UNIT V

Optical Rotatory Dispersion and Circular Dichroism (ORD and CD)

Many transparent compounds characterized by lack of symmetry in their molecule or crystal structure have the property of rotating the plane of polarised radiation. The most important optically active inorganic compounds are complexes of transition metals containing two or three chelate rings. Transition metal complexes of several transition metal ions especially Co (III), Cr (III) Rh (III), Ir (III) and Pt (II) give kinetically inert complexes so that resolution of optical isomers is possible and the rates of racemization are slow enough for spectroscopic studies. Detailed studies of optical activity require a clear understanding of the energy levels and electronic spectra of complexes.

Polarised light : A beam of ordinary natural light is a packet of rays. It can be considered as a wave front (having an electric vector and perpendicular magnetic vector) in which vibrations occur in all planes perpendicular to the direction of propagation. Each of these vibrations can be thought of as being resultant of two vibrations at right angle to one another, but the polarised light has vibration only in one plane.

Types of polarised light

(1) **Linearly polarised or plane polarised light :** If natural light is passed through a polariser e.g. nicol prism or a sheet of polaroid having the property of absorbing one of these components, the emerging light beam vibrates only in one plane. This is referred to as plane polarised light or linearly polarised light. If this plane polarised light is allowed to pass through chiral or dis-symmetric molecule, the plane of emerging beam is rotated through an angle which depends upon the temperature, concentration and wavelength of polarised light. Two linearly polarised light beams with equal amplitudes but with their plane of polarisation at right angles may be considered to give different types of vibrations.

(2) **Circularly polarised light :** Consider two linearly polarised light beam, *AB* and *CD*. If the vibrations commence at *A* and *C* simultaneously and also reverse at *B* and *D* simultaneously, resultant will still be plane polarised light *EF*. Linearly polarised ray is obtained when difference of phase is either an even number of quarter wavelength or zero. If the vibration commences at *C* first when the *AB* vibration is passing through, the resultant of two linear vibrations is a circular rotation. This circular rotation may be either in the clockwise or anticlockwise direction depending upon whether the linearly polarised ray *AB* is moving to the right or left through *O* when *CD* commences its motion from *C*. Circularly polarised light, thus, represents a wave spiralling around the direction of propagation of the ray either clockwise or anticlockwise. Hence a plane polarised ray may be represented as the vector sum of the two circularly polarised rays having the same amplitude of vibration but one moving clockwise and the other anticlockwise.

(3) **Elliptically polarised light :** It results when the phase difference between two linear vibrations at right angles is neither zero nor exactly even or odd number of the quarter wavelengths.

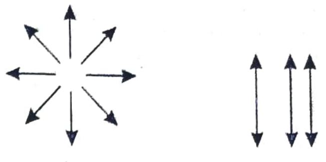
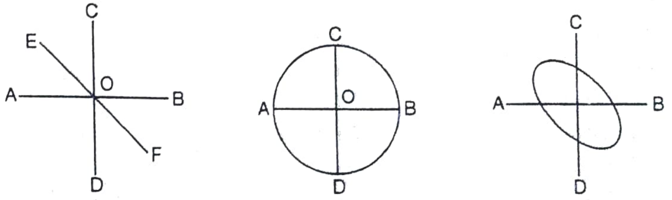

(a) (b)

Fig. 5.1 : (a) Ordinary light
(b) Plane polarised light



(a) (b) (c)

Fig. 5.2 : Different types of polarisation
(a) Plane polarised light
(b) Circular polarised light
(c) elliptically polarised light.

Optical rotatory power : Optical activity in a molecule can be expected when the molecule is so structured that it can not super-impose on its mirror-image. An optically active molecule must not possess a centre of symmetry or a plane of symmetry. Such a molecule is said to be dissymmetric or chiral (Greek : hand). They have the property of rotating the plane of polarised radiation such as quartz and sugars. The extent to which the plane of polarised radiation is rotated varies widely from one optically active compound to another. The rotation is said to be dextro (+) if it is clockwise to an observer looking towards the light source and laevo (−) if anticlockwise. The six-coordinate complexes of the types [M (bidentate ligand)$_3$] and cis-[M (bidentate ligand)$_2$ X$_2$] which have symmetries D_3 and C_2, respectivley are optically active compounds.

For any given compound, the extent of rotation depends on the number of molecules in the path of radiation e.g., in case of solutions, on the concentration and the length of the containing vessel and also dependent on the wavelength of radiation and temperature.

The optical rotatory power of a pure substance mainly in the liquid state is usually expressed in terms of specific rotatory power or optical rotation α.

$$[\alpha]^t = \alpha / dc \qquad \text{...(5.1)}$$

where α = is the angle (measured in degrees) through which the plane of polarised light rotated by a solution

c = concentration (c grams of solute per milliliter of solution)

d = length of sample cell (in decimeter),

t = temperature

The wavelength is commonly specified as 589.3 nm, the *D* line of a sodium-vapour lamp.

Table : 5.1 : Specific rotation of solutions (at 20°C).

Active substance	Solvent	$[\alpha]_D^{20}$
Camphor	Alcohol	+ 43.8°
Calciferol (vitamin D_1)	Chloroform	+ 52.0°
Calciferol (vitamin D_2)	Acetone	+ 82.6°
Cholesterol	Chloroform	− 39.5°
Quinine sulphate	0.5 F HCl	− 220°
l-Tartaric acid	Water	+ 14.1°
Ro chelle salt	Water	+ 29.8°
Sucrose	Water	+ 66.5°
β-*d*-glucose	Water	+ 52.7°
β-*d*-fructose	Water	− 92.4°
β-Lactose	Water	+ 55.4°
β-Maltose	Water	+ 130.4°

The angle of rotation of a plane polarised light caused by an optically active compound can be measured by an instrument called polarimeter. The polarimeter consists of light source, polarizer, sample cell, analyser and graduated circle to measure the extent of rotation. Mono chromatic radiation from a sodium vapour lamp or mercury vapour lamps used as light source is made parallel by a collimator. Sodium vapour lamp emits a doublet (589.0, 589.3 nm) while mercury vapour lamp emits prominent lines at wavelengths 435.0, 491.6, 546.1, 577.0 and 579.1 of which the green mercury line at 546.1 nm is taken as standard wavelength and the rest are removed by using filters. Radiations are polarised by a calcite prism. Following the polariser, there is placed a small auxillary calcite arranged to intercept one-half of the beam. The radiation then passes through the sample which is contained in a glass tube of known length, closed at both ends by glass plates and then through the analyers to the eye piece for visual observation. In principle, the polarimeter could function without the small auxillary prism. But the auxillary prism is permanantly oriented with its polarising axis at an angle of a few degrees from that of the polariser. There is then a particular, position of the analyser at which the radiations passed in the two halves of the beam are just equal in power. This provides a more satisfactory reference point than does the position of complete extinction. Since the visual observation consists of matching exactly the powers of two half-beams at some intermediate level for which application the eye is well suited. The movement of the analyser is recorded by means of vernier fixed to the analyser.

Measurement : The polarimeter tube is filled with the sample. It rotates the plane of polarised light to a certain angle and the analyser is rotated in the clockwise direction to obtain the uniform illumination of field. The angle through which the analyser is rotated is the angle of rotation of the compound at known concentration.

Applications : (1) The most extensive application of analysis by optical rotation is in the sugar industry. In the absence of other optically active material, sucrose can be determined quantitatively by a direct application of equation (5.1) which may be written in the form :

$$c = \frac{\alpha}{d\,[\alpha]_D^{20}} = \frac{\alpha}{2 \times 66.5} = \frac{\alpha}{133.0} \qquad ...(5.2)$$

For sucrose in the 2-*dm* tube at a temperature of 20°C. The rotation of an unknown sugar sample can be substituted in equation (5.2) and the concentration is thus determined. If, other active substances are present, a more general treatment is required. Sucrose, alone among common sugars, can be made to undergo a hydrolysis reaction in the presence of acid as follows :

$$\underset{\substack{\text{Sucrose} \\ [\alpha]_D^{20}\,(+\,66.5)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{acid}} \underset{\text{Glucose }(+\,52.7°)}{C_6H_{12}O_6} + \underset{\text{Fructose }(-\,92.4°)}{C_6H_{12}O_6} \qquad ...(5.3)$$

The resulting mixture of glucose and fructose is called invert sugar and the reaction inversion. During the inversion process, the specific rotation changes from +66.5 to − 19.8°, corresponding to an equimolor mixture of the products. By measuring the rotation before and after inversion, it is posssible to calculate the amount of sucrose present.

The usual procedure is to start with a sample of 100 ml volume, measure its rotation and then add 10 ml. of concentrated hydrochloric acid. The acidified solution must stand for at least 24 hours at 20°C, 10 hours at 25°C or 10 minutes at 70°C to ensure completion of reaction. The rotation is then redetermined. Under these conditions, the weight of sucrose in the original sample is :

$$w_s = -\,1.17\,\Delta\alpha - 0.00105\,[\alpha]_{D\,(x)}\,\omega_x \qquad ...(5.4)$$

α = observed changes in angle of rotation

$[\alpha]_{D\,(x)}$ = specific rotation of any other active material which may be present.

w_x = Weight of this active impurity

If nearly all the active material present is sucrose, the second term is negligible, but if sucrose is present as a minor constituent in a large portion of another active substance, the second term can be evaluated and the weight of sucrose calculated from the observed $\Delta\alpha$.

(2) Optical rotation method can be used for simultaneos determination of penicillin and the **enzyme penicillinase.** Penicillin is destroyed quantitatively by the enzyme at a rate which is directly dependent on the amount of enzyme present but independent of the penicillin concentration. A graph of rotation against time gives a straight line which terminates when the penicillin is all used up. The slope of the line is a measure of the concentration of the enzyme. The curve tails off an effect due to secondary reactions (figure 5.4). The exact time of disappearance of penicillin is found by the intersection of the extra-polated straight portions. The concentration can be determined with a precision of about ± 1 percent for the penicillin, and about ± 10 percent for the enzyme.

Circular birefringerance : The wavelength dependence of optical activity, known as optical rotatory dispersion (ORD) is a more useful source of information about asymmetric compounds than is the specific rotation at a single wavelength. An ordinary beam of light can be resolved into two plane polarised beam and plane polarised radiation can be further resolved in into two beams which

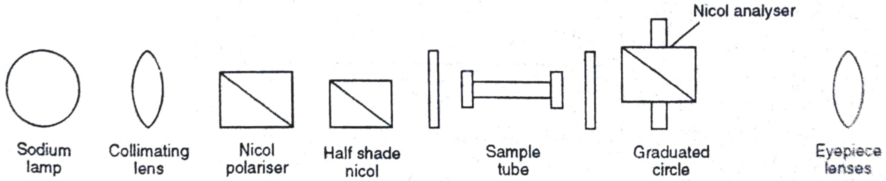


Fig. 5.3 : Schematic Diagram of polarimeter.

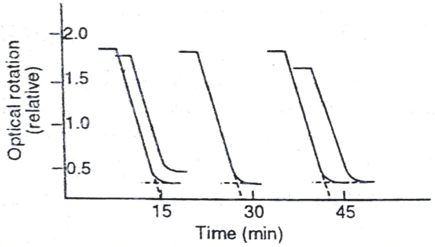


Fig. 5.4 : Relative concentration of the enzyme.

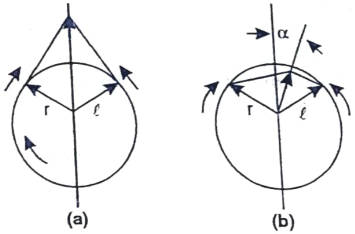


Fig 5.5 (a) An instantaneous view along the direction of propagation of the of two vector r and *l* of the circulatory polarised beams and their resultant which lies in vertical plane. (b) In $n_L > n_R$ the beam l is retarded relative to beam r, thus causing the plane of the resultant to be tilted by an angle α.

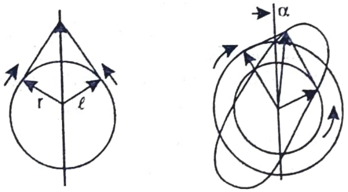


Fig. 5.6 : (a) Same as figure 5.5(a) (b) If $n_L > r_L$ and also $\in_L > \in_R$, the vectors r and l will be affected and they will give rise to a resultant which comes out as the indicated ellipse.

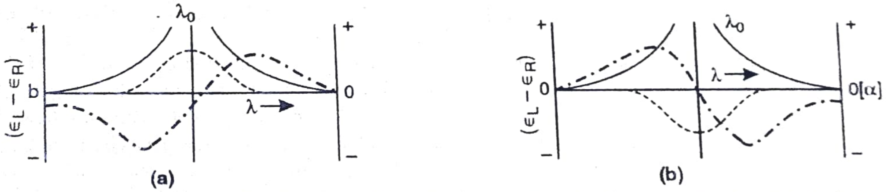


Fig. 5.7 : Cotton effect (a) Positive cotton effect (b) negative cotton effect i.e., $(\in_L - \in_R)$ circulr dichroism and ORD $[\alpha]$ as would be given by a dis-symmetric compound with an absorption band centred at λ_0 [—Absorption, ...CD _ _ _ORD]

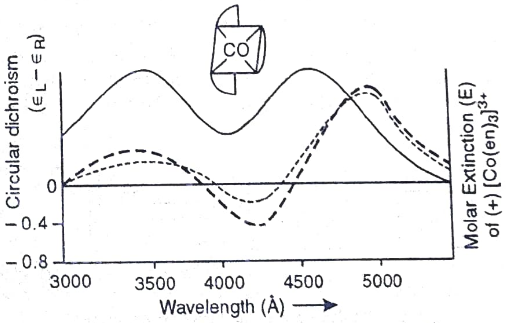


Fig. 5.8 : The visible spectrum of (+) $[Co(en)_3]^{3+}$, (---) CD of (+) $[Co(en)_3]^{3+}$ (...) CD of (+) $[Co(i - pn)_3]^{3+}$.

are circularly polarised in opposite directions. For example, there are molecules AB consisting of two separately dis-symmetric halves say $A\,(+), A\,(-)$ and $B\,(+), B\,(-)$ which are different substances, for example, the diastereoisomers $A\,(+), B\,(+)$ and $A\,(-), B\,(+)$ having numerically different physical properties, so the physical interactions of the two circularly polarised beams with a given enantiomorph of a dissymmetric molecule. The refractive indices for left and right circularly polarised light may not be the same and will be designated as n_L and n_R, respectively. For an isotropic medium $n_L = n_R$ e.g., for glass or water. The index is independent of the state of polarisation. If $n_L \neq n_R$, a phase difference appears between the two components which is equal to saying that the plane of polarisation has been rotated, i.e., the angle $\alpha \neq 0$.

The angle of rotation is given by (as expressed in radians) if $n_L > n_R$, plane of the emergent linearly polarised light is rotated to the right.

$$\alpha = \pi/\lambda\,(n_L - n_R)\,d \qquad \text{...(5.5)}$$

The quantity $(n_L - n_R)$ is called the circular birefringence. Optical rotation is dependent on wavelength, especially in the region of an electronic absorption band of the atom or ion lying at the "centre of dissymmetry". Moreover, at a given wavelength, the values of $(n_L - n_R)$ for one enantiomorph are equal and opposite to those for the other enantiomorph.

Ellipticity and *CD* : The molar absorbances $\in_1$ and $\in_2$ will be different for left and right circularly polarised light. The simultaneous existence of a difference between $\in_1$ and $\in_2$ means that the rotated plane is no longer strictly a plane. Since one rotating electric vector is not exactly equal in length to the other after the two components have transversed the optically active medium, their resultant, describes an ellipse whose principal axis defines the plane of the rotated beam and whose minor axis is equal to the absolute difference $(\in_L - \in_R)$. This diffference is usually very small so that, it is a very good approximation to speak of rotating "the plane", it can be measured and constitutes the circular dichroism (*CD*). It is also dependent on wavelength and at a given wavelength, the value for $(\in_L - \in_R)$ for one enantiomorph is equal and opposite to those for the other enantiomorph.

If $\in_1 \neq \in_2$, then one component is absorbed more strongly than the other, the vector diagram representing the polarisation turns out to be elliptical with the eccentricity. θ is a measure of $(\in_L - \in_R)$ Ellipticity θ is expressed as–

$$\theta = \frac{1}{4}(\in_L - \in_R)\,d \qquad \text{...(5.6)}$$

The specific ellipticity $[\theta]$ may be given by

$$[\theta] = \theta/lc\ (l = \text{length in cm}). \qquad \text{...(5.7)}$$

The molar ellipticity per unit length is expressed as

$$[\theta]\,M = [\theta]\,.\,M/100 \qquad \text{...(5.8)}$$

Cotton effect : Cotton effect is studied very much, as in an empirical way it is used to correlate the configurations of related dissymmetric molecules and thus to follow the steric course of certain reactions. Both theoretical and experimental work is in progress to establish generally reliable criteria for determining spectroscopically the absolute configurations of molecules.

Aime Cotton (1895) made pioneering studies of the wavelength dependent aspects of rotation and ellipticity. The variation of the angle of rotation with wavelength is optical rotatory dispersion, which coupled with circular dichroism and the introduction of ellipticity in the rotated beam are all together called the Cotton effect.

The use of ORD and CD data in making empirical correlations of configuration is increasingly important. The basic idea is that electronic transitions of similar nature in similar molecules should have the same signs for CD and ORD effects when the molecules have the same absolute chirality. The chief uncertainty in the conclusions arises from failure to satisfy adequately the criteria of similarity in the nature of electronic transition and in the structures of the moleculces themselves. There is an abrupt reversal of rotation in the vicinity of an absorption band. If the complex is initialy laevo-rotatory, the ORD curve falls to a minimum, rises rapidly to a maximum and then slowly falls. If the complex was initially dextrorotatory, the effect is reversed with the ORD curve rising first to a maximum, then falling, These represent positive and negative cotton effects, respectively. Figure 5.8 shows the CD curves for $(+)[Co(en)_3]^{3+}$ and $(+)[Co(i-pn)_3]^{3+}$ where the $(+)$ sign indicates that these are enantiomers having positive values of $[\alpha]$ at the sodium D-line. These two complex ions must have the same absolute configurations. The structure of the $(+)[Co(en)_3]^{3+}$ ion has been determined by means of anomalous X-ray method.

In cases where the ligands themselves have electronic transitions in the ultra violet region that persist in perturbed state but can be identified in the complexes, ORD or better CD data give a reliable method of assigning absolute configurations without employing any reference compound of known configuration. This is based on the fact that when two or three such ligands are in close proximity in the complex, their individual electric dipole transition moments can couple to produce excitaton splitings. Each component of the split band will have a different sign for its circular dichroism and that this sign may be predicted from the absolute configuration. The types of ligand discussed above are exemplified by bipyridine and phenanthroline which have strong near ultra-violet transitions. In the case of $[Fe(phenan)_3]^{2+}$ X – ray crystallographic determination method confirms it. CD curves will often pin point hidden absorption maxima, on the other hand ORD curves are affected to a considerable degree by more distant chromophoric bands and hence are more characteristic of specific compounds than CD.

Faraday effect : All the substances rotate the plane of polarization of light and exhibit ORD and CD effects when placed in a magnetic field that has a component in the direction of propagation of the polarised radiation. These effects are, collectivley called the faraday effect. It is analogous to ordinary optical activity and the Cotton effect, but their interpretation and application to chemical problems are more complicated and less advanced.

Because all substances, including solvents, cell window etc. exhibit Faraday effect, it is, only possible to get interpretable results by measuring the magnetic circular dichroism (MCD) through the electronic absorption bonds of the complex under study. This can be done with apparatus normally used for conventional CD measurements by surrounding the sample cell with a small super conducting solenoid.

MCD spectra are chiefly useful in testing or confirming the assignments of orbitally allowed electronic transitions such as charge transfer bands.

Note : A positive elliptical polarisation (or CD) results when $(\epsilon_L - \epsilon_R)$ and if $\epsilon_R > \epsilon_L$, a negative CD results. A positive Cotton effect thus denotes a positive CD as well as a particular type of variation of α with λ. The wavelength at which α is zero and the CD is a maximum or minimum coincides with that of a maximum in the electronic absorption spectrum of the optically active species (The condition $n_L > n_R$ in the longer wavelength region in which an optically active medium showing a positive Cotton effect implies $\epsilon_L > \epsilon_R$ holds in the shorter wavelength region where light is absorbed.

For the $[Fe(CN)_6]^{3-}$, there are three charge transfer bands in the visible and near ultraviolet spectra. All of them must involve transition from orbitals of t_{1u} and t_{2u} symmetry on the ligands to the vacancy in the metal d-orbitals of t_{2g} symmetry. It is possible to show theoretically that a $t_{1u} \rightarrow t_{2g}$ transition should have a positive MCD effect, while a $t_{2u} \rightarrow t_{2g}$ transition should have a negative MCD effect. From the observed MCD spectrum, it is clear, that the $t_{2u} \rightarrow t_{2g}$ transition lies between the two $t_{1u} \rightarrow t_{2g}$. In favourable circumstances the shape and/or magnitude of the MCD effect can show that a transition involves an excited state that is degenerate.

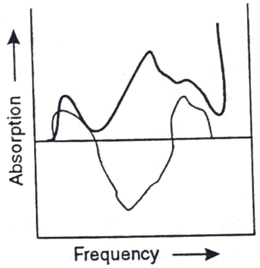


Fig. 5.9 : The absorption spectrum (bold curve) and MCD spectrum (thinner line) of $[K_3Fe(CN)_6]$ in the region of charge transfer bands.

Assignment of electronic transitions : In a molecule, there are electrons in different kinds of orbitals, i.e., bonding, non-bonding, π-bonding and, antibonding with different energies in the ground state. Electrons from these different orbitals can be excited to higher energy molecular orbitals giving rise to many possible excited states. Thus, many transitions from the ground state to different excited states are possible in one molecule.

There are several conventions used to designate these different electronic transitions. Molecular orbital configuration of carbonyl group in formaldehyde is :

$$\sigma^2, \pi^2, (n_a = n_b)^4, (\pi^*)^0, (\sigma^*)^0$$

n_a and n_b are two non-bonding molecular orbitals containing the lone pairs of oxygen. Relative energies of these orbitals are $\sigma < \pi < n_a = n_b < \pi^*, \sigma^*$. The observed transitions are referred to as $n \rightarrow \pi^*, n \rightarrow \sigma^*, \pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$.

Electron excitations can occur with or without a change in the spin of the electron. Many more transitions are observed than predicted by the simple representation of electronic transition because levels that would otherwise be degenerate are split by electronic interactions.

If the energies of the molecular orbitals in all molecules could be set up, the assignment of transitions to the observed bands would be simplified. The $n \rightarrow \pi^*$ transition would be lower in energy than $\pi \rightarrow \pi^*$ which, in turn, would be lower in energy than $\sigma \rightarrow \pi^*$. In addition to different electron-electron repulsions in different states, two other factors complicate the picture by affecting the energy and the degeneracy of the various states. These factors are spin orbit coupling and higher state mixing.

Spin-orbit coupling : There is a magnetic interaction between the electron spin magnetic moment $(m_s = \pm 1/2)$ and the magnetic moment due to the orbital motion of an electron. Magnetic field created by the orbital motion of an electron can interact with the spin magnetic moment of the electron giving rise to spin-orbit interaction. The orbital moment may either complement or oppose the spin moment, giving rise to two different energy states. The splitting of the doubly degenerate energy states ($s = \pm 1/2$) of the electron has occurred, lowering the energy of one and raising the energy of the other. Whenever an electron can occupy a set of degenerate orbitals which permit circulation about the nucleus, this interaction is possible.

For example, if an electron can occupy the d_{yz} and d_{xz} orbitals of a metal ion, it can circle the nucleus around the z-axis.

Higher state mixing : If a high energy orbital has the same symmetry as a lower energy orbital, accurate wave function for each of these obitals may include contribution from both orbitals. The lower energy orbital will be lower in energy than that predicted by the simple model and transitions involving this orbital will be at different energies from those predicted by simple model. In the case of higher state mixing.

$$\psi^0 = a\psi_1 \pm b\psi_2 \qquad \ldots(5.9)$$

where ψ^0 – accurate wave function

ψ_1 – wave function for the simple model ground state

ψ_2 – simple model excited state wave function

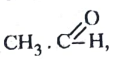
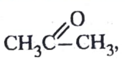
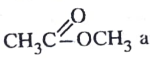
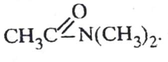
It is adequate for many purposes to employ the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ designation for electronic transitions. But we should consider the possible complexity of the excited states too. The following phenomena are characteristics of an $n \rightarrow \pi^*$ transition and can be used to help in making this assignment.

(1) The molar absorptivity of the transition is generally less than 2000.

(2) A blue shift (hypsochromic shift or shift toward shorter wavelength) is observed for $n \rightarrow \pi^*$ transition in high dielectric or hydrogen bonding solvents. This indicates that the energy difference between the ground and excited state is increased in a high dielectric or hydrogen bonding solvents. For solvent shifts, it is often difficult to ascertain whether the excited state is raised in energy or the ground state is lowered. The shift may also result from a greater lowering of the ground state relative to the excited state or a greater elevation of the excited state relative to the ground state. It is thought that the solvent shifts in the $n \rightarrow \pi^*$ transition results from a lowering of the energy of the ground state and an elevation of the energy of the excited state. In a high dielectric solvent, the solvent molecules arrange themselves about the absorbing solute so that the dipoles are properly oriented for maximum interaction ,*i.e.,* solvation which lowers the energy of the ground state. When the excited state is produced, its dipole will have different orientation from the ground state. Since solvent molecules can not rearrange to solvate the excited state during the time of a transition, the excited state energy is raised in a high dielectric solvent.

Hydrogen bonding solvents cause pronounced blue shifts due to hydrogen bonding of the solvent hydrogen with the lone pair of electrons in the non-boding orbital undergoing the transition. In the excited state, there is only one electron in the non-bonding orbital, the hydrogen bonding is weaker and as a result, the solvent does not lower the energy of this state nearly as much as that of the ground state. In this hydrogen-bonding system, an adduct is formed and this specific solute-solvent interaction is the main cause of the blue shift. If there is more than one lone pair of electrons on the donor, the shift can be accounted for by the inductive effect of hydrogen-bonding.

(3) The $n \rightarrow \pi^*$ bond often disappears in acidic media due to protonation or upon formation of an adduct that ties up the lone pair ,e.g., $BCH_3^+I^-$. This behavior is very characteristic if there is only one pair of non-bonding electrons on B. ,i.e., B-base molecule containig the non-bonding electrons.

(4) Blue shifts occur upon the attachment of an electron donating group to the chromophore, i.e., the series  $CH_3.C(=O)H$,  $CH_3C(=O)CH_3$,  $CH_3C(=O)OCH_3$ and  $CH_3C(=O)N(CH_3)_2$. A molecular orbital treatment indicates that this shift results from a raising of the excited. π^* level relative to the non-bonding level.

(5) The absorption band corresponding to the $n \rightarrow \pi^*$ transition is absent in the hydrocarbon analogue of the compound.

(6) Usually, but not always, the $n \rightarrow \pi^*$ transition gives rise to the lowest energy singlet-singlet transition.

$\pi \rightarrow \pi^*$ transitions have a high intensity. A slight red (bathochromic shift) shift is observed in high dielectric solvents and upon introduction of an electron donating group. In the above systems, only the difference in energy between the ground and excited states can be measured from the frequency of the transition, so only the relative energies of the two levels can be measured.

Oscillator Strengths or *f*-number : A parameter for expressing the intensity of an absorption band is the oscillator strength or f-number is given

$$f = 4.315 \times 10^{-9} \int \in d\bar{\nu} \qquad \ldots(5.10)$$

$\in$ – molar absorptivity, $\bar{\nu}$ – frequency (in cm^{-1}). The concept of oscillator strength is based on a simple classical model for an electronic transition. The value of $f = 1$ indicates an allowed transition. The quantity f is evaluated graphically by plotting $\in$ versus the wave number $\bar{\nu}$ in cm^{-1} and calculating the area of the band. Values of f from 0.1 to 1 correspond to molar absorptivities in the range 10,000 to 100,000 depending on the width of the peak. For a single symmetrical peak, f can be approximated by the expression :

$$f \approx (4.6 \times 10^{-9}) \in_{max} \Delta V_{1/2} \qquad \ldots(5.11)$$

where $\in_{max}$ – Molar absorptivity of the peak maximum

$\Delta V_{1/2}$ – half intensity band width (the width at 1/2 $\in_{max}$)

Applications of ORD and CD

(1) **Determination of absolute configuration of complexes :** The determination of the absolute spatial relationship of the atoms in a dissymmetric coordination compound is a problem. It is not possible to assign the absolute configuration simply on the basis of the direction of rotation of plane of polarised light. However, through analysis of rotatory properties of enantiomers, strong clues can be provided as to the configuration.

The simplest method is notation of the experimental direction of rotation of polarised light, (+) or d, (−) or l, thus $(+)_{589} - [Co\,(en)_3]^{3+}$ is said dextro rotatory with respect to light of wavelength equal to 589 nm. This label identifies enantiomers with respect to each other, but serves little purpose. By using certain techniques and assumptions, strong clues can be provided with regard to configuration.

We can arbitrarily assign the *D* configuration to (+)- $[Co(en)_3]^{3+}$and can compare all known configuration with it. This now immediately tells us the configuration of *D*-isomer by comparing it with a figure of *D*- $[Co(en)_3]^{3+}$, but the *D*-symbol is an arbitrary one.

A systematic basis can be found by viewing a tris (chelate) complex, the most common species of chiral coordination compounds, down the three fold rotation axis. If the helix viewed is right-handed, the isomer is the Δ isomer and its mirror image is Λ-isomer. The D^-, L^-, Δ^- and Λ^- isomers may be presented below. It is a result of these systems that $\Lambda \neq L$ and $\Delta \neq D$.

X-ray diffraction method gives exactly the same diffraction pattern for both enantiomers and thus, this method gives no information on the absolute configuration about the metal atom. Once one absolute configuration is known, correlation of other compounds can be found by other methods. The absolute configuration of *D* (+)- $[Co(en)_3]^{3+}$ has been determined as the chloride and bromide salts and L-(−)- $[Co\,(R-pn)_3]^{3+}$ as the bromide. (*en* = ethylene diamine, *R-pn* → *l*- or (−) propylene diamine.

If one of the ligands is chiral and its absolute configuration is known, we can readily determine the absolute configuration at the metal atom by *X*-ray diffraction or neutron diffraction. Of the two enantiomeric structures consistent with the *X*-ray data, the one having the correct configuration about the known chiral center is chosen. For example, consider, tris (*R*-propylene diamine) cobalt (III). The following synthesis of tris (*R*-propylenediamine) cobalt (III) is stereospecific.

$$[Co\,(CO_3)_3]^{3-} + 3R{-}pn \rightarrow [Co\,(R{-}pn)_3]^{3+} + 3CO_3^{2-}$$

We obtain only one isomer which is identified as the Δ- or *L*-isomer. Since we know the absolute configuration of the asymmetric carbon in *R*-propylene diamine, we choose the enantiomeric solution of the data that provides the correct configuration for that carbon, thus automatically fixing the correct configuration about cobalt. This method is especially useful when studying complexes of naturally occurring *L*-amino acids such as alamine and glutamic acid.

Tris (ethylene diamine) cobalt (III) ion shows a similar electronic transition and a very similar visible spectrum to that of hexa amine cobalt (III) ion. Optical rotatory dispersion and circular dichroism can be associated with *d-d* transitions to assign absolute configurations of complexes. On the basis of Cotton effect a general rule may be stated as : If, in analogous compounds, corresponding electronic transitions show Cotton effects of the same sign, the compounds have the same configuration.

Optical rotatory dispersion involves measuring the variation of optical rotation with wavelength. There is an abrupt reversal of rotation in the vicinity of an absorption band. If the complex is initially laevorotatory, the optical rotatory dispersion curve falls to a minimum, rises rapidly to a maximum and then slowly falls. If the complex was initially dextro rotatory, the effect is reversed with the optical rotatory dispersion curve rising first to a maximum then falling. These represent positive and negative Cotton effects, respectively.

Optical rotatory dispersion curves (ORD) are useful in the assignment of absolute configurations. For example, the configurations of the enantiomers of tris (ethylene diamine) cobalt (III), tris (alaninato) cobalt (III) and bis (ethylenediamine) glutomato cobalt (III) are known from *X*-ray diffraction technique and it is found that the three Λ − (*D* −) enantiomers of these complexes have similar ORD spectra. On this basis, the Λ-configuration could have been assigned to any of these in the absence of *X*-ray data simply on the basis of the similarity of the ORD spectra to one of known configurations.

Although ORD was used extensively because of simpler instrumentation, circular dichroism (CD) is much more useful. The CD effect arises because there is differential absorption of left and right circularly polarized light associated with transitions such as $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$. The CD is the difference between the molar absorptivities of left and right polarized light $(\in_1 - \in_2)$. Complexes having the same sign of CD for a given absorption band will have the same absolute configurations.

Table : 5.2 : Circular dichroism data for some Λ − (*D*) -and Δ − (*L*)-tris (chelate) complexes of cobalt (III)

Formula of complex	ν (cm^{-1})	$(\in_L - \in_R)$	**Absolute Configuration**
$(+)_{589} - [Co\,(en)_3]^{3+}$	20,280 23,310	+ 2.18 − 0.20	Λ
$(-)_{589} - [Co\,(en)_3]^{3+}$	20,280 23,310	− 2.18 + 0.20	Δ
$(+)_{589} - [Co\,(S-pn)_3]^{3+}$	20,280 22,780	+ 1.95 − 0.58	Λ
$(+)_{589} - [Co\,(.R-pn)_3]^{3+}$	21,000	+ 2.47	Λ
$(+)_{589} - [Co\,(S-ala)_3]$	18,500 21,000	+ 1.3 − 0.2	Λ
$(+)_{495} - [Co\,(S-glu)(en)_2]^{2+}$	19,600	+ 2.5	Λ

(2) Isomerism due to non-planarity of chelate rings : In addition to the dis-symmetry generated by the tris (chelate) structure of octahedral complexes, ligands also have dis-symmetric structure, for example, the gauche confirmation of ethylene diamine could be resolved. Attachment of the chelate ligand to a metal retains the chirality of gauche form, but the two enantiomers can still interconvert through a planar confirmation at a very low energy. Thus, it is possible in principle to describe two enantiomers of a complex such as $[Co\,(NH_3)_4\,(en)]^{3+}$. In practice it proves to be impossibnle to isolate them because of the rapid interconversion of the ring conformers.

If two or more rings are present in one complex, they can interact with each other and certain conformations might be expected to be stabilised as a result of possible reduction in interatomic repulsions. For example, consider a square planar complex containing two chelated rings of ethylene diamine. We might expect to find three structures, which may be formulated $M\delta\delta$, $M\lambda\lambda$ and $M\delta\lambda$ (identical to $M\lambda\delta$). The first two molecules lack a plane of symmetry, but $M\,\delta\lambda$ is a meso form. According to Carey and Bailar, the $M\delta\delta$ and $M\lambda\lambda$ should predominate over the meso form since the meso form has unfavourable H−H interactions of the axial-axial and equatorial-equatorial type between the two rings. The enatiomeric $M\delta\delta$ and $M\lambda\lambda$ forms are expected to be about 4 kJ mole^{-1} more stable than the meso isomer.

For octahedral tris (chelate) complexes, we might expect $M\delta\delta\delta$, $M\delta\delta\lambda$, $M\delta\lambda\lambda$ and $M\lambda\lambda\lambda$.These will all be optically active from the tris structure as well, so there are expected to be eight isomers formed. In general, a much smaller number is found, usually only two.

This stereo selectivity is easily observed by using a chiral ligand such as propylene diamine $CH_3CH(NH_2)CH_2NH_2$. The five-membered chelate ring will give rise to two types of substituent positions, those that are essentially axial and those that are essentially equatorial. All substituents larger than hydrogen will cause the ring to adopt a conformation in which the substituent is in an equatorial position. As a result of this strong confirmation tendency $R-(-)$ propylene diamine bonds preferentially as a λ chelate and $S-(+)$ propylene diamine bonds as a δ-chelate. This reduces the number of expected isomers to four

$$D-M\delta\delta\delta\ (= D-M\delta\delta\delta),\ D-M\lambda\lambda\lambda\ (= D-M\lambda\lambda\lambda),\ D-M\delta\delta\delta\ (= L-M\delta\delta\delta)$$

and

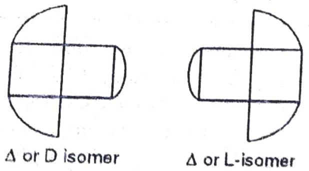
$$\Delta-M\lambda\lambda\lambda\ (= L-M\lambda\lambda\lambda)$$

where Λ, Δ D and L refers to the absolute configuration about the metal related to $\Lambda-(+)_{589}-[Co(en)_3]^{3+}$ (= the D-enantiomer).

In a reaction such as oxidation of cobalt (II) chloride in the presence of recemic R, S propylene diamine, only two isomers are formed.

$$[Co(H_2O)_6]^{2+} + R-pn + S-pn \xrightarrow{[O]} \Lambda\,[Co(S-pn)_3]^{3+} + \Delta\,[Co(R-pn)_3]^{3+}$$

The difference in stability between the various isomers has been related to preferred packing arrangements of chelate rings about the central metal atom. Thus, the S-propylene diamine forms a δ-chelate ring. The most efficient method of fitting around a metal will be in the form of a left handed helix which minimizes the various repulsions. It has been termed the "|*lel*|" isomer since the C–C bonds are parallel to the three-fold axis of the complex. The alternate isomer in which the ligands form a right handed helix about the metal, is known as the "ob" isomer since the C–C bonds are oblique to the three fold axis. The interactions between the hydrogen atoms of the various rings stabilize the "|*lel*|" isomer by a few kJ per mole.



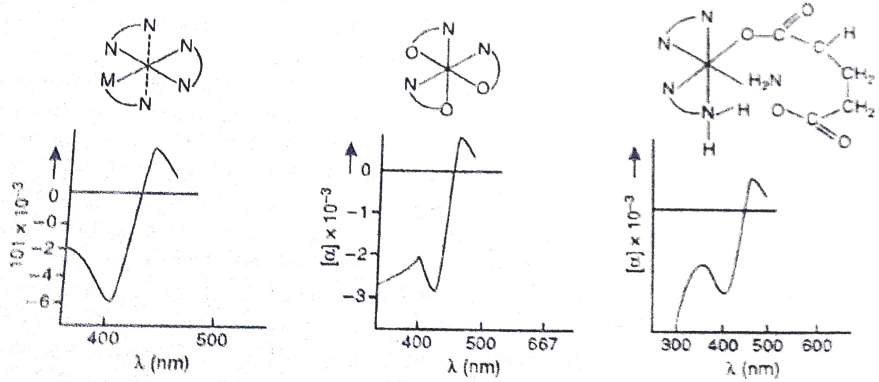


Fig. 5.10 : The absolute configurations and ORD spectra of (a) Λ-$[Co(en)_3]^{3+}$
(b) Λ-$[Co(S\text{-}ala)_3]$ [S-ala → anion of S-(L)-alanine.
(c) Λ-$[Co(en)_2(S\text{-}glu)]^+$ [S-glu = dianion of S-(L) glutamic acid)

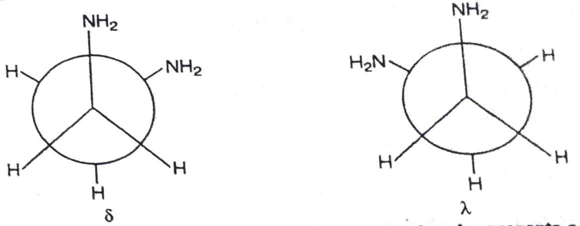


Fig. 5.11 : Enantiomeric conformations of gauche ethylene di-amine. δ represents a right handed helix and λ a left handed helix.

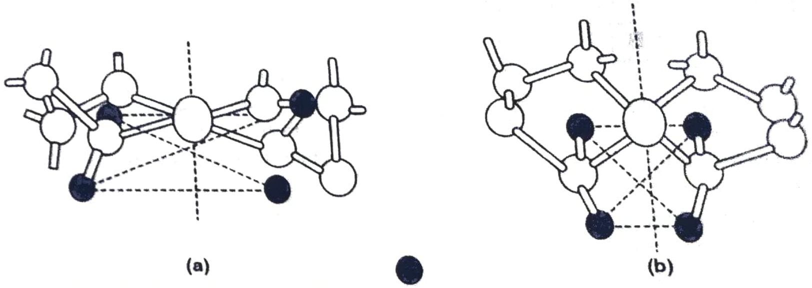


Fig. 5.12 : Conformational interactions in bis-(chelate) square planar complex (a) $\lambda\lambda$ form (b) A δ from (dashed line represents inter ring —H repulsions).

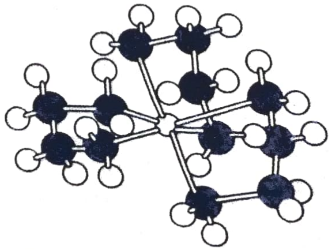


Fig. 5.13 : The lel conformer of the Λ and D enantiomer of the tris (diamine) metal complexes (dashed circles positions of methyl groups in the propylene diamine complex. For propylenediamine, this represents the A$\delta\delta\delta$ or D$\delta\delta\delta$ isomer)