



Optical Rotatory Dispersion and Circular Dichroism

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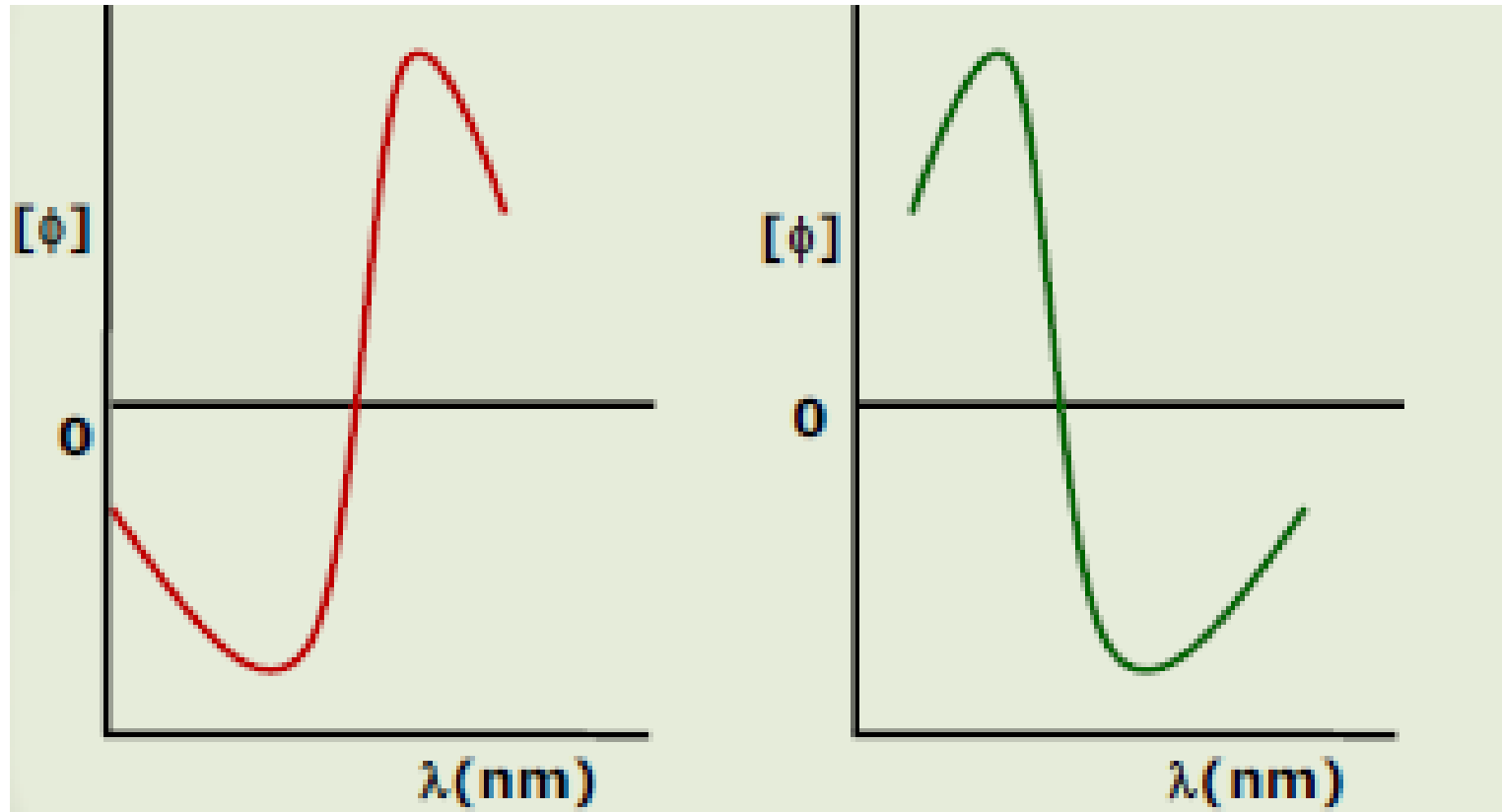
Spectroscopic Methods for determination of Absolute Configuration of Coordination Complexes

As we are aware that lowest d-d transitions in the hexaminecobalt(III) complex is $1A_{1g} \rightarrow 1T_{1g}$. Thus, for the complex $[\text{Co}(\text{en})_3]^{3+}$, a very similar electronic transition and visible spectrum will be observed. There are two spectroscopic methods for the determination of the absolute configuration. (i) Optical Rotatory Dispersion (ORD) (ii) Circular Dichroism (CD) These methods depend on the behavior of polarized light passing through a solution (usually) of the optically active compound. The results have to be interpreted by comparison with a similar compound of known absolute configuration.

Assignment of Absolute Configuration using ORD

Optical Rotatory Dispersion (ORD) involves measuring the variation of optical rotation with wavelength. There is abrupt reversal of rotation in the vicinity of absorption band. If the complex is **levorotatory**, the ORD curve falls to a minimum, rises rapidly to a maximum and then slowly falls. If the complex is **dextrorotatory**, the effect is reversed for the ORD curve rising first to a maximum, then falling etc. These represent **positive and negative Cotton effects**.

Assignment of Absolute Configuration using ORD



Laevorotatory

Positive Cotton Effect Curve

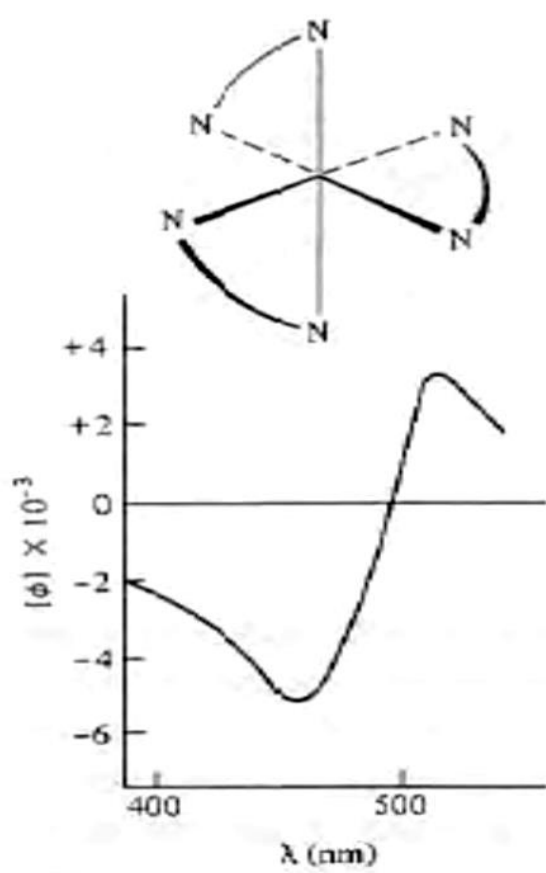
Dextrorotatory

Negative Cotton Effect Curve

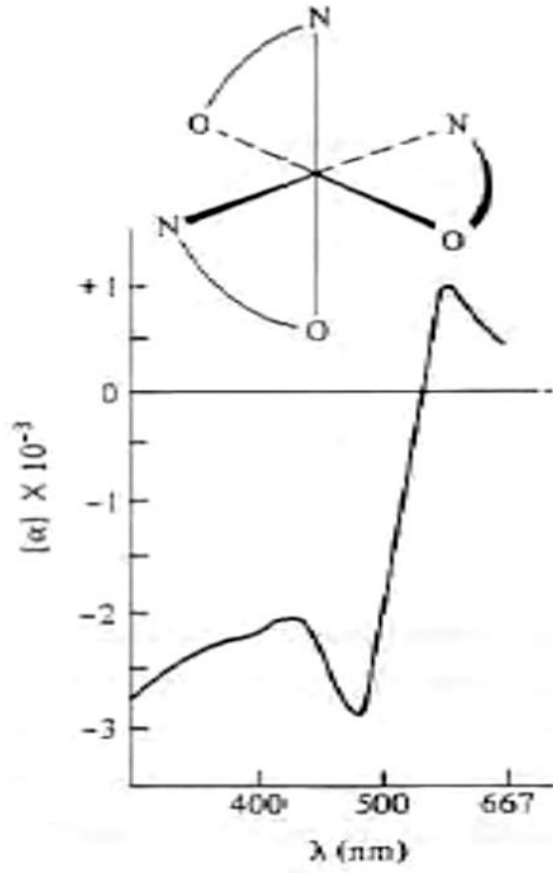
Assignment of Absolute Configuration using ORD

ORD curves are useful in the assignment of the absolute configurations. For example, configurations of the enantiomers of tris(ethylenediamine)cobalt(III), tris(alaninato)cobalt(III) and bis(ethylenediamine)glutamatocobalt(III) are known from X-ray diffraction technique. It is found that three Λ -(+)-enantiomers or Λ -(D)-enantiomers of these complexes have similar ORD spectra. On the basis of Λ -configuration, these complexes can be assigned to any known configuration in the absence of X-ray data simply on the basis of the similarity of ORD spectra.

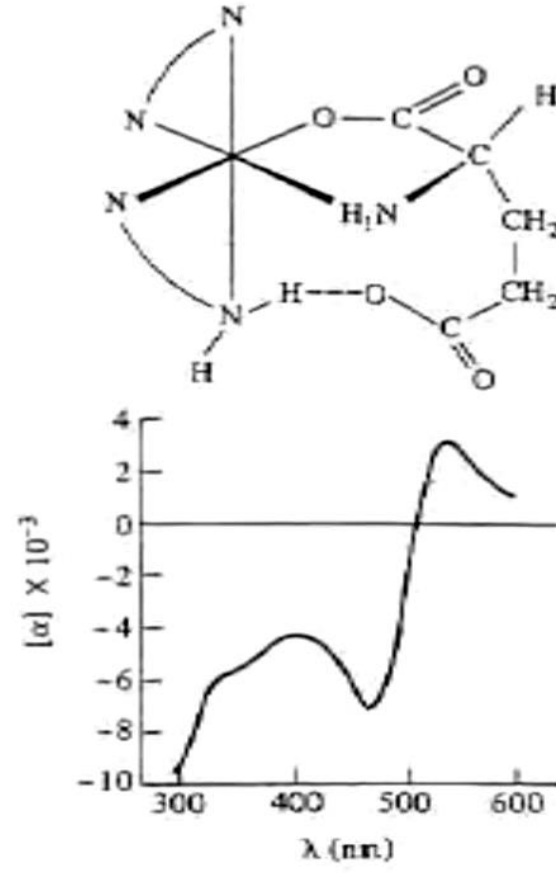
Assignment of Absolute Configuration using ORD



(a)



(b)



(c)

Assignment of Absolute Configuration using ORD

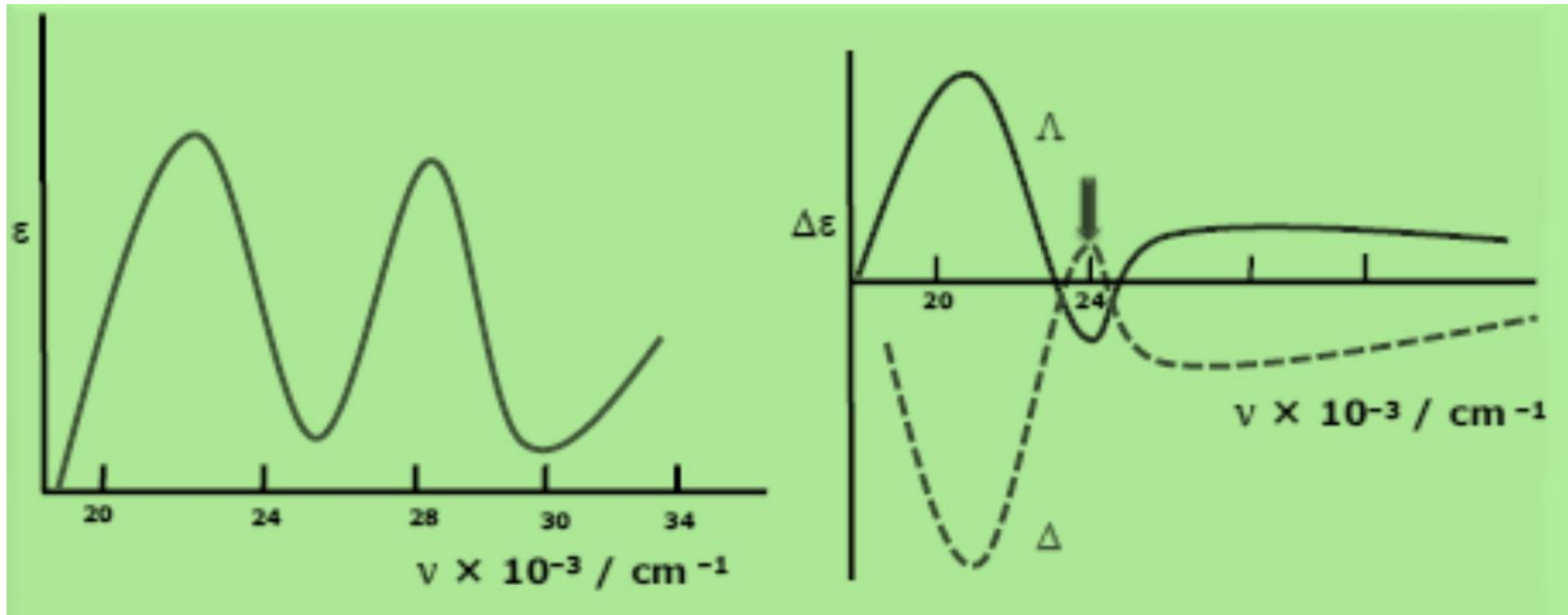
For ORD spectrum to be instantly recognizable, no other absorption must be nearby. The ORD spectra of Λ -[Co(en)₃]³⁺, Λ -[Co(S-ala)₃]³⁺, and Λ -[Co(en)₂(S-glu)]³⁺ are shown in figure. All these complexes represent positive Cotton effect. (Where en refers to ethylenediamine, S-ala refers to the anion of S-(L)-alanine and S-glu refers to the dianion of S-(L)-glutamic acid. All of these complexes have the Λ or D configuration.)

Assignment of Absolute Configuration using Circular Dichroism (CD)

The **circular dichroism (CD)** refers to differential absorption of left and right circularly polarized light, $\epsilon_L - \epsilon_R$.

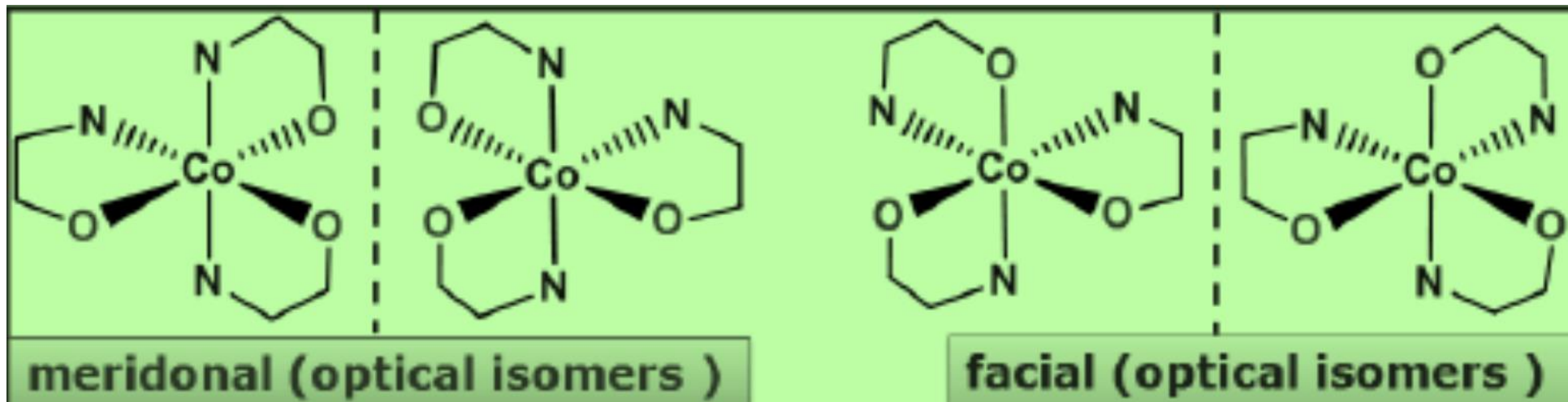
Complexes having same sign of CD for a given absorption band will have the same absolute configuration. The absolute configuration of $[\text{Co}(\text{en})_3]^{3+}$ had to be determined first for assignment of the absolute configuration of other related complexes. The CD spectrum of $[\text{Co}(\text{en})_3]^{3+}$ suggest that Λ - $[\text{Co}(\text{en})_3]^{3+}$ isomer shows **positive deflections**, however Δ - $[\text{Co}(\text{en})_3]^{3+}$ isomer shows **negative deflections** in CD spectrum which also corresponds to the sign of Cotton effect. The CD spectrum of $[\text{Co}(\text{en})_3]^{3+}$ also shows the presence of another absorption band at $\sim 24 \times 10^{-3}$ that is not obvious from the absorption spectrum.

Assignment of Absolute Configuration using Circular Dichroism (CD)



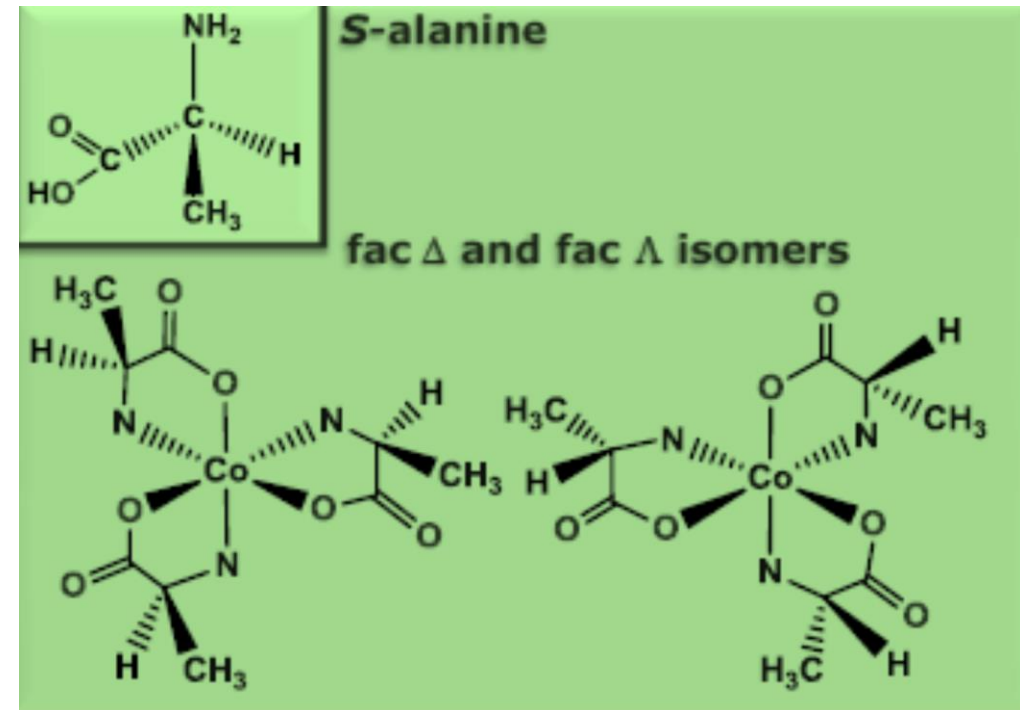
Assignment of Absolute Configuration using Circular Dichroism (CD)

Tris(aminoacido)cobalt complexes were prepared using amino acids. CD spectra of these complexes illustrate the application of circular dichroism for the determination of configuration. If three glycinate ligands are bound to a metal ion, two diastereomers: *fac* and *mer* are possible and each of these will have an enantiomer.



Assignment of Absolute Configuration using Circular Dichroism (CD)

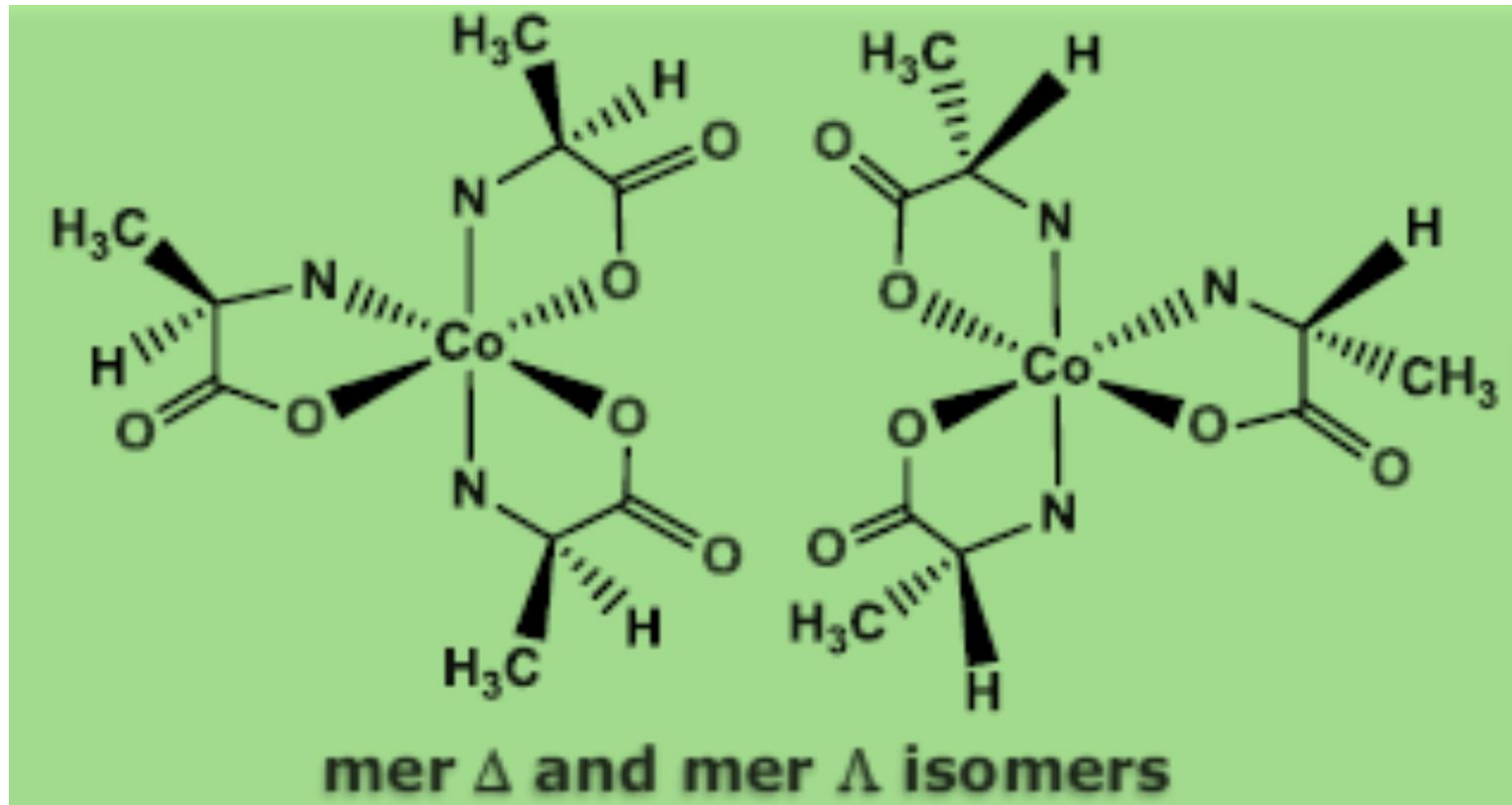
However, if a substituted amino acid such as alanine (R-alanine or S-alanine) is used, complex can still exist as two geometrical isomers both of which are chiral, i.e. *fac* and *mer*. The arrangement of ligands about metal ion can result in Λ or Δ chirality. However, right-handed *fac* isomer is not enantiomeric with the left-handed *fac* isomer. For example, the use of S-alanine can give the *fac* Λ isomer.



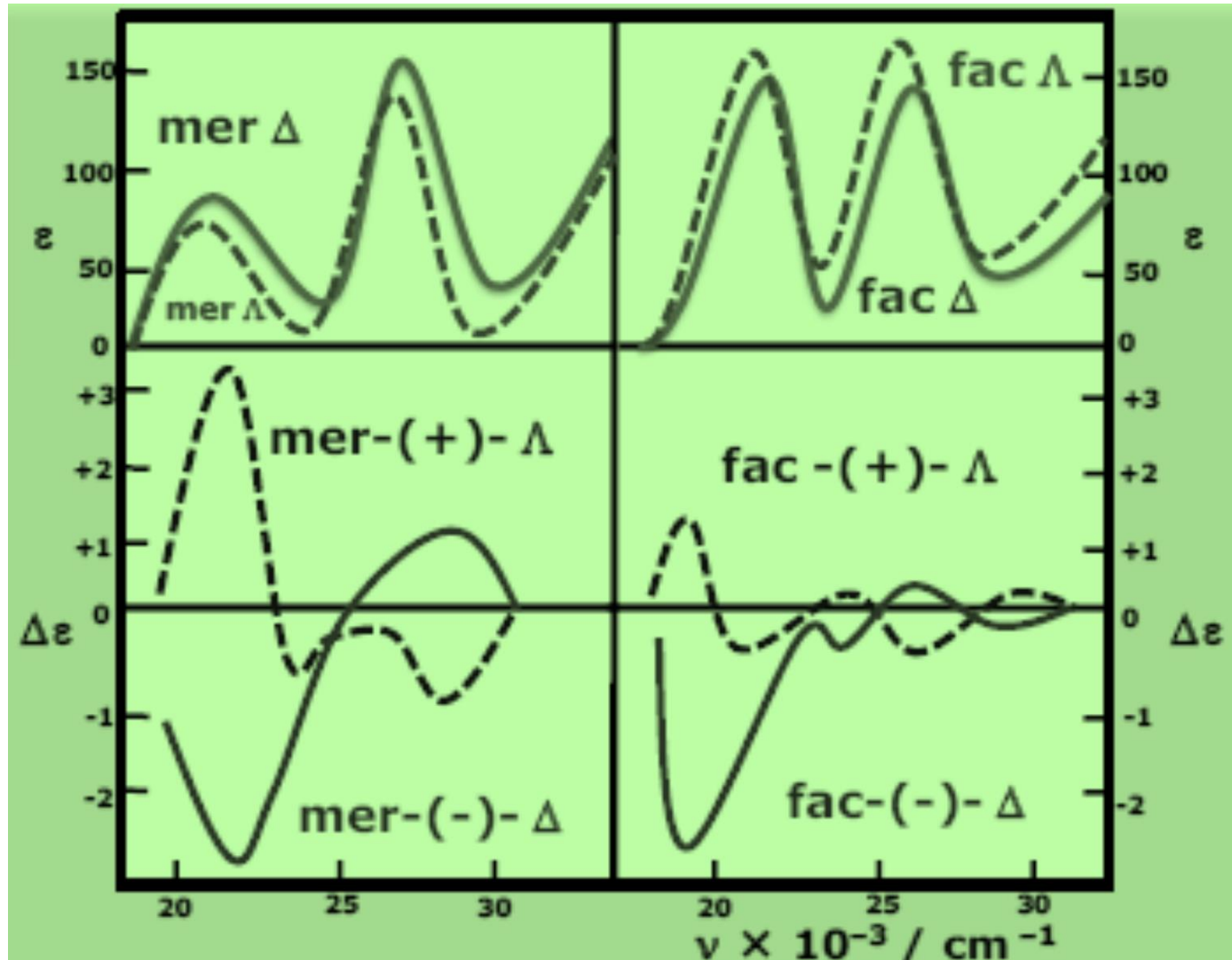
Assignment of Absolute Configuration using Circular Dichroism (CD)

A mirror image of this compound cannot be generated with S-alanine because the enantiomer necessarily contains R-alanine. Therefore, *fac* Δ isomer is a diastereomer of *fac* Λ . This is the same case with *mer* isomers. The net result is that, if glycine is used while *fac* and *mer* isomers have an enantiomeric partner, however, an optically active amino acid will give a diastereoisomer for each chirality of each *fac* or *mer* isomer. All the four isomers shown in figures are diastereomers, easily separable from one another under achiral conditions. Each one of them is having different physical properties.

Assignment of Absolute Configuration using Circular Dichroism (CD)



Assignment of Absolute Configuration using Circular Dichroism (CD)



Assignment of Absolute Configuration using Circular Dichroism (CD)

The *fac* and *mer* isomers show distinct spectroscopic properties from one another. The *fac* isomers give rise to similar UV-visible spectra; similarly *mer* isomers also give similar UV-visible spectra.

The absolute configuration of the optically pure alanine complexes can be assigned by comparing their CD spectra to those for optically pure $[\text{Co}(\text{en})_3]^{3+}$. The absorption and CD spectra for the four diastereomers of $[\text{Co}(\text{S-alaninate})_3]$ are shown in figure. The sign of the Cotton effect for the lowest energy CD band of the *fac*-(+) and *mer*-(+) isomers is positive just as it is for Λ -(+)- $[\text{Co}(\text{en})_3]^{3+}$. This result strongly suggests that these complexes have the same absolute configuration, Λ .

Assignment of Absolute Configuration using Circular Dichroism (CD)

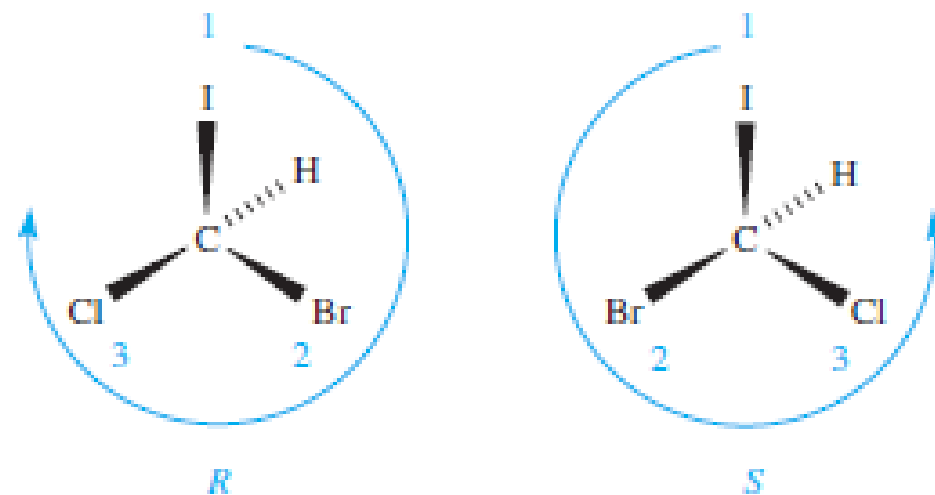
The negative sign of the Cotton effect for the lowest energy CD band of the *fac*-(-) and *mer*-(-) isomers suggests that they have an absolute configuration opposite to that for the (+)- isomers. This result suggests that these complexes have the same absolute configuration, Δ .

It should be noted that CD curves for the (+) and (-) isomers are not exactly mirror images of one another. This is due to the fact that, while complexes have opposite absolute configurations based on the positioning of chelate rings, they are in fact diastereomers as mentioned above, this arises because only S-alaninate was used as a ligand.

| Formula of complex ^b | ν (cm ⁻¹) | $\epsilon_1 - \epsilon_r$ | Absolute configuration |
|--|---------------------------|---------------------------|------------------------|
| (+) ₅₈₉ -[Co(en) ₃] ³⁺ | 20,280 | +2.18 | Λ |
| | 23,310 | -0.20 | |
| (-) ₅₈₉ -[Co(en) ₃] ³⁺ | 20,280 | -2.18 | Δ^c |
| | 23,310 | +0.20 | |
| (+) ₅₈₉ -[Co(<i>S</i> -pn) ₃] ³⁺ | 20,280 | +1.95 | Λ |
| | 22,780 | -0.58 | |
| (+) ₅₈₉ -[Co(<i>R</i> -pn) ₃] ³⁺ | 21,000 | +2.47 | Λ |
| (+) ₅₈₉ -[Co(<i>S</i> -ala) ₃] | 18,500 | +1.3 | Λ |
| | 21,000 | -0.2 | |
| (+) ₄₉₅ -[Co(<i>S</i> -glu)(en) ₂] ²⁺ | 19,600 | +2.5 | Λ |

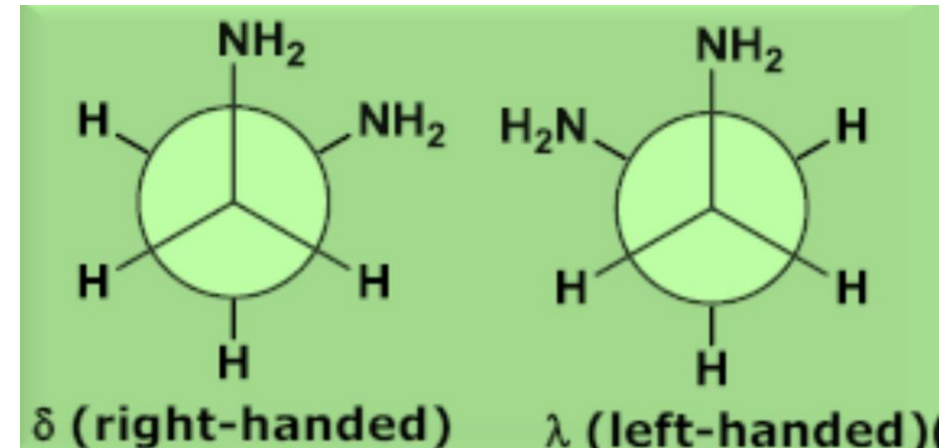
R and S prefixes:

The convention for labelling chiral carbon atoms (tetrahedral with four different groups attached) uses the Cahn–Ingold–Prelog notation. The four groups attached to the chiral carbon atom are prioritized according to the atomic number of the attached atoms, highest priority being assigned to highest atomic number, and the molecule then viewed down the CX vector, where X has the lowest priority. The R- and S-labels for the enantiomers refer to a clockwise (rectus) and anticlockwise (sinister) sequence of the prioritized atoms, working from high to low. Example: CHClBr , view down the CH bond:



Isomerism due to non-planarity of chelate rings

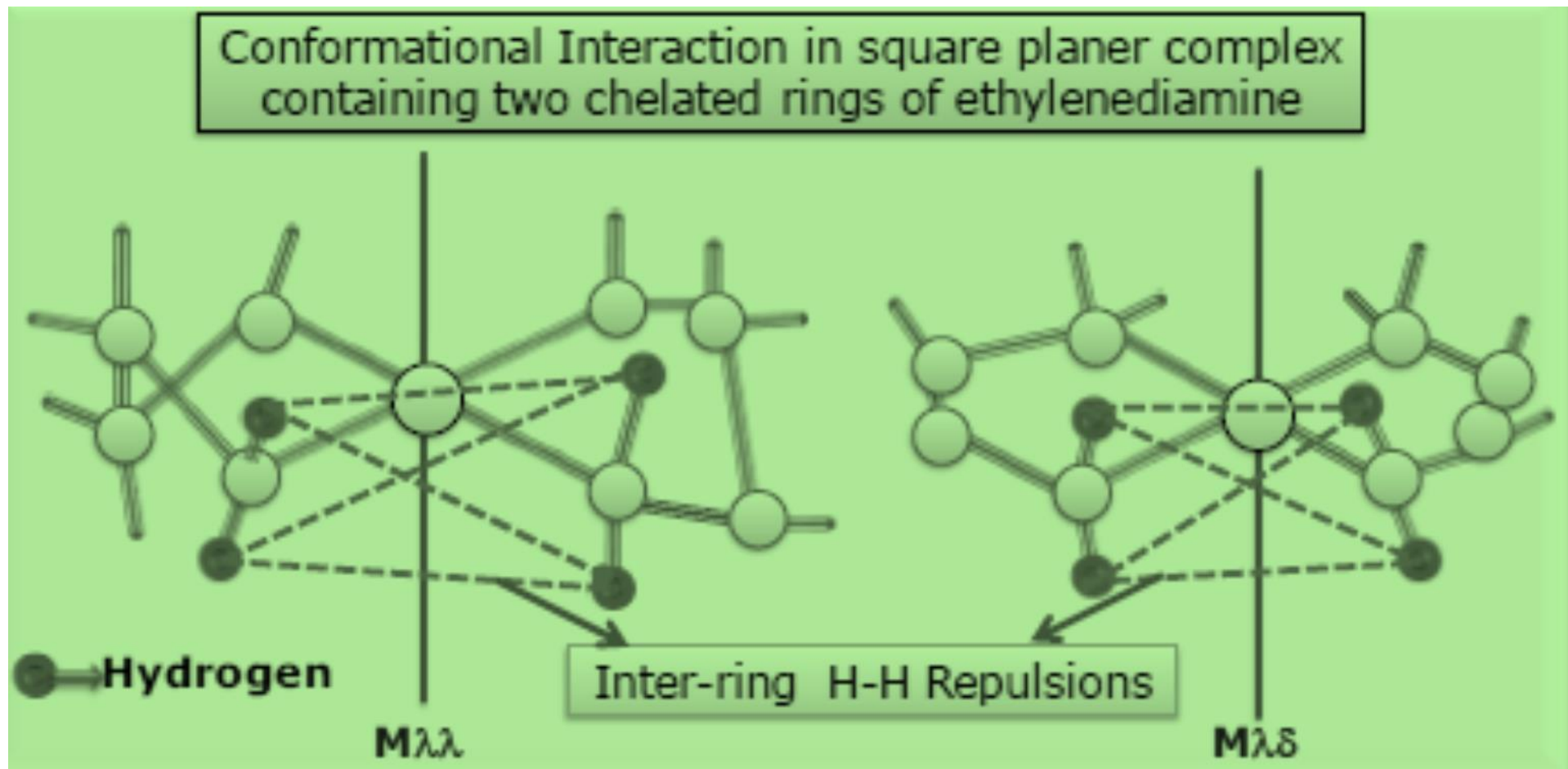
As we are aware that in tris(chelate) octahedral complexes, dissymmetry can also be generated by using dissymmetric ligand. For example, the gauche conformation of ethylenediamine is dissymmetric and could be resolved were it not for the almost complete absence of an energy barrier preventing racemization. Attachment of the chelate ligand to a metal retains the chirality of the gauche form, but the two enantiomers can still interconvert through a planer conformation at a very low energy, similar to the interconversion of organic ring systems. Thus, although it is possible to have two enantiomers of a complex such as $[\text{Co}(\text{NH}_3)_4(\text{en})]^{3+}$, but it is impossible to isolate them due to rapid interconversion of the ring conformers. In this case, two enantiomers of a complex are possible due to δ or λ chirality of the ethylenediamine-metal ring.



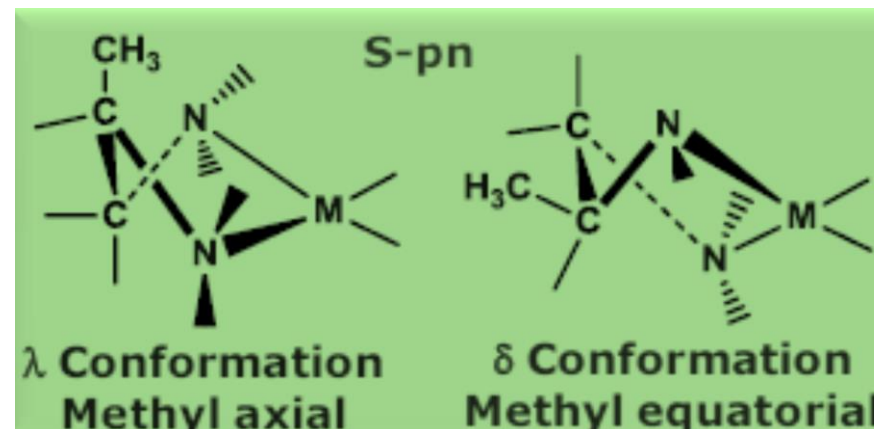
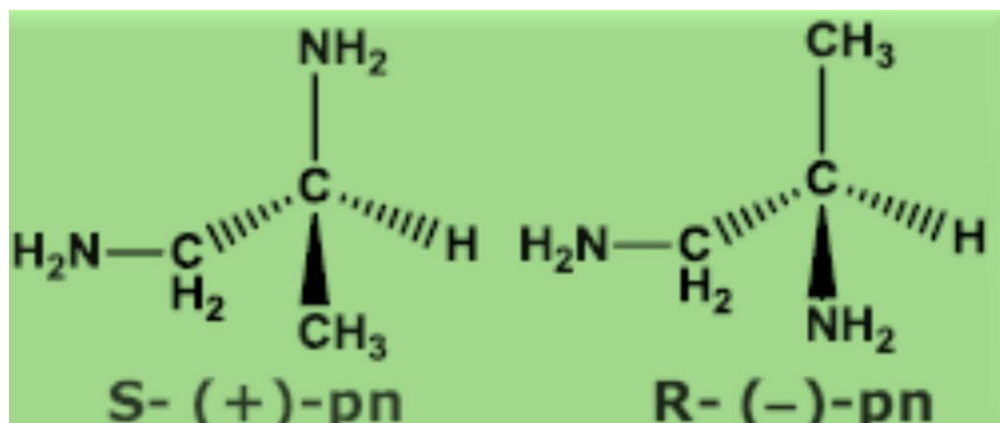
Isomerism due to non-planarity of chelate rings

If two or more rings are present in one complex, they can interact with each other and certain conformations might be expected to be stabilized as a result of possible decrease in the interatomic repulsions. For example, consider a square planer complex containing two ethylenediamine rings. It can assume three possible structures; $M\delta\delta$, $M\lambda\lambda$ and $M\lambda\delta$ (or $M\delta\lambda$). The first two lack a plane of symmetry, but $M\lambda\delta$ is a meso form. Corey and Bailer showed that $M\delta\delta$ and $M\lambda\lambda$ are more stable as compared to $M\lambda\delta$ (meso). This is due to the fact that meso compound has unfavorable **H-H interactions** of axial-axial and equatorial-equatorial type between the two chelate rings.

Isomerism due to non-planarity of chelate rings



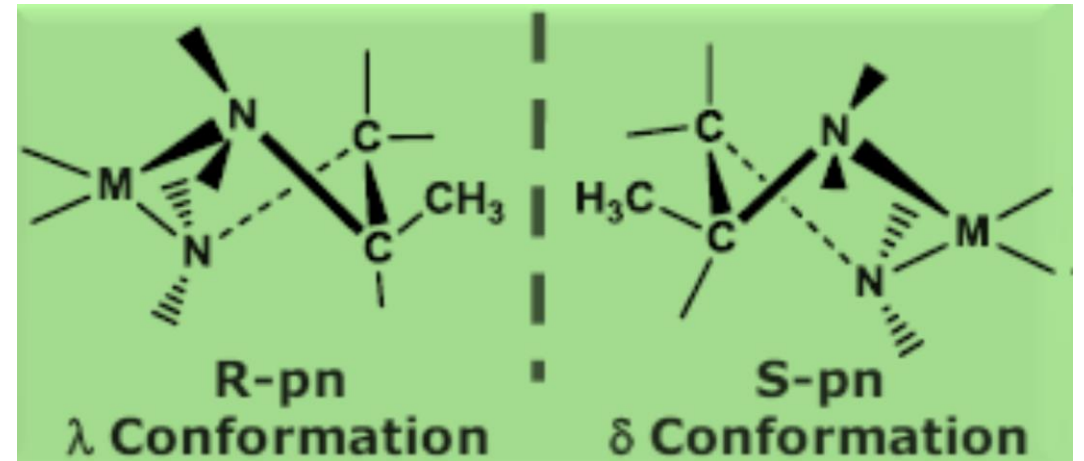
Isomerism due to non-planarity of chelate rings



Similarly for an octahedral tris(chelate) complex we might expect to have $M\delta\delta\delta$, $M\delta\lambda\lambda$, $M\delta\delta\lambda$ and $M\lambda\lambda\lambda$ forms. All these forms are optically active, so there can be in total eight isomers, but only two isomers have been isolated. This stereoselectivity is most easily followed by using a chiral ligand such as propylenediamine (pn), $CH_3CH(NH_2)CH_2NH_2$. The configuration of the (+) enantiomer of the ligand has been shown to be S . If the molecule in this configuration is attached to a metal, two conformations are possible. The conformation with the CH_3 group in an equatorial position (*i.e.*, δ) is more likely as compared to one with the CH_3 group in axial position (*i.e.*, λ).

Isomerism due to non-planarity of chelate rings

Note that the S-pn δ conformation is the mirror image of the R-pn λ conformation; therefore, if the diamine or R configuration is used, the conformation of greater stability should be λ .



Isomerism due to non-planarity of chelate rings

If R -pn is treated with cobalt(III) sulfate and oxygen, two isomers of empirical formula $[\text{Co}(R\text{-pn})_3]^{3+}$ are isolated and they are not enantiomeric to one another. Instead of having equal and opposite rotations as expected for enantiomers, they have specific rotation of -24° and $+214^\circ$. S -pn also gives two diastereoisomers, but these have rotation of $+24^\circ$ and -214° . It is clear that R -pn and S -pn have given two pairs of enantiomers, one pair having R - or S - ligands with specific rotation $\pm 24^\circ$ and another pair, again with R - or S - ligands with specific rotation $\pm 214^\circ$. An X-ray analysis of the $(-)-[\text{Co}(S\text{-pn})_3]^{3+}$ isomer indicates that

1. All the three chelate methyl groups are cis to one another
2. The absolute configuration is Δ
3. The pn chelate rings are in the expected δ conformation.

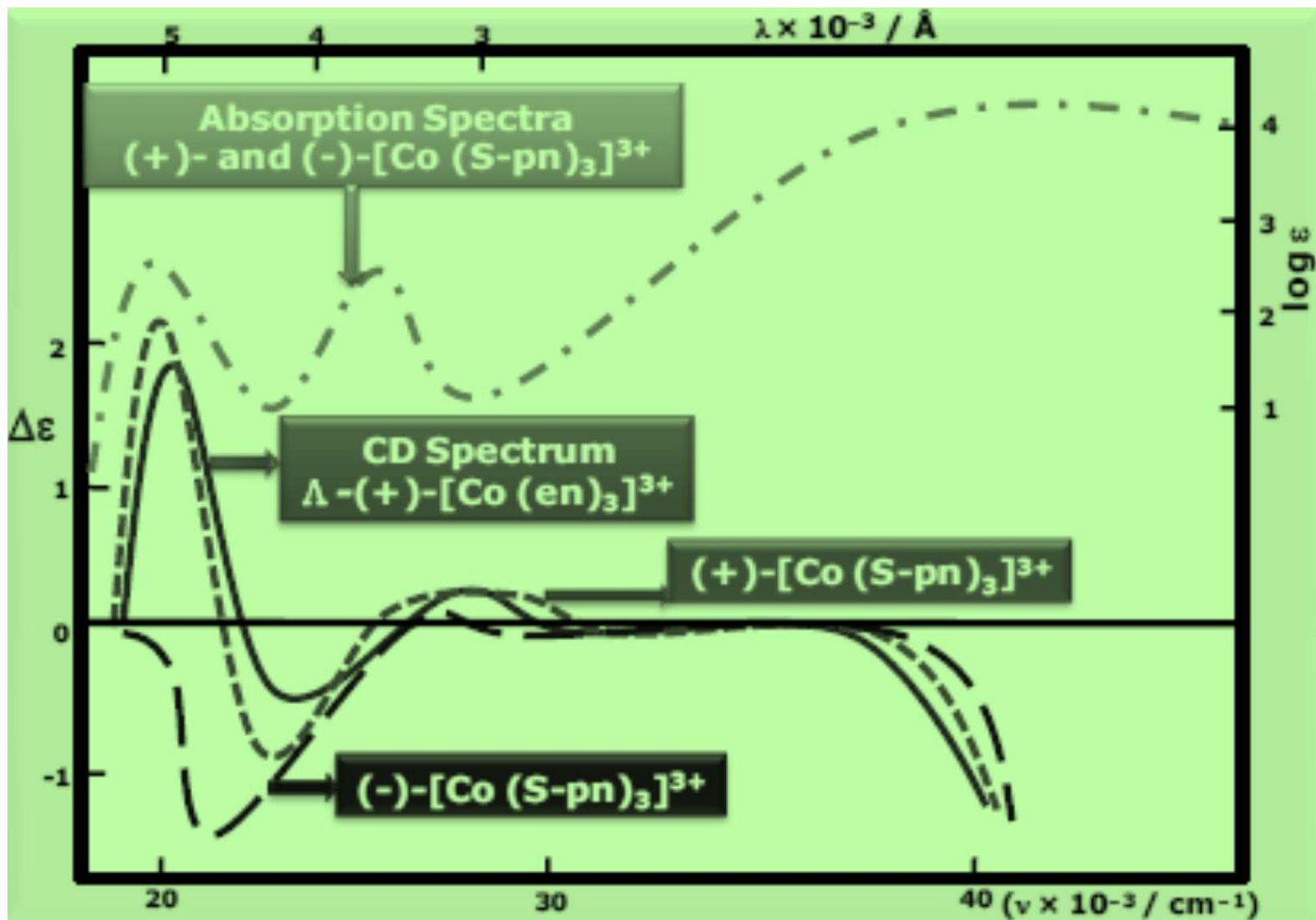
Isomerism due to non-planarity of chelate rings

| Complex | Configuration | Ligand Conformation | Specific Rotation $[\alpha]_D$ |
|------------------------------------|---------------|-------------------------|--------------------------------|
| $[\text{Co} (\text{S-pn})_3]^{3+}$ | Λ | $\delta\delta\delta$ | $+24^\circ$ |
| $[\text{Co} (\text{R-pn})_3]^{3+}$ | Δ | $\lambda\lambda\lambda$ | -24° |
| $[\text{Co} (\text{S-pn})_3]^{3+}$ | Δ | $\delta\delta\delta$ | -214° |
| $[\text{Co} (\text{R-pn})_3]^{3+}$ | Λ | $\lambda\lambda\lambda$ | $+214^\circ$ |

Isomerism due to non-planarity of chelate rings

Therefore, assuming that methyl groups are cis to one another in all of the complexes, the enantiomeric (+)-[Co(*R*-pn)₃]³⁺ must have Λ configuration with rings arranged in λ conformation. Likewise, the configurations and ring conformations of the remaining isomers are given in table. The authenticity of this analysis can be confirmed by the CD spectrum of (+)-[Co(*S*-pn)₃]³⁺, which is similar to that of Λ -(+)-[Co(en)₃]³⁺; in contrast, the CD spectrum of (-)-[Co(*S*-pn)₃]³⁺, is opposite to that of Λ -(+)-[Co(en)₃]³⁺.

Isomerism due to non-planarity of chelate rings



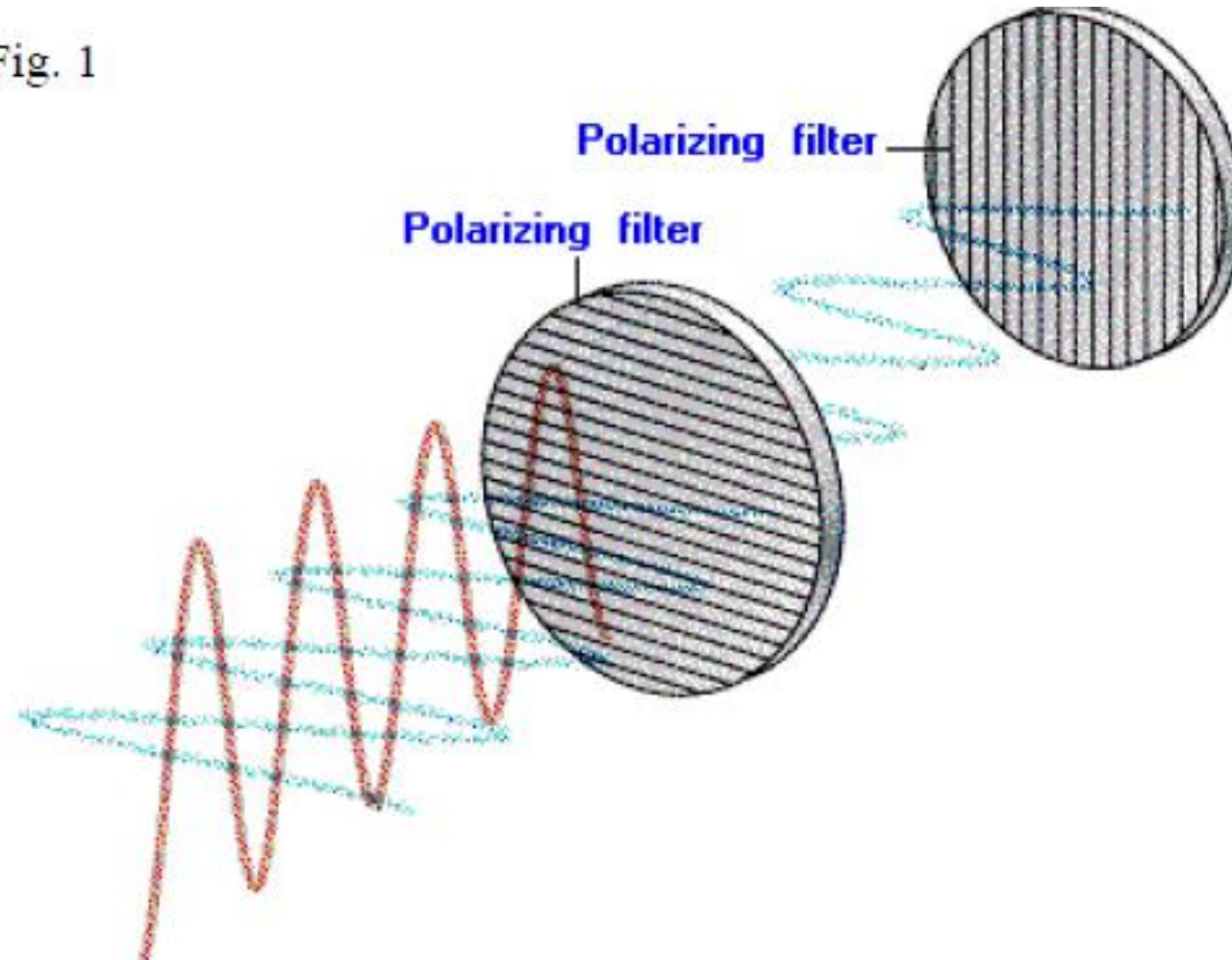


Faraday effect and Kerr effect

Though discovered over a century ago, the Faraday and Kerr Effects of polarized light are two of the most instrumental components of optical communication technology today. The nature of these properties is the manner in which the polarization of light is affected by an electromagnetic field; the **Faraday Effect** concerns light transmitted through a magnetic field where as the **Kerr effect** concerns light reflected off a magnetized surface.

Faraday effect and Kerr effect

Fig. 1



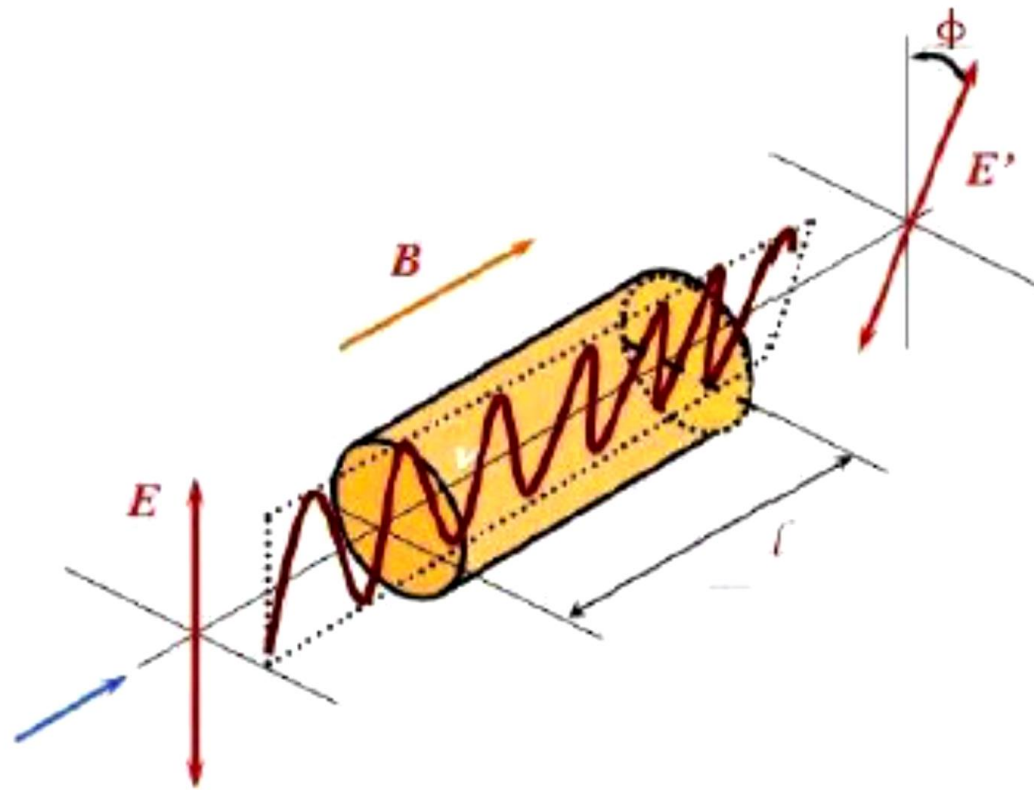
Faraday effect and Kerr effect

Light is electromagnetic radiation that varies in wavelength ranging from around 4,000 (violet) to around 7,700 (red) angstroms. This kind of light may be apparent to the average unaided human eye. Light vibrates at different frequencies and travels at different speeds. When light in which electromagnetic vibrations oscillate repeatedly in multiple directions, the light is then considered a non-polarized light. Natural light is made up of photons that scatter in a random pattern, travelling in many different directions; rather, the light is not correlated.

Faraday effect and Kerr effect

However, certain materials can be used to filter or align the light in one direction. The resulting light is called polarized light. In Fig., the beam of light is shown with two distinct wave directions. It passes through the first polarizing filter which only allows the horizontally polarized light through while blocking the other. Then, upon passing through a vertically polarized filter, all the light is blocked. Polarized lenses are used in sunglasses and cameras to cut glare and sharpen the image. Polarized light can also be used to read stored data on optical drives.

Faraday Effect



Faraday effect is discovered in 1845. Faraday showed that linearly polarized light would undergo a rotation of the plane of polarization upon being transmitted through a medium that has a magnetic field applied along the direction of propagation. Therefore, a longitudinal magnetic field results in the medium becoming optically active.

Faraday Effect

In its simplest form the rotation, ϕ , as expressed in Eq. is proportional to the strength of the magnetic field, B , and the length of the sample, l ,

$$\phi = V Bdl \quad \theta = V l B$$

V is called the Verdet constant, which depends upon both the properties of the medium, the ambient temperature wavelength, λ , of the incident light. It is the strength of the faraday effect in material.

The sense of the angle of rotation, ϕ , depends on the direction of the applied magnetic field, and by convention, V is positive when its sense is the same as the direction of the positive current that generates the magnetic field

Kerr Effect



The Kerr effect was discovered in 1875 by John Kerr, a Scottish physicist. The **Kerr effect**, also called the **quadratic electro-optic (QEO) effect**, is a change in the refractive index of a material in response to an applied electric field. All materials show a Kerr effect, but certain liquids display it more strongly than others.

Two special cases of the Kerr effect are normally considered, these being the Kerr electro-optic effect, or DC Kerr effect, and the optical Kerr effect, or AC Kerr effect.

Kerr Effect

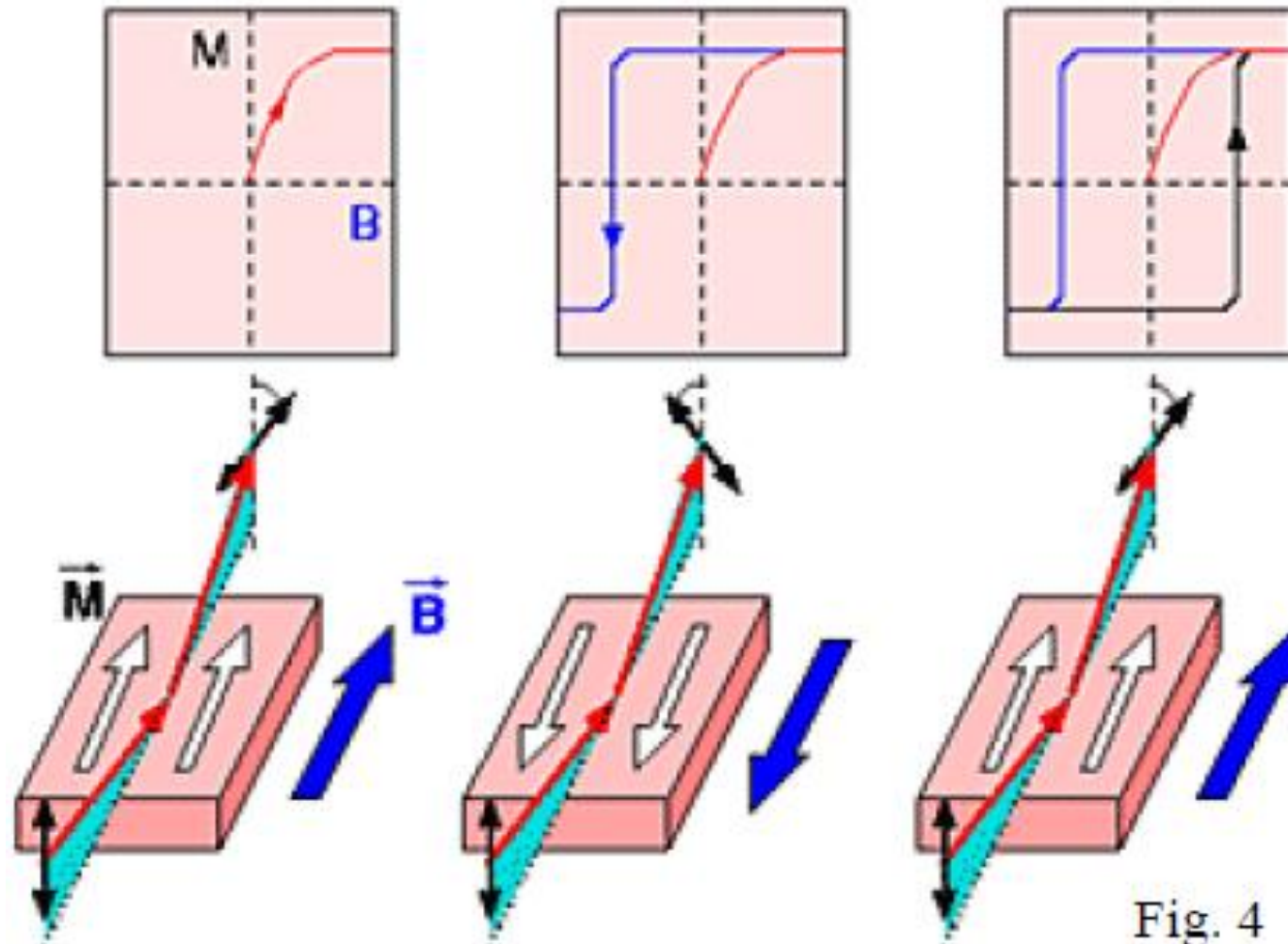


Fig. 4

Kerr Effect

The Kerr electro-optic effect, or DC Kerr effect, is the special case in which a slowly varying external electric field is applied by, for instance, a voltage on electrodes across the sample material. Under this influence, the sample becomes birefringent, with different indices of refraction for light polarized parallel to or perpendicular to the applied field. The difference in index of refraction, Δn , is given by

$$\Delta n = \lambda K E^2$$

where λ is the wavelength of the light, K is the *Kerr constant*, and E is the strength of the electric field.

Kerr Effect



This difference in index of refraction causes the material to act like a waveplate when light is incident on it in a direction perpendicular to the electric field. If the material is placed between two "crossed" (perpendicular) linear polarizers, no light will be transmitted when the electric field is turned off, while nearly all of the light will be transmitted for some optimum value of the electric field. Higher values of the Kerr constant allow complete transmission to be achieved with a smaller applied electric field.

Kerr Effect

Some **polar** liquids, such as nitrotoluene ($C_7H_7NO_2$) and nitrobenzene ($C_6H_5NO_2$) exhibit very large Kerr constants. A glass cell filled with one of these liquids is called a *Kerr cell*. These are frequently used to modulate light, since the Kerr effect responds very quickly to changes in electric field. Light can be modulated with these devices at frequencies as high as 10 GHz.