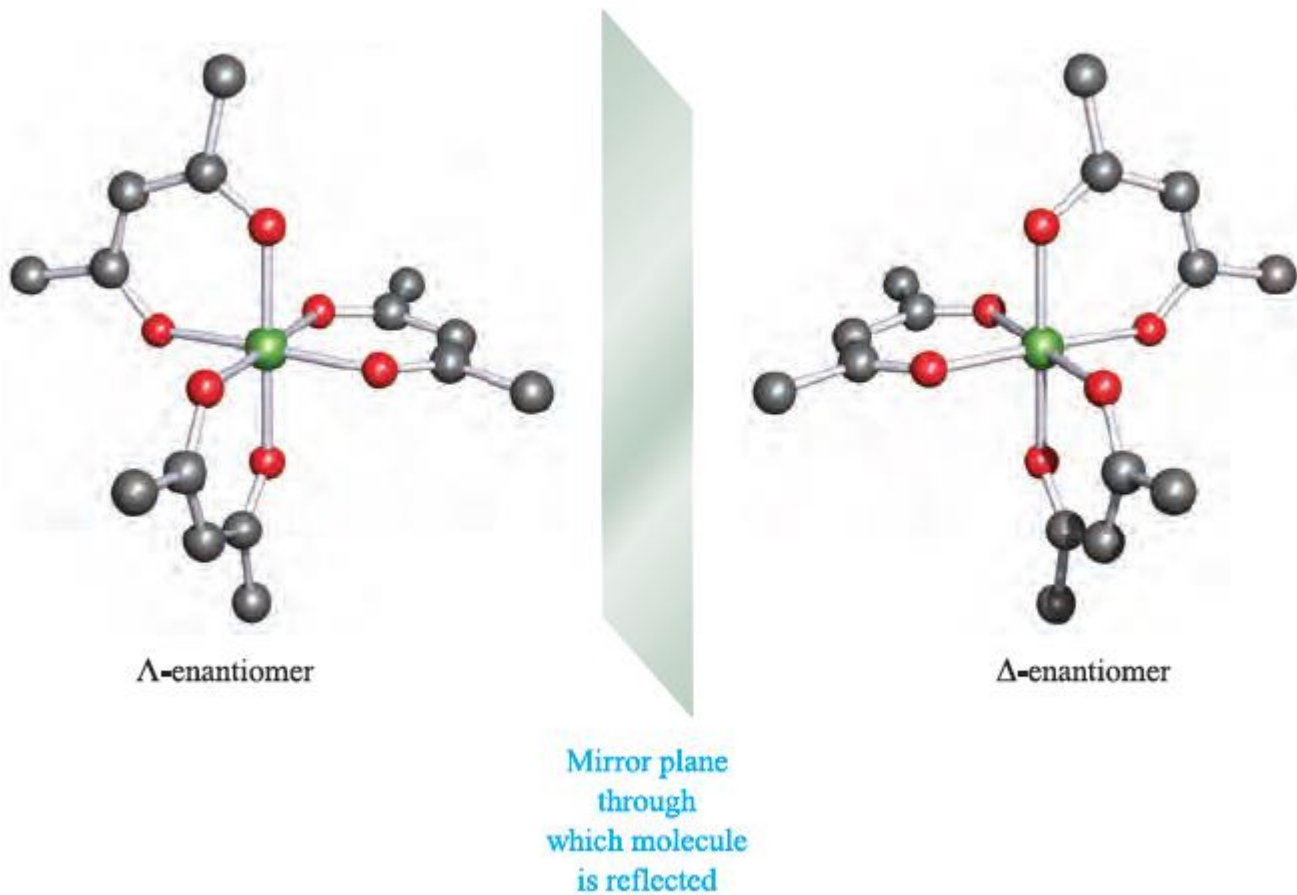Now you put a solution of an optically active substance into the tube.

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.
- **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.

Plane-polarized light

Plane-polarized light after rotation of the plane through a°

Direction of wave propagation

Polarimeter tube containing a solution of a chiral compound

[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

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

- α = observed rotation, l = path length of solution in the polarimeter (in dm) and c = concentration (in g/cm^3).
- **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° 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.

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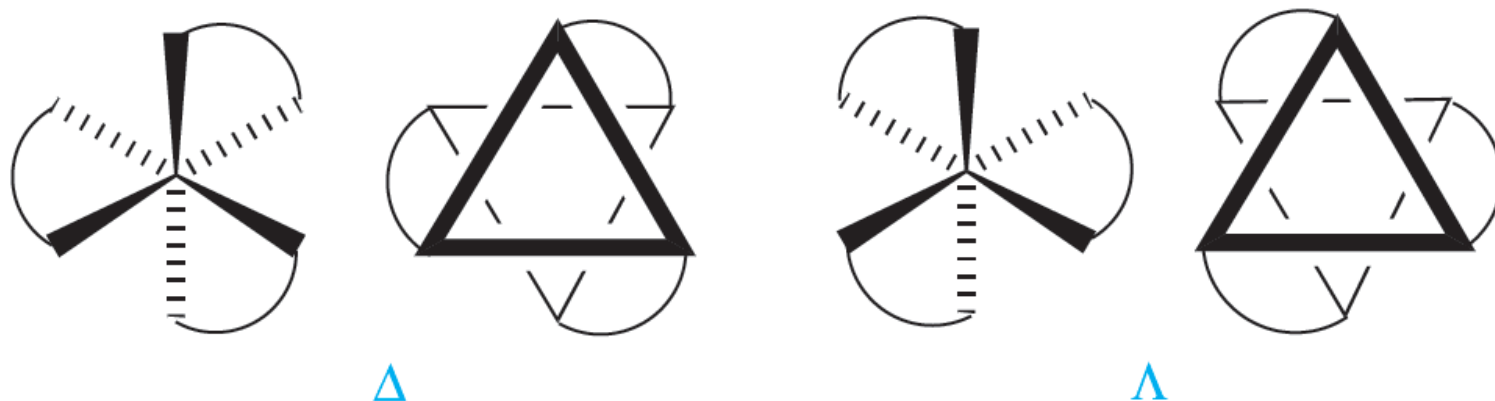
- The octahedron is viewed down a three-fold axis, and the chelates then define either a right- or left-handed helix.

- The enantiomer with right-handedness is labelled Δ , and that with left-handedness is Λ.

right- or left-handedness of a helix

Δ   Λ
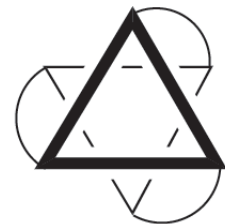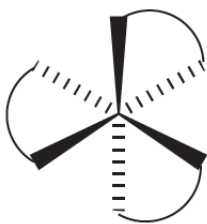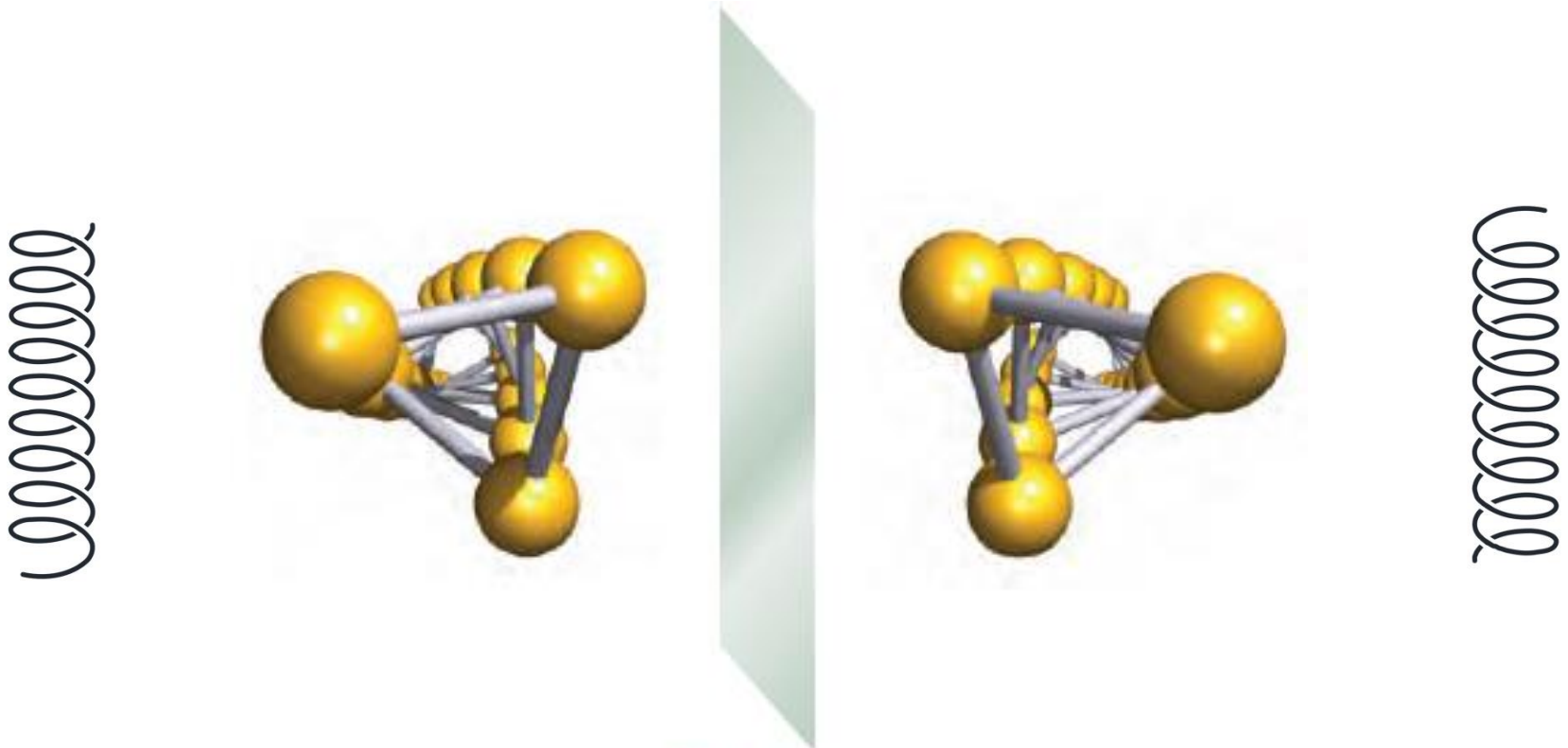
optical isomers
tris-chelate complexes.

- The simplest case of optical isomerism among d-block complexes involves a metal ion surrounded by three didentate ligands

- $[Cr(acac)_3]$ or $[Co(en)_3]^{3+}$.

- Pairs of enantiomers such as Δ and Λ $[Cr(acac)_3]$ 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 $[Co(en)_3]^{3+}$, 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 {Δ·(+)} and {Λ·(—)} is enantiomeric as is the pair {Δ·(—)} and {Λ ·(+)} .

- However, with a given anion chirality, the pair of salts {Δ·(—)} and {Λ·(—)} 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