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THE OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM OF COORDINATION COMPOUNDS

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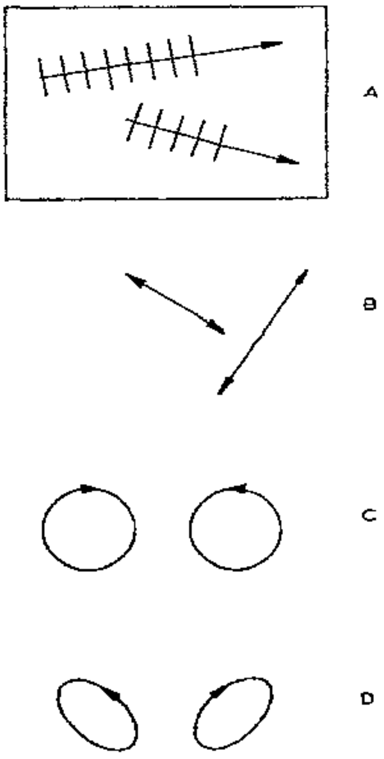
CONTENTS

A. INTRODUCTION

(i) Polarized Light

Optical activity is a change in the direction of the line of polarization of linearly polarized light[1], as it passes through optically anisotropic matter. Optically active chemical compounds are said to rotate the plane of polarization of polarized light, which, by convention, is the plane that contains the electric vector of the light (with the magnetic vector being in a perpendicular plane). Strictly speaking, however, it is preferable to use the term "linear polarized light" rather than "plane polarized light" because the same "plane of polarization" can contain many different directions of linear polarized light (*i.e.*, polarized light with the electric vectors all being in the same plane, see Fig. 1). Consequently, in physics, there appears to be some preference[2] to refer to linear polarized light and to the direction of vibration of the electric vector, rather than to plane polarized light. However,



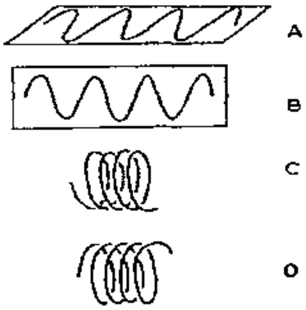


Fig. 1. Two light beams in the same plane of polarization (plane A) possessing different directions of their electronic vibrations (hatch marks), all of which are in plane A; orthogonal pairs of light beams polarized linearly (B), circularly (C), and elliptically (D).

Fig. 2. Forms of a beam of monochromatic light which is polarized linear vertically (A), linear horizontally, right circularly (C), and left circularly (D).

because the term "plane polarized light" has received widespread acceptance in the chemical world, and because its use does not usually introduce any confusion or misunderstanding in chemistry, this term will also be used in this review.

Polarized light[2] is light whose vibration pattern exhibits preference with regard to transverse direction (plane or linear polarized light) or to chirality* (elliptically or circularly polarized light). Fig. 2 contains a representation of plane polarized light travelling from left to right with its electric vector in the plane of the page. The magnetic vector would, of course, be confined to a plane which is perpendicular to the page. Fig. 2 also shows a representation of right-handed circularly polarized light (or elliptically polarized light of which circularly polarized light may be considered a special case in which both axes of the ellipse are equal). Some chemists[1,3] disagree with others[4] and with some physicists[2] regarding the definitions of right-and left-handed circularly polarized light. This author prefers the definition used by the last group, which defines as right-handed circularly polarized light that light in which the wave head of the electric vector traces out a right-handed helix as it rotates continuously around the axis of propagation. The pitch of the helix would correspond to the wavelength, and the radius to the amplitude of the circularly polarized light. This definition is superior to that used by authors who define right circularly polarized light as light whose wave-head travels in a clock-wise direction *when viewed as it travels from the source toward the viewer*, because a right-handed helix (or screw) continues to appear right-handed regardless of the observer's viewpoint. Plane polarized light may be regarded as being the resultant of two interfering components of circularly polarized light of equal amplitude and opposite sense of rotation, as in Fig. 3.

The history of man's knowledge of polarized light dates back to 1669 with the discovery of the phenomenon of double refraction by the Danish scientist Erasmus Bartholinus[5]. Shortly after (1690) Christian Huygens[6] demonstrated the phenomenon of polarization of light by means of two calcite prisms aligned in series with each other. However, it was not until more than a century later that scientists became very interested in polarized light. In 1808 Entienne-Louise Malus, a French physicist, discovered the phenomenon of the polarization of light by reflection[7,8] in a most interesting way. He happened to be looking through a calcite crystal in the Luxembourg Palace in Paris. The light was coming from a palace window at an oblique angle, and Malus noticed that, as he rotated the crystal, the two images produced by the birefringent calcite were alternately extinguished. In 1811, F. Arago discovered the phenomenon of optical rotation[9,10] by certain crystals and J. Biot[11] studied this property of crystals in some detail. In 1812 a Scottish physicist, David Brewster, discovered a relationship concerning polarization of light by reflection, which has since become known as "Brewster's Law"[12]. Biot[13] discovered the phenomenon of dichroism in tourmaline in 1815, and in

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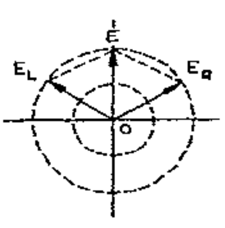
* Handedness, *e. g.*, "right-handed" or "left-handed" (circularly polarized light).

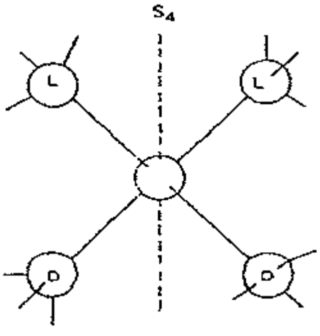
1817 he reported[14] that the ability to rotate the plane of polarized light is not confined to crystals, but is also exhibited by solutions of certain substances such as camphor, sugar, etc. In 1845 the British physicist Michael Faraday discovered the phenomenon of magnetic rotation, the rotation of linearly polarized light by normally optically inactive samples upon their being subjected to a magnetic field[15]. In 1847 the Austrian mineralogist Wilhelm Haidinger discovered[16] the effect known as "circular dichroism" and in 1848 Louis Pasteur, in an elegant paper, outlined criteria necessary for molecules to be able to rotate the plane of polarized light[17].

(ii) Fundamental symmetry requisites for optical activity

Considerable work was done in the late nineteenth and early twentieth centuries on the application of optical rotation to the study of optically active molecules containing tetrahedral atoms of carbon[18,19], boron[20], silicon[21], tin[22], phosphorus[23], arsenic[24], nitrogen[25], sulfur[26], selenium[27], and tellurium[28]. Further, such studies were also carried out with molecules which are optically active because of their over-all dissymmetric structure, even though no asymmetric atom is present, such as in spiro compounds[29], allylenes[30], binuclear aromatics with hindered rotation[31], helicene[32], twisted biphenyls[33], etc.

As a result, it has been determined that the basic stereochemical requirement for a molecule to exhibit optical activity is the absence of a rotation–reflection symmetry axis [34]. Practically speaking, it is not sufficient to state that a molecule will show optical activity if it lacks a center or plane of symmetry; rather, the molecule will exhibit optical activity if its mirror image is non-superposable on the molecule itself[1]. Fig. 4 is an example of a molecule with a four-fold reflection





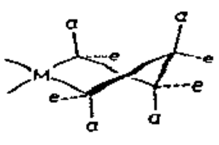


Fig. 3. The resultant of right and left circularly polarized beams of equal amplitude, wavelength, and velocity—a plane polarized beam (OE) of light travelling out of (or into) the page.

Fig. 4. A molecule (with a tetrahedral central atom) containing a four-fold mirror axis but no center or plane of symmetry. The D and L terms refer to *dextro* and *levo* tetrahedral groups on the central tetrahedral atom.

Fig. 5. Optical activity in a complex due to the conformation of a coordinated ligand (ethylenediamine); a = axial H, e = equatorial H.

axis, possessing neither a plane nor a center of symmetry, which is superimposable with its mirror image (and which is therefore optically inactive).

For coordination compounds, optical activity may be expected to occur when (a) an optically active ligand is coordinated to a metal ion in a complex which would otherwise be optically inactive (*e.g.*[35], $[Co(NH_3)_5(l\text{-menthoxyacetate})](NO_3)_2]$, (b) the *configuration* of optically inactive, coordinated ligands about a metal ion produces a dissymmetric molecule or ion (*e.g.*, $[Si(acac)_3]^+$, where acac = acetylacetonate anion[36], [Pt(*meso*-stilbenediamine) (*iso*-butylene-diamine)]$^{2+}$ [37], $[Pt(pyridine)(NH_3)(NO_2)(I)(Cl)(Br)]$[38]), (c) the *conformation* of an optically inactive coordinated ligand produces a dissymmetric molecule[39,40a], (*e.g.*, $[Co(NH_3)_4(en)]^{3+}$, see Fig. 5), or (d) optical activity is induced in a ligand atom upon coordination of the ligand[40b] (*e.g.*, $[Pt(NO_2)_2(N\text{-methyl-}N\text{-ethylglycinate})]^-$, see Fig. 6).

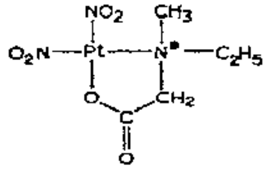
It was not until 1911 that the first optically active coordination compound was resolved into its enantiomers by Alfred Werner[41,42], who, three years later, also resolved the first optically active coordination compound which contains no carbon[43]. Excellent reviews of the application of optical rotatory disperion and circular dichroism techniques to coordination compounds have been published by Woldbye[1,44], Mason[34], Kuhn[45], Gillard[46], Sargeson[47], and Jaeger[48]. In addition, several interesting reviews dealing with theories of optical rotatory power in general have also appeared[49–69].

In this work the primary concern is with the interaction of polarized light (both plane and circular) with matter, and with the information which can be obtained by studying this interaction, especially with regard to the determination of structure of optically active coordination compounds.

B. PRODUCTION AND NATURE OF POLARIZED LIGHT

(i) *Linear (plane) polarized light*

Linearly polarized light (see Introduction) can be produced from natural (unpolarized) light in several ways[3], utilizing for example, double refraction,



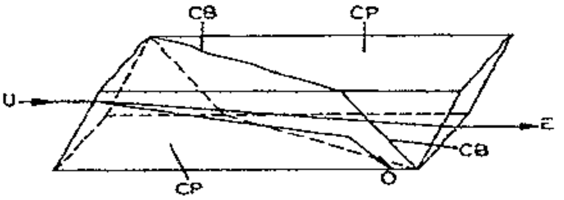


Fig. 6. The induction of optical activity in a ligand atom upon coordination (1).

Fig. 7. A schematic drawing (not to scale) of a Nicol prism, showing the unpolarized beam (U), the ordinary (O) and extraordinary (E) beams, the calcite prisms (CP) and the Canada balsam cement (CB).

reflection, and filter transmission (*e.g.*, Polaroid discs) techniques[1–3]. The usual method used by chemists to produce linearly polarized light of a high degree of polarization with minimum absorption is to pass unpolarized light through a prism constructed of certain birefringent (*i.e.*, "doubly refracting") substances. Anisotropic (rigorously, refractoanistropic) crystals such as calcite ($CaCO_3$) and sodium nitrate exhibit the interesting property of *birefringence* – the ability to split a beam of unpolarized light into two beams (called "ordinary" and "extraordinary" beams), which are refracted differently within the crystal and which emerge at different locations *orthogonally polarized* to each other. By cementing two such crystals with a cement of intermediate refractive index (*e.g.*, Canada balsam for calcite), it is possible to divert one of the beams to a crystal face with a black coating (thereby absorbing it), thus allowing only one of the polarized beams (usually the extraordinary beam) to emerge. This is the principle by which polarizing crystals such as the Nicol and Glan-Thompson polarizers are constructed (Fig. 7). Calcite prisms are usually used for the wavelength region 300 to 800 mμ. For work in the ultra-violet region below 300 mμ, quartz Rochon prisms are frequently used.

(ii) Circular and elliptical polarized light

Both circularly and elliptically polarized light may be produced from a beam of linearly polarized light by resolving it into two beams of linearly polarized light of equal amplitude (travelling in the same direction and polarized orthogonally to each other), one of which is *retarded* with respect to the other. Either circularly or elliptically polarized light will be produced, depending upon the extent of retardation. Circularly polarized light is produced when the retardation is 90° ($\pi/2$) or 270° ($3\pi/2$) and elliptically polarized light is produced at all other retardation values (except 180° [π], which results in a beam of linear polarized light that has been rotated by 90°). Fig. 8 shows how retarding one of two interacting, orthogonal, linearly polarized beams by 90° gives a resultant beam which traces out a left-handed helix of circular cross-section as it progresses[3]. The part of the helix represented by the solid line H is on the reader's side of plane A and above plane B (*vice versa* for the dotted part of the helix), and curves 1 and 2 are the linearly polarized beams which are travelling in the same direction and whose planes of polarization are orthogonal.

The most common methods of producing two orthogonal, linearly polarized waves (one of which is retarded with respect to the other) from a single linearly polarized beam are by passing the beam through a Fresnel rhomb, through a natural crystal* (*e.g.*, quartz, mica, gypsum), or through certain crystals (*e.g.*,

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* When retardation by a crystal of 90^0 ($2\pi/4$), a quarter of one wavelength) is produced, the result is the conversion of a beam of plane polarized light into circularly polarized light. Such a crystal is known as a "quarter-wave plate." For light of wavelength 589 mμ, a quarter-wave plate made of mica has a thickness of 0.032 mm.

ADP [ammonium dihydrogen phosphate]) to which an electric field has been applied along the z-axis (the Pockels' Effect[70–72]). The retardation (phase difference) is proportional to the length of the light path in the crystal (and to the applied electric field, in the Pockels' Effect case), making it relatively simple to produce elliptically (or circularly) polarized light of any desired ellipticity by adjustment of these parameters. Further, the sense of rotation of the transmitted circularly or elliptically polarized light may be reversed by rotating the plane of the incident beam (or the crystal) by 90°, or, in the case of the Pockels cell, by reversing the direction of the applied electric field.

C. INTERACTION OF POLARIZED LIGHT WITH OPTICALLY ACTIVE MATTER

(i) Absorption and dispersion

Dispersion is the wavelength dependence of refractive index. That is, a curve of refractive index of a substance *vs.* wavelength of the incident radiation is known as a dispersion curve because it indicates how light of various frequencies would be dispersed by a prism made of the substance in question[73]. A *dispersion curve* for an optically inactive substance obtained with non-polarized light would be identical to that obtained with linearly or circularly polarized light of either chirality. When light travels from a vacuum into another medium, its frequency remains constant but its velocity and its wavelength are reduced. The index of refraction of the medium ($n_{med.}$) is defined[1] as:

$$n_{med.} = \frac{c_{vac.}}{c_{med.}} = \frac{\lambda_{vac.}}{\lambda_{med.}} \tag{1}$$

Absorption is the reduction of the intensity of incident light (I_0) as it passes through a substance[1,74]. This absorption increases exponentially with increasing

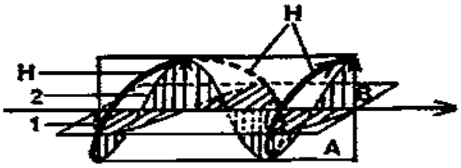


Fig. 8. A schematic diagram showing the conversion of linearly polarized light, into circularly polarized light, by resolution of the linearly polarized light into two orthogonal linearly polarized beams, one of which is then retarded with respect to the other (see text).

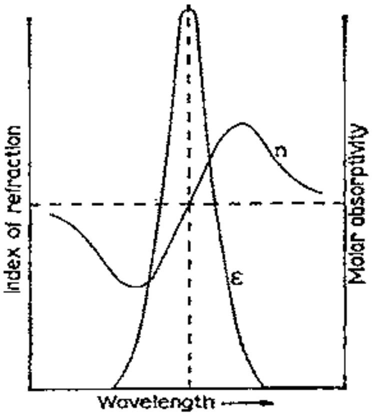


Fig. 9. Theoretical absorption (n) and dispersion (ϵ) curves of a substance.

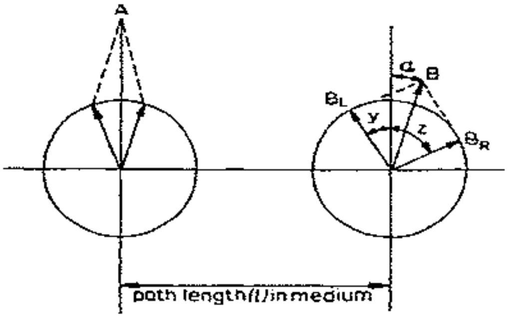


Fig. 10. A. Linear polarized light (A) [as it enters an optically active medium] considered as a resultant of two like beams of circularly polarized light of opposite chirality; B. the rotation of the line of polarization of linearly polarized light by an optically active substance (shown as it leaves that substance) which slows (retards) beam B_L more than beam B_R.

distance travelled in the medium, and, for solutions, with increasing concentration of the solute, according to the equation:

$$I = I_0(10^{-\varepsilon lc}) \tag{2}$$

where I is the intensity of the transmitted light, c is the molar concentration, l the path length, and ε the molar extinction coefficient (a characteristic of each substance). The wavelength dependence of the absorption of light of different frequencies by a substance is known as its *absorption spectrum*. Theoretical absorption and dispersion curves are shown in Fig. 9.

(ii) Optical activity

As was mentioned earlier, *optical activity* (I) is the change in direction (rotation) of the plane (strictly, the line) of polarization of plane (linear) polarized light by an anistropic medium (a pure substance or a solution).

Linear polarized light may be regarded as the resultant of beams of right and left circularly polarized light of equal intensity and frequency (Fig. 10). A medium will exhibit optical rotation[1,3] if it possesses different indices of refraction for right and left circularly polarized light; such a medium is said to be *circularly birefringent*[3,44]. Fig. 10 illustrates how the differences in indices of refraction (velocities) of the two beams result in the rotation of plane of polarization. Consider that the two beams enter the optically active medium in phase as linear polarized light, with their resultant wave heads at point A. As they travel through the medium, consider that one of the beams (B_L) travels more slowly (is retarded more) than the other (B_R). It can be seen that, upon emerging from the medium, the resultant beam is *still linearly polarized*, with its plane of polarization having been rotated by an amount α.

If the path length of the beam in the optically active medium (between points A and B of Fig. 10) is represented by l, then, from equation [1], the wavelengths of the two beams of circularly polarized light are $\lambda_{vac.}/n_L$ and $\lambda_{vac.}/n_R$. Further, in the distance l there are contained $ln_L/\lambda_{vac.}$ and $ln_R/\lambda_{vac.}$ full waves of the two beams B_L and B_R. The difference in the number of waves is therefore $l(n_L-n_R)/\lambda_{vac.}$, and the phase difference $(z-y)$ is $2\pi l(n_L-n_R/\lambda_{vac.}$, or

$$z = y+2\pi l(n_L-n_R)/\lambda_{vac.} \tag{3}$$

$$\alpha = (z-y)/2 = \pi l(n_R-n_L)/\lambda_{vac.} \tag{4}$$

Equation [4] is the Fresnel equation[75] for optical rotation (α).

It should be emphasized at this point that optical rotation is a property which is extremely sensitive to small variations in structure (*e.g.*, the type of difference between *meso*- and *dextro*-tartaric acid) which give rise to small differences in refractive index. For example, if one solves equation [4] for n_L-n_R for a sucrose solution (0.3 g./100 ml water) at 20° C in a 10 cm tube at the sodium D line ($\lambda = 5890\times10^{-8}$ cm) which has an observed optical rotation of 0.2°, then n_L-n_R is 6.5×10^{-9}. That is, the difference between the indices of refraction of the solution for right and left circularly polarized light is less than one part in one hundred million—and this difference is easily detected polarimetrically!

Optical rotation is also the quantity (radians or degrees) by which an anisotropic medium rotates the line of linearly polarized light. Chemists customarily measure the *observed optical rotation*, $\alpha^t_{\lambda\ \mathrm{obs.}}$, in terms of degrees per decimeter[1,3] and they report the wavelength of the incident radiation and the temperature of the sample. In practice, the observed rotation of a sample is measured by reading the angle indicated by a polarimeter containing the sample (either a pure substance or a solution) in sample tube (often one decimeter long) and subtracting from this reading the angle indicated for the tube containing only the solvent (in the case of solutions) or the tube containing air (in the case of pure substances), all measurements being made at the same temperature and with incident radiation of the same wavelength.

Since, under ordinary conditions, optical rotation is proportional to concentration, the *specific rotation*, $[\alpha]^t_\lambda$, is often reported for solutions containing optically active solutes, as:

$$[\alpha]^t_\lambda = \alpha^t_{\lambda\mathrm{obs.}}/cl_d \tag{5}$$

where c is the concentration in grams per milliliter of the solute (or density, for a pure substance), and l_d is the path length in decimeters. Although this quantity has been widely used for solutions of a compound at different concentrations, it should be emphasized that the specific rotation is not a constant under all conditions[3,76]. The experimental units of specific rotation[3] are degrees-cm^2 g$^{-1}\times10$, although these are usually not reported with specific rotation data in the literature.

In order to compare different compounds containing the same optically active unit (*e.g.*, $[Co(en)_3]Cl_3$ and $[Co(en)_3]Br_3$), it is advantageous to utilize the *molecular rotation*, $[M]^t_\lambda$, since (assuming that the optically inactive anions exert identical effects on the rotation of the cation) the two compounds will not show the same specific rotation (because they have different numbers of optically active groups per gram), but they will show the same molecular rotation (since they have the same number of optically active groups per mole). Molecular rotation (or molar rotation, [M] or [ϕ]) is defined[1,3] as:

$$[M]_\lambda^t = [\alpha]_\lambda^t \left(\frac{M}{100}\right) = \frac{\alpha_{\lambda\text{obs.}}^t}{[C]l_m} \tag{6}$$

where M is the molecular weight of the solute, [C] is its molar concentration, and l_m = the path length in meters. A recent proposal[1,3], with which this author concurs, is to name the unit of specific rotation after Biot, 1 Biot [B] = 1.74533 [α], and the unit of molecular rotation after Cotton, 1 Cotton [C] = 1.74533 [M].

For a comparison of compounds containing the same optically active unit, but different numbers of this unit per molecular unit (*e.g.*, $[Co(en)_3](NO_3)_3$ and $[Co(en)_3]_2(SO_4)_3$, in which the latter contains two optically active complex ions per formula unit, whereas the former contains only one), it is of considerable advantage to employ the *equivalent rotation*, $[E]_\lambda^t$, since (again assuming that the anions exert identical effects on the rotation of the cation) the two compounds will not have the same specific or molecular rotations, but they will have the same equivalent rotation[77]. Equivalent rotation is defined[77] as:

$$[E]_\lambda^t = \frac{[M]_\lambda^t}{\bar{n}} \tag{7}$$

where n is the number of optically active units per molecule or formula unit.

(iii) Optical rotatory dispersion

Optical rotatory dispersion (ORD) is the wavelength dependence of optical rotation. The indices of refraction of a medium for circularly polarized light (n_L and n_R) are not constant, but vary with the wavelength of the incident radiation, according to the Sellmeier equation[53]:

$$n^2 = 1 + \Sigma[(D_m{}^2)/(\lambda^2 - \lambda_m{}^2)] \tag{8}$$

where D_m is a constant which is a function of the oscillator strength at the wavelength of the absorption band, λ_m, and which is characteristic of the medium, λ is the wavelength of incident radiation, and λ_m refers to the wavelengths of the absorption bands. P. Drude developed an equation[53,78] to describe the ORD of a substance in the wavelength region outside an optically active absorption band:

$$[\alpha] = \Sigma[(c_m)/\lambda^2 - \lambda_m{}^2)] \tag{9}$$

where c_m is a constant that depends on the number of absorption peaks and other factors of a given medium. The Drude equation is usually expressed with one or

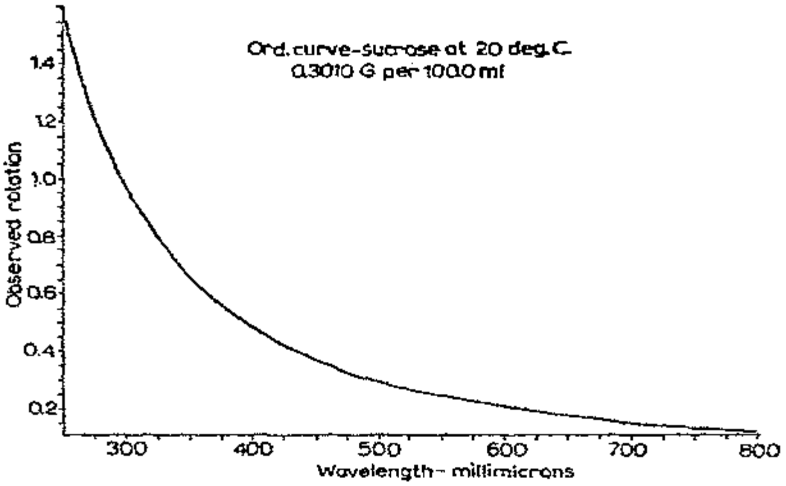


Fig. 11. A computer-produced and drawn normal optical rotatory dispersion curve for *dextro*-sucrose at 20° C.

two terms, depending upon the number of important absorption bands. Additional terms may be necessary if more than two absorptions influence the normal ORD outside the absorption region:

$$[\alpha] = \frac{C_1}{\lambda^2 - \lambda_0{}^2} + \frac{C_2}{\lambda^2 - \lambda_1{}^2} \tag{10}$$

where λ_0 and λ_1 are the wavelengths of the absorption bands ($\lambda_0 > \lambda_1$). It is possible to program a computer[79] to produce a normal optical rotatory dispersion curve from a Drude equation (see Fig. 11). It is also possible to determine graphically, by a method described by Heller[80], whether a one-term Drude expression adequately describes the optical rotatory dispersion of a system outside its absorption band. Rearrangement of equation [10] as a one-term Drude expression gives:

$$\frac{1}{[\alpha]\lambda^2} = \frac{1}{C_1} - \frac{\lambda_0{}^2}{C_1\lambda^2} \tag{11}$$

and it can be seen that, if the data are adequate, a plot of $1/[\alpha]\lambda^2$ *vs.* $1/\lambda^2$ will give a straight line, the slope and intercept of which can give C_1 and λ_0. The use of Drude equations of more than one term is more complex[3,53].

(iv) Optical circular dichroism

It should be emphasized that the previous discussion of optical activity and optical rotatory dispersion was confined to those phenomena as they appear for substances being studied in wavelength regions outside their absorption bands. The same phenomena also occur inside the absorption regions, but some other phenomena also occur in these wavelength regions which do not occur outside them. *Optical circular dichroism* (CD) is the differential absorption by a medium of right and left circularly polarized light[1,3,4,54]. Further, incident *linear* (plane) polarized light (considered a resultant of like beams of right and left circularly polarized light), having a wavelength inside the absorption band of a circularly dichroic medium, leaves that medium both with its line (plane) of polarization having been rotated *and* also with itself having been converted into *elliptically* polarized light. The medium is said to exhibit "circular dichroism", which results from the different electronic transition probabilities when optically active molecules are excited by right and left circularly polarized light inside an optically active absorption band[81,82]. Fig. 12 shows the conversion of linear polarized light (Y) into elliptically polarized light as a result of unequal absorption of the right and left circularly polarized components of the incident linear (plane) polarized light. The greater absorption (smaller transmission) of the left component is shown in this diagram as a shorter vector (E_L), and, as the two vectors (E_L and E_R) in this diagram rotate counter-clockwise and clockwise, respectively, the resultants (E) at all points in time lie on the ellipse shown.

Further, Fig. 12 also shows how the "line" of polarization has been rotated from Y to B (by the angle α) as a result of the unequal velocities of transmission of the two beams (E_L and E_R) through the optically active medium (α is the angle between the incident beam and the major axis of the ellipse). Still further, Fig. 12 shows the angle of ellipticity (ψ) of the elliptically polarized light, which is the angle formed by the major axis (OB) and a line (OD) drawn from the origin through the end of the minor axis (OA) which has been displaced to the tip of the ellipse (BD).

Since the major and minor axes of the ellipse represent the vector sum and difference, respectively, of the amplitudes (p) of the two circular components of the elliptically polarized light which emerges from the medium, then the tangent of the angle of ellipticity (ψ) is:

$$\tan(\psi) = \frac{p_R - p_L}{p_R + p_L} \tag{12}$$

Since the intensity (I) of this radiation is proportional to the square of the amplitude of the electric vector, and since

$$I_L = (\tfrac{1}{2}) I_0 \times 10^{-\varepsilon_L lC} \qquad \text{and} \qquad I_R = (\tfrac{1}{2}) I_0 \times 10^{-\varepsilon_R lC} \tag{13}$$

then

$$\tan(\psi) = \frac{10^{-(\frac{1}{2})\varepsilon_R lC} - 10^{-(\frac{1}{2})\varepsilon_L lC}}{10^{-(\frac{1}{2})\varepsilon_R lC} + 10^{-(\frac{1}{2})\varepsilon_L lC}} \tag{14}$$

Now, if a and b are defined as:

$$a = -(\ln 10) lC \left(\frac{\varepsilon_L + \varepsilon_R}{4}\right) \tag{15}$$

$$b = (\ln 10) lC \left(\frac{\varepsilon_L - \varepsilon_R}{4}\right) \tag{16}$$

then

$$\tan(\psi) = \frac{e^{a+b} - e^{a-b}}{e^{a+b} + e^{a-b}} = \tanh b \tag{17}$$

Since the ellipticity (ψ) is normally quite small (because the difference in the absorption of right and left circularly polarized light by a medium is normally quite small), then[1]:

$$\psi \text{ (in radians)} \cong \tan \psi \text{ (ψ in degrees)} = \tanh\left[(\ln 10)lC\left(\frac{\varepsilon_L - \varepsilon_R}{4}\right)\right] \cong (0.576)lC(\varepsilon_L - \varepsilon_R) \tag{18}$$

where C is the molar concentration and l is the path length in cm.

Under ordinary circumstances specific and molar ellipticity are defined analogously to specific and molar rotation, that is, specific ellipticity, $[\psi]^t_\lambda$, is

$$[\psi]^t_\lambda = \frac{\psi^t_\lambda}{c l_d} \tag{19}$$

where c is the concentration in g/ml and l_d is the path length in dm (for solutes in solution). For pure substances, c in equation [19] is replaced by ρ, the density of the substance. Molar ellipticity, $[\theta]^t_\lambda$, is

$$[\theta]^t_\lambda = [\psi]^t_\lambda (M/100) = \frac{\psi^t_\lambda}{C l_m} \tag{20}$$

where M is the molecular weight of the substance (or solute), C is the molar concentration of the solute, and l_m is the path length in meters.

From equations [18] and [20] the molar ellipticity is

$$[\theta]^t_\lambda = 57.6(\varepsilon_L - \varepsilon_R) \text{ (in radians-cm}^{-1}\text{mole}^{-1}\text{ml} \times 10^1\text{)} \tag{21}$$

or, more commonly,

$$[\theta]^t_\lambda = 3300(\varepsilon_L - \varepsilon_R) \text{ (in deg-cm}^{-1}\text{mole}^{-1}\text{ml} \times 10^1\text{)} \tag{22}$$

Usually circular dichroism curves are plots of wavelength *vs.* $[\theta]$ or $(\varepsilon_L - \varepsilon_R)$. Experimentally, $\Delta\varepsilon$ (the circular dichroic absorption) may be determined[54] from the equation:

$$\Delta\varepsilon = \Delta D / Cl \tag{23}$$

where ΔD is the circular dichroic optical density ($D_L - D_R$, or circular dichroic absorbance, $A_L - A_R$), C is the molar concentration, and l is the path length in cm.

D. THE COTTON EFFECT

In the late nineteenth century, Cotton[83] studied optical rotatory dispersion curves of compounds in the region of their absorptions, where both optical rotation and circular dichroism occur simultaneously. He noticed that not only is it possible to observe the circular dichroism and ellipticity in an absorption region, but also that the shape of optical rotatory dispersion (ORD) curves inside the absorption region differs markedly from their shape outside these regions. For many years ORD curves inside absorption regions were referred to as "anomalous" ORD curves, but this is erroneous, since this shape is the usual one for ORD curves inside these regions. The combination of the appearance of circular dichroism (and ellipticity) and an "S"-shaped ORD curve for an optically active compound inside its absorption region is today known as the *Cotton Effect.*

In the early part of the twentieth century, Natanson[84] noticed a relationship between the ORD and CD spectra of a compound, which is now known as *Natanson's Rule.* It states that the contribution to the circular birefringence of a compound on the high wavelength side of a given absorption band has the same sign as the circular dichroism of that compound in that band. It should be noted that the sign of the optical rotation of a compound on the high wavelength side of a given absorption band may not be identical with the sign of the circular dichroism in that band because of relatively strong effects of other absorption bands in the compound. Fig. 13 shows the relationship between ORD and CD curves in the region of an optically active absorption band. The smoothly ascending or descending ORD curves observed outside absorption regions are called "plain" or "normal" dispersion curves, and the sign[4] of such an ORD curve is commonly referred to as "positive" or "negative" depending upon whether the optical rotation becomes more positive or more negative with *decreasing wavelength.*

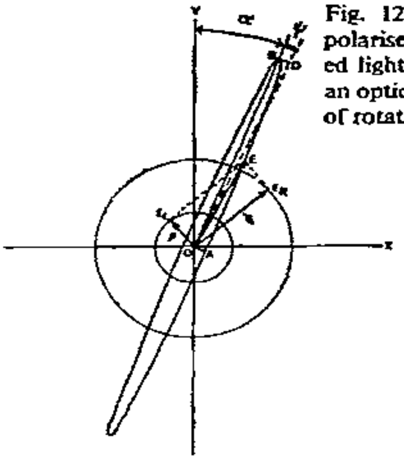


Fig. 12. The conversion of plane polarised light to elliptically polarized light in the absorption region of an optically active medium; α, angle of rotation; ψ, angle of ellipticity.

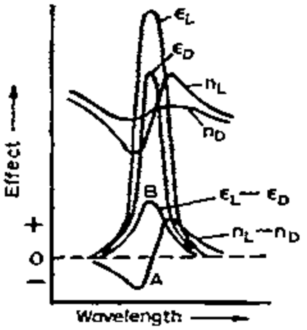


Fig. 13. An idealized Cotton Effect inside an absorption band. A: an ORD curve; B: a CD curve in the same band.

The sign of the Cotton Effect inside absorption regions is commonly referred to as "positive" or "negative" depending upon whether $\varepsilon_L - \varepsilon_R$ is positive or negative, or depending upon whether the peak (most positive rotation) of an ORD curve occurs at higher or lower wavelengths than the trough (most negative rotation). Heller (ref. 3, p. 2312) points out some cautions to note when using this terminology.

The molecular amplitude (a) of a Cotton Effect measured by ORD[85,4] is defined as the difference between the molecular rotation at the extremum (peak or trough) at the higher wavelength ($[M_1]$) and that at the lower wavelength ($[M_2]$), divided by 100:

$$a = \frac{[M_1]-[M_2]}{100} \tag{24}$$

For a compound exhibiting a positive Cotton Effect which has a molar rotation of +6950° at 312 mμ and −6870° at 276 mμ, the molecular amplitude will be +138°. The *breadth* (b) of a Cotton Effect measured by ORD is the difference (in mμ) between the wavelengths of the peak and trough of the curve. In the above example, b is 36 mμ. When Cotton Effects are measured by ORD techniques, the *crossover wavelength* (λ_0) is also usually mentioned. This is the wavelength at which the optical rotation is zero (as the curve goes from positive to negative rotations, or *vice-versa*.

When the Cotton Effect is measured by CD techniques, the sign of the curve and the wavelengths and molar ellipticities (or $\varepsilon_L - \varepsilon_R$) of the maxima and minima are usually identified, and the *bandwith* Γ, (the difference in mμ between the two wavelengths of the curve at half the maximum height) is also often mentioned[4].

(i) Relationships between ORD and CD

Compounds do not exhibit any circular dichroism at all in wavelength regions where $\varepsilon_L = \varepsilon_R$, (*e.g.*, in regions of no absorption), and the interaction of such substances with polarized light in these wavelength regions may be studied only by polarimetric or ORD techniques. Further, the applicability of the Drude equation to the quantitative study of ORD curves is limited to regions outside the absorption band. However, for wavelength regions inside absorption bands, Kuhn and Braun [86,87] have developed quantitative expressions to describe the Cotton Effect, and have also developed equations describing the relationship between $\varepsilon_L - \varepsilon_R$ and $n_L - n_R$. Kronig[88] and Kramers[89] have demonstrated that it is possible to predict a dispersion curve over the entire spectral range from a knowledge of the corresponding absorption as a function of wavelength. The Kronig–Kramers relationships are well-described in a paper by MacDonald and Brachman[82,90]. Moffitt and Moscowitz[32,50,51,59,91] in several excellent papers have developed general relationships between ORD and CD. One of the most useful is the expression:

$$a = 0.0122[\theta] \tag{24}$$

which relates the molecular amplitude of an ORD curve to the molecular ellipticity of the corresponding CD curve.

Rotatory strength. In his work mentioned above, Kuhn utilized a "coupled oscillator" model as the basis for his descriptions (*vide infra*). Condon [51] and Moscowitz[50,91] used quantum mechanical treatments and obtained essentially identical results. In the quantum mechanical studies by these latter workers and by Rosenfeld[92a], the contribution to the total optical rotation of an electronic transition from state a to state b is determined by the Rotatory Strength (R_{ba}) of that transition, where the Rotatory Strength is defined as the imaginary part of the scalar product of the electric and magnetic dipole moments associated with that transition. Selection rules for these electronic transitions are described by Mason[34], and it should be pointed out that it is possible to calculate rotatory strengths from ORD and CD data[1].

(ii) Theories of optical activity in coordination compounds

There are three primary models which theoreticians have utilized in attempts to explain the optical activity of coordination compounds. They are the coupled oscillator model of Kuhn and Bein[92b,51], the ionic (or crystal field) model utilized by Moffitt[51] and extended by Hamer[92c], Piper and Karipides[92d], Poulet[92e], and Sugano Shinada[92f], and the molecular orbital model used by Liehr[55], Mason and McCaffery[34,92g], Caldwell and Eyring[92h], and Maaskant and Oosterhoff[92i]. All three have had some success in describing and predicting the structure of certain optically active systems. The first is being revised because of incorrect predictions of absolute configuration. The second and third have proven quite attractive and are being expanded by several investigators.

(iii) Instrumentation

Optical rotation. The technical considerations attendant upon the measurement of optical rotation, optical rotatory dispersion, and circular dichroism are already well-described in the literature[1–4,49,50,53,54,57,93]. Some of the major manufacturers of commercial instruments designed to measure optical rotation at one or a few wavelengths are Rudolph[94], Zeiss[95], Galileo[96], Perkin-Elmer[97], Bellingham and Stanley[98], Hilger[99], Bendix[100], DuPont[101], Polyscience[102], and Schmidt and Haensch[103]. There is a wide variation in accuracy (0.1 to 10^{-4}

degrees of arc), principle of operation, degree of flexibility, detection methods (*e.g.*, use of the eye *vs.* photoelectric cells), and price.

Optical rotatory dispersion. Instruments designed to determine the ORD of optically active compounds, either manually or by recording the ORD curves automatically, also vary greatly in accuracy, mode of detecting optical rotation (oscillating analyzer or polarizer, Faraday effect, etc.), sensitivity, cost, and other factors. Some of the manufacturers mentioned above[94,95,97,98] also produce ORD instruments designed to measure optical rotation as a function of wavelength in the visible and ultra-violet regions. In addition, such instruments are produced by others, including Cary[104], Jasco[105], and Shimadzu[106]. Kirschner and co-workers[107], Keston and Lospalluto[108], Woldbye[109], Carroll and co-workers[110], Savitzky and coworkers[111a], and Nebbia and co-workers[111b], have constructed such instruments in their own laboratories. In addition to the investigators just mentioned, Snatzke[112] and Roy and Carroll[113] have described some of the principles of operation of ORD and CD instruments.

Circular dichroism. Some of the manufacturers mentioned above also produce instruments for the determination of circular dichroism, either manually[106], or by automatic recording devices[104,105], usually in conjunction with ORD instruments. Beckman[114] and Jouan[114] manufacture instruments which automatically record CD only, and Cary[104] and Rehovoth[115] produce attachments for spectrophotometers for the determination of CD curves. CD instruments and attachments also vary considerably with regard to the factors mentioned above for ORD instruments, and with regard to the methods used for the production of circularly polarized light[1]. The most commonly used methods involve quarter-wave plates, Fresnel rhombs, or crystals of ammonium dihydrogen phosphate (ADP), upon which is imposed an alternating longitudinal electric field. An interesting technique for the determination of CD has also been described by Arvedson and Larsen[116].

(iv) The production of optically active coordination compounds

Reviews by Kirschner[77], Woldbye[1], and Jones[117] have been published which deal with techniques for the synthesis and resolution of optically active coordination compounds, and the reader is referred to them for information in this field.

(v) Environmental effects on the ORD and CD of optically active coordination compounds

Temperature. It is important that the temperatures at which optical rotations, ORD curves and CD curves are determined, be reported. Temperature changes may result in changes of optical rotation[1,3] as a result of volume changes and changes in the optical rotatory power of molecules themselves. The latter changes may be due to solvation changes, dipole–dipole interaction changes, changes in the degree of ion and/or molecule association, changes in equilibria between solute and solvent, changes in configurations and/or conformations of optically active species, and changes in the rates of configuration or conformational changes. Tartaric acid is a notorious example in that its specific rotation may vary by more then 10% per degree centigrade at 25 °C. Insufficient work has been done in this area of ORD and CD and there is a need for additional studies on the temperature dependence of the ORD and CD of optically active compounds.

Solvent. The effect of solvent on ORD and CD is another area where far too little work has been done. There is little question that the refractive index of a solvent plays an important role in the observation of different rotations for the same compound in different solvents[82,118]. Kauzmann, Walter, and Eyring[51], Condon[51], and Weigang[119] have studied this problem from a theoretical approach, but more remains to be done. Kirschner and co-workers[120] have studied the ORD of the ionic complex $[Ru(o\text{-phenanthroline})_3](ClO_4)_2$, and have noted that in solvents of low dielectric constant, both ionic association and optical rotation are enhanced. In solvents of high dielectric constant (*e.g.*, water) there is very little association between the perchlorate anion and the complex cation, but there is considerable association between the polar solvent and the complex, which results in a marked enhancement of the optical rotation of the complex. Similar solvent effects have also been observed in organic systems[121]. Bosnich [121a] has observed the appearance in the visible region of an interesting negative CD peak for the $[PtCl_4]^{2-}$ anion in an optically active, colorless solvent, *d*(−)-2,3-butanediol.

Concentration. It should be emphasized at this point that although the specific rotation described by equation [5] is usually constant under normal experimental conditions, it is by no means constant at all concentrations. Heller[3] describes the situation in some detail and gives some equations for the concentration dependence of specific rotation. Woldbye[2] has studied the effect of salt concentration and Larsson[122] has interpreted the observed effects in terms of "outer-sphere" complexation. McReynolds and Witmeyer[123] and Kirschner and his co-workers[107,120,124] have studied the effects of optically inactive ions on the ORD of optically active complex ions. The latter authors have concluded that the primary effect is an alteration of the rotatory strength at the peak and trough wavelengths in the absorption region, and that this effect depends upon the degree of association of the ions of opposite charge. McReynolds and Witmeyer[123] have also worked on this problem. Smith and Douglas[125] have described the effects of optically inactive ions on the CD of complex cations and have also observed that the rotatory strengths of the observed transitions are quite sensitive to changes in the symmetry of the complex ion as a result of interactions with the inactive anions. Mason and Norman[126] have studied "outer-sphere" complex formation, and the effects of this phenomenon on the CD of some systems containing optically active, colorless, organic species which interact with optically inactive, colored complex cations. They describe the appearance of a CD curve at a visible absorption peak of the optically inactive complex cation and attribute its appearance to the formation of hydrogen bonds between ligands of the complex and the optically active organic compound.

E. THE PFEIFFER EFFECT

An important environmental effect on optical rotation is one which has been observed by Pfeiffer and Quehl[127], and which is now referred to as the "Pfeiffer Effect." They observed that the optical rotation of a solution of an optically active substance (*e.g.*, ammonium *d*-α-bromocamphor-π-sulfonate, also called the optically active "environment" compound) changes upon the addition of solutions of racemic mixtures of certain coordination compounds (*e.g.*, D, L-[Zn(*o*-phenanthroline)$_3$](NO$_3$)$_2$). Kirschner and Magnell[128] describe the effect in some detail. The effect has also been studied by Brasted[129] and his students[130–132], Dwyer and co-workers[133], and Kirschner and co-workers[134]. Kirschner, Nasir and Magnell[135] have reported the rate of appearance of the effect is exactly the same as the rate of racemization of the complex itself, and they have also found that the effect can be applied to the resolution of certain complexes. Fig. 14 shows the ORD of the Pfeiffer Effect for the system in which an environment compound (ammonium *d*-α-bromocamphor-π-sulfonate) in water is treated with racemic [Ni(*o*-phenanthroline)$_3$]SO$_4$. Kirschner and Magnell[128] have proposed a quantitative treatment of the Pfeiffer Effect in a manner analogous to that used for optical rotation. The *observed Pfeiffer rotation* $(\mathrm{P}^t_\lambda)_{\mathrm{obs.}}$ is defined as:

$$(\mathrm{P}^t_\lambda)_{\mathrm{obs.}} = \pm(\alpha_{e+c} - \alpha_e) \tag{25}$$

where α_{e+c} is the observed rotation of the solution containing both the complex and environment compounds, and α_e is the observed rotation of the solution containing only the environment compound. The sign to be used before the parentheses is the same as the sign of α_e. *The specific Pfeiffer rotation*, $[\mathrm{P}]^t_\lambda$, is defined as:

$$(\mathrm{P}^t_\lambda)_{\mathrm{obs.}} = (\mathrm{P})_{\mathrm{obs.}}/(c)\,(e)\,(l_\mathrm{d}) \tag{26}$$

where *c* and *e* are the concentrations (in g/ml) of the complex and environment compounds, respectively, and l_d is the path length in decimeters (see eq. [5]). Equation [26] holds for Pfeiffer active systems, but its accuracy falls off at high concentrations (also see p. 478). *Molar Pfeiffer rotation* $[\mathrm{P_M}]^t_\lambda$ is correspondingly defined as:

$$[\mathrm{P_M}]^t_\lambda = \frac{\mathrm{P_{obs.}}}{[C]\,[e]\,d_m} \tag{27}$$

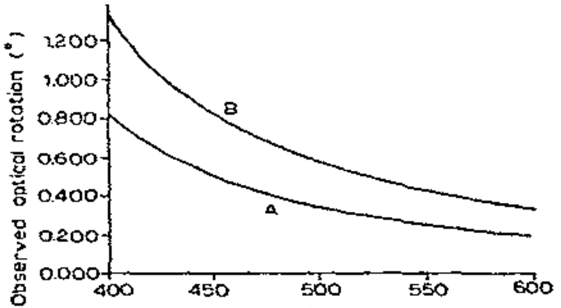
where $[C]$ and $[e]$ are the molar concentrations of the complex and environment compounds, and d_m is the path length in meters (see eq.[6]).

Dwyer and Gyarfas[133] have proposed that a shift in the equilibrium between the enantiomers of the optically labile complex occurs in the presence of an optically active environment substance, and there is some evidence in support of this idea[128].

F. ABSOLUTE CONFIGURATION AND CONFORMATION

One of the most important applications of ORD and CD studies has been in the area of absolute configuration and conformation of dissymmetric coordination compounds. Early work in the field was based upon the supposition that closely related compounds of the same absolute configuration should exhibit similar ORD and CD curves[48,136]. However, it was not until the work of Saito and co-workers[137] that coordination chemists had an X-ray structure which gave the absolute configuration of a complex. These workers demonstrated that the absolute configuration of the $[Co(en)_3]^{3+}$ cation (en = ethylenediamine) in crystalline $2(+)_{589}$-$[Co(en)_3]Cl_3 \cdot NaCl \cdot 6H_2O$ is that shown in Fig. 15. In this figure, the curved line represents a bidentate ethylenediamine ligand.

The use of curved lines to represent multidentate chelating agents can be misleading, they give the appearance that the chelate rings are planar. Actually these rings are often non-planar and, in an important paper in 1959, Corey and Bailar[39] undertook a conformational analysis of such non-planar rings. They found that, upon chelation, the ethylenediamine adopts either of two enantiomorphic conformations (which they call *k* and *k'*), in which the ligand chains form segments of left- and right-handed helices, respectively. Further, for a complex with three such bidentate rings, four possible conformational isomers may exist[138], with the rings



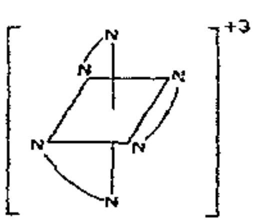


Fig. 14. The Pfeiffer Effect. A: ORD of 0.016 *M* ammonium *d*-α-bromocamphor-π-sulfonate in water; B: The ORD of an aqueous solution of 0.016 *M* ammonium *d*-α-bromocamphor-π-sulfonate which is also 0.008 *M* in D, L-$[No(o\text{-}phen)_3]SO_4$.

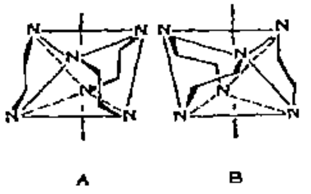
Fig. 15. The absolute configuration of the $(+)_D$-$[Co(en)_3]^{3+}$ cation.

being *kkk*, *kkk'*, *kk'k'*, and *k'k'k'*. That all four conformers of both the $(+)_D$-$[Co(en)_3]^{3+}$ cation and its opposite enenatiomer may exist is in conformity with thermodynamic considerations[44]. Fig. 16 shows schematic diagrams of the conformations of these rings for the *kkk* isomers of $(+)_D$-$[Co(en)_3]^{3+}$ (called *lel* because the carbon–carbon bonds of the ligands are parallel to the three-fold $[C_3]$ symmetry axis) and of the $(-)_D$-$[Co(en)_3]^{3+}$ cation (called *ob* because the C—C bonds of the ligands are oblique to the C_3 axis). Dwyer and co-workers[40a,139] have shown that the *lel* conformation is more stable than the *ob* by a free energy of 0.6 kcal per ring.

(i) Nomenclature

There has been some confusion among coordination chemists and others regarding the nomenclature used to represent the absolute configuration of optically active coordination compounds. Although there has been practically unanimous agreement that the isomer depicted in Fig. 15 should be used as the "standard" of comparison for tris bidentate chelate compounds (and probably also for *cis*-bis(monodentate)–bis(bidentate) complexes as well), there is as yet no unanimity regarding the designation of the complex in Fig. 15. Early workers referred to the absolute configuration of this ion as D or D*, but because many persons use the symbols D, d, and (+) interchangeably, and because there is no necessary correlation between the sign of rotation of a complex at a given wavelength and its absolute configuration, some confusion has arisen. Woldbye[140] has recently summarized various proposals for the nomenclature of these compounds. In this author's judgment, it has now become important that some universally accepted system of nomenclature be adopted to represent both the *conformation* of the ligands in coordination compounds as well as their *configuration* about a metal ion.

Piper[141] has proposed that the nomenclature for absolute configuration be based upon the type of helix generated by a tris bidentate complex about its three-fold symmetry (C_3) axis. Whenever this has the appearance of a right-handed helix (see Fig. 17) he proposes that the absolute configuration be known as "Δ"



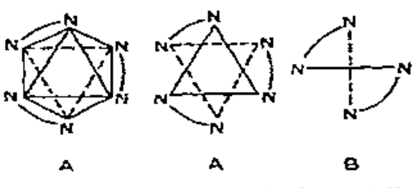


Fig. 16. A: The *kkk* conformation (*lel*) of the ethylenediamine chelate rings in $(+)_D$-$[Co(en)_3]^{3+}$ and in $(+)_D$-$[Co(+_Dpn)_3]^{3+}$; B: The *kkk* conformation (here, *ob*) of the chelate rings in $(-)_D$-$[Co(en)_3]^{3+}$ and $(-)_D$-$[Co(+_Dpn)_3]^{3+}$ (pn = propylenediamine).

Fig. 17. The helicity of $(+)_D$-$[Co(en)_3]^{3+}$ viewed along A: a three-fold symmetry axis; B: a two-fold symmetry axis. Note that A generates a left-handed helix and B generates a right-handed helix.

and that the opposite enenatiomer be "Λ". For the complex in Fig. 15 the absolute configuration would therefore be "Λ". Mason and co-workers have pointed out[142,143] that if the two-fold symmetry axis (C_2) is used as the reference axis, then the resulting "two-bladed" propeller produces a helix of the opposite chirality (handedness) to that which is produced when the C_3 axis is chosen (see Fig. 17). Further, they make use of the symbols "P" and "M" (for Plus and Minus) to represent the absolute configuration when it is determined from the C_2 axis. Gillard[46] uses the symbols "R" and "S" in a similar way. Hawkins and Larsen[144] defined an "octant sign" (see "octant rule" for organic carbonyl compounds[4] and Djerassi[51]) to characterize the helicity of both conformations and configurations of tris bidentate and *cis*-bis monodentate-bis bidentate complexes. Legg and Douglas[145] have proposed the use of the two-fold symmetry axis (C_2) for helicity reference and a "ring-pairing" technique for multidentate ligand complexes. An interesting proposal for the nomenclature of absolute configuration and conformation of octahedral complexes described by Douglas[146] is now under study by an I.U.P.A.C. nomenclature committee for possible adoption by I.U.P.A.C. It eliminates the need to identify symmetry elements or axes (sometimes a difficult task), and is based upon the facts that two skew, non-orthogonal lines define a unique helical system and that *cis*-bis bidentate and tris bidentate chelate ligands which span edges of octahedra can be regarded as skewed non-orthogonal lines. This proposal uses the "Δ" and "Λ" terminology for complexes whose skewed edge lines define right-handed and left-handed helices, respectively. The results are similar to those of Piper, who uses a C_3 symmetry axis to define Δ and Λ helices. Further, this proposal also defines the helicity of ligands, and this definition is related to definitions proposed by Cory and Bailar[39] and Sargeson[40a] as follows:

Douglas	*Corey and Bailar*	*Sargeson*
δ	k'	k
λ	k	k'

Thus the absolute configuration and conformation of the $(+)_D$-$[Co(en)_3]^{3+}$ ion determined by Saito *et al.*[137] would be represented in this proposal by $\Lambda(+)_{589}$-$[Co(en)_3\delta\delta\delta]^{3+}$. If the ligands are themselves optically active and their absolute configuration is known, then this is so indicated using the system described by Cahn, Ingold, and Prelog[147] for the organic ligands, where R and S are used to indicate absolute configurations. Thus the absolute configuration and conformation of the propylenediamine complex of cobalt(III), which was determined (using anomalous X-ray scattering techniques) by Saito and co-workers[148] are represented by $\Delta(-)_{589}[Co[(R)(-)pn]_3\lambda\lambda\lambda]^{3+}$. The absolute configurations of some other complexes have been determined by Pepinsky[149] and Saito and co-workers[150]. Table I lists complexes whose absolute configurations or conformations have been determined by X-ray studies.

TABLE I

COMPLEXES WHOSE ABSOLUTE CONFIGURATIONS AND/OR CONFORMATIONS HAVE BEEN DETERMINED BY X-RAY STUDIES

*Compound**	*Ref.*	*Compound*	*Ref.*
$[Co(en)_3]^{3+}$	137, 149	$[Cr(ox)_3]^{3-}$	159f
$[Co(l\text{-}pn)_3]^{3+}$	148, 159a	$[Co(tn)_3]^{3+}$	150a
$[Co(d\text{-}pn)_3]^{3+}$	150a	$[Co(d\text{-}cptn)_3]^{3+}$	150a
[Fe(mecptdn) (carb-mecptdn)]	149a	$[Co(d\text{-}chxn)_3]^{3+}$	150a
$[Cu(en)_2]^{2+}$	150b	*cis*-$[Co(en)_2(CN)_2]^+$	150g
trans-$[Co(en)_2Cl_2]^+$	150c	$[Co(H_2O)_3(l\text{-}asp)]$	149
trans-$[Co(en)_2Br_2]^+$	150d	$[Cr(NH_3)_3(NCS)_3]$	149
trans-$[Co(l\text{-}pn)_2Cl_2]^+$	150, 150e		

* Ligand abbreviations: en = ethylenediamine; pn = propylenediamine; ox = oxalate; mecptdn = methylcyclopentadienide; carb-mecptdn = 1-methyl-3-carboxyl-cyclopentadienide; tn = trimethylenediamine; cptn = cyclopentanediamine; chxn = cyclohexanediamine; asp = aspartate.

Mason and co-workers[138,151] have suggested an interesting criterion for the absolute configuration of dihedral complexes by an examination of the circular dichroism of such complexes in the solid state (polarized crystal spectra) with the circularly polarized light directed along the trigonal axis. By this technique it may be possible to assign rotatory strengths to particular transitions, and, by comparison with solution circular dichroism studies, to assign chirality to dihedral complexes. Mason and Norman[152] have recently reported evidence in support of their absolute configuration assignment by this technique for the (-)([Fe(*o*-phenanthroline)$_3$]$^{2+}$ cation by an X-ray study[153]. Piper and co-workers[154] have also applied ORD and CD techniques and polarized crystal spectra studies to the determination of absolute configuration and conformation of complexes, and have discussed the influence of chelate ring conformation on absolute configuration.

Absolute configurations have been determined by chemical techniques, (*e.g.*, by Busch[154a], the [Co(edta)]$^-$ anion (edta = ethylenediaminetetraacetate) and several absolute configurations have been proposed on the basis of ORD and CD studies[1,40a,44,46,48,92g,154]. X-ray studies[153,150] have confirmed two of the structures whose absolute configurations have been proposed on the basis of ORD-CD studies by Mason and co-workers[152] and Mathieu[155]. Gillard and co-workers[156] have reported several absolute configurations based upon ORD-CD data, and they also report a case[157] in which configurational relationships could not accurately be determined by ORD. An example of the technique used to predict absolute configurations from ORD data is given in Fig. 18, which contains ORD curves[158] for $(+)_{589}[Co(en)_3]^{3+}$, $(-)_{589}[Co(+chxn)_3]^{3+}$, and $(-)_{589}[Co(+cptn)_3]^{3+}$. All three of these ions are predicted[44] to have the same absolute configuration ($\Lambda[C_3]$) on the basis of these curves. Mason and co-workers[158a] have assigned the absolute configurations of (+)- and (−)-$[Co(+pn)_3]^{3+}$ on the basis of circular dichroism measurements (see Fig. 19). They point out that

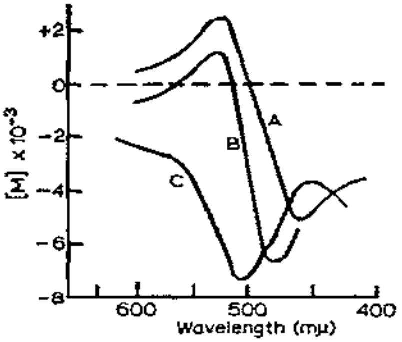
TABLE 2

SOME COORDINATION COMPOUNDS STUDIED BY ORD AND/OR CD TECHNIQUES

*Compound**	*Ref.*	*Compound**	*Ref.*
$[As(cat)_3]^-$	187	$[Co(EDTA)Cl]^{2-}$	166
$[Co(ala)_3]$	166, 181	$[Co(EDTA)(NO_2)]^{2-}$	166
$[Co(asp)_3]^{3-}$	171	$[Co(gly)_3]$	166, 181
Cobalamine complexes	54	$[Co([OH]_2Co[NH_3]_4)_3]^{6+}$	182
$[Co(-CDTA)]^-$	47	$[Co(+hmc)_3]$	180
trans-$[Co(-chxn)_2Cl_2]^+$	168	$[Co(NH_3)_5(menac)]^{2+}$	161
$[Co(en)_3]^{3+}$	47, 162	$[Co(ox)_3]^{3-}$	47
$[Co(en)_2acac]^{2+}$	173	$[Co(NH_3)_5(-phalaH)]^{3+}$	169
$[Co(en)_2CO_3]^+$	47	$[Co(penten)]^{3+}$	138
$[Co(en)_2(ox)]^+$	47	$[Co(+PDTA)]^-$	47, 162
$[Co(en)_2(glut)]^+$	162	$[Co(-pn)_3]^{3+}$	47
$[Co(en)_2(-pn)]^{3+}$	47	$[Co(-pn)_2(+pn)]^{3+}$	40
cis-$[Co(en)_2(NH_3)_2]^{3+}$	47, 138	*trans*-$[Co(-pn)_2(NH_3)_2]^{3+}$	168
cis-$[Co(en)_2F_2]^+$	178	*trans*-$[Co(-pn)_2Cl_2]^+$	168
cis-$[Co(en)_2Cl_2]^+$	47	*trans*-$[Co(-pn)_2(NCS)_2]^+$	168
cis-$[Co(en)_2(CN)_2]^+$	138	*trans*-$[Co(-pn)(EDDA)]^+$	166
cis-$[Co(en)_2(NO_2)_2]^+$	181, 156	$[Co(NH_3)_4(sar)]^+$	183
$[Co(en)(-pn)_2]^{3+}$	40, 47	$[Co(NH_3)_4(+tart)]^+$	161
$[Co(en)(malon)_2]$	166	$[Co(ox)_2(gly)]^{2-}$	184
$[Co(en)(ox)_2]^-$	47, 166	$[Cr(en)_3]^{3+}$	47, 136, 138, 162
cis-$[Co(en)_2(H_2O)_2]^{3+}$	47	$[Cr(ox)_3]^{3-}$	47
cis-$[Co(en)_2(H_2O)(NO_2)]^{2+}$	181	$[Cr(-pn)_3]^{3+}$	138
cis-$[Co(en)_2(H_2O)Cl]^{2+}$	47	$[Cr(+PDTA)(H_2O)]^-$	162
cis-$[Co(en)_2(NH_3)(H_2O)]^{3+}$	47	$[Cu(amac)_2]$, $[Co(ox)(amac)_2]^-$	169, 179, 185
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	47, 156	$[Cu(-pn)_2]^{2+}$	162
cis-$[Co(en)_2(NH_3)(NO_2)]^{2+}$	47, 181	$[Cu(-prol)_2]$	169
$[Co(NH_3)_5(amac)]^{3+}$	172	$[Cu(-ser)_2]$	169
$[Co(NH_3)_5(l\text{-}mal)]^{2+}$	162	$[Cu(+tart)_2]^{2-}$	162
$[Co(NH_3)_5(l\text{-}lac)]^{2+}$	162	$[Cu(-thr)_2]$	169
$[Co(NH_3)_5(+tart)]^+$	161	$[Dy(-PDTA)]^-$	170
$[Co(TET)]^+$	47	$[Fe(o\text{-}phen)_3]^{2+}$	47
$[Co(trien)(-pn)]^{3+}$	173	$[Ir(en)_3]^{3+}$	47, 136, 162
$[Co(trien)(+pn)]^{3+}$	173	$[Ir(ox)_3$	47
cis-$[Co(trien)(NH_3)_2]^{3+}$	173	$[Ni(o\text{-}phen)_3]^{2+}$	47
$[Co(en)(trien)]^{3+}$	173	$[Os(o\text{-}phen)_3]^{2+}$	47
$[Co(trien)(ox)]^+$	173	$[Rh(-ala)_3]$	181
$[Co(trien)(H_2O)Cl]^{2+}$	173	$[Rh(+hmc)]$	180
trans $[Co(trien)Cl_2]^+$	173, 186	$[Rh(en)_3]^{3+}$	47, 136, 138, 162
$[Co(-val)_3]$	171	$[Rh(ox)_3]^{3-}$	47
$[Cr(dipy)(ox)_2]^-$	189	$[Rh(-pn)_3]^{3+}$	138, 162
$[Co(acac)_2(ox)]^-$	184	$Ru(o\text{-}phen)_3]^{2+}$	47, 162
$[Co(Co(en)_2(OH)_2)_3]^{6+}$	188	$[Ru(cptdn)(oxotm\text{-}cptdn)]$	191
$[Co(Co(NH_3)_4(OH)_2)_3]^{6+}$	190	$[Pd(phetam)_2Cl_2]$	193
$[Co(en)_2(NCS)(Cl)]^+$	156	$[Pt(en)_3]^{4+}$	192
$[Co(EEE)]^+$	47	$[Pt(pn)_3]^{4+}$	192
$[Co(EDTA)]^-$	47	$[Si(acac)_3]^+$	182
$[Co(EDTA)Br]^{2-}$	166		

* For abbreviations, see bottom of opposite page.

$(+)$-$[Co(+pn)_3 3^+$ and $(+)$-$[Co(en)_3]^{3+}$ have very similar CD spectra, and suggest that these have the same absolute configuration of the ligands about the metal ion, while the CD curve of $(-)$-$[Co(^+pn)_3]^{3+}$ indicates that it possesses the opposite configuration. It is this author's opinion, however, that additional confirmatory evidence (*e.g.*, *via* X-ray structure determinations) should be available for many more complexes whose absolute configurations have been predicted by ORD and CD before these techniques are used definitively to assign absolute configurations. Table 2 lists some compounds for which ORD and/or CD studies have been carried out.



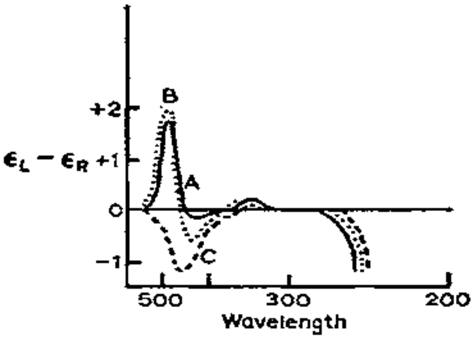


Fig. 18. ORD curves of A: $(+)_D[Co(en)_3]^{3+}$, B: $(-)_D[Co(+chxn)_3]^{3+}$, C: $(-)_D[Co(+cptn)_3]^{3+}$ (+chxn = $(+)_D$ cyclohexanediamine; +cptn = $(+)_D$cyclopentanediamine).

Fig. 19. Circular dichroism spectra of A (solid line): $(+)$-$[Co(en)_3]^{3+}$; B (dotted line): $(+)$-$[Co(+pn)_3]^{3+}$; C (dashed line): $(-)$-$[Co(+pn)_3]^{3+}$.

Abbreviations in Table II:

acac = acetylacetonate
ala = alaninate
amac = amino acid anion
asp = aspartate
cat = catechyl
CDTA = cyclohexanediaminetetraacetate
chxn = cyclohexanediamine
dipy = 2,2′-dipyridyl
EEE = 1,8-bis(salicylideneamino)-3,6-dithiaoctane
EDDA = ethelenediaminediacetate
EDTA = ethylenediaminetetraacetate
en = ethylenediamine
glut = glutamate
gly = glycinate
hmc = hydroxymethylenecamphor
lac = lactate
mal = malate

malon = malonate
menac = menthoxyacetate
ox = oxalate
penten = pentaethylenehexamine
PDTA = propylenediaminetetraacetate
phalaH = phenylalanine
o-phen = *ortho*-phenanthroline
phetam = phenylethylamine
pn = propylenediamine
prol = prolinate
sar = sarcosinate
ser = serinate
tart = tartrate
TET = 1,10-bis(salicylideneamino)-4,7-dithiadecane
thr = threoninate
trien = triethylenetetramine
val = valinate

G. OTHER STUDIES

(i) Spectropolarimetric titrimetry

Kirschner and co-workers[159] have applied the spectropolarimeter to the determination of metal ions, strong and weak acids and bases, optically active and inactive ligands, and the number of ligands per metal ion in complexes. For strong acids, for example, an optically active indicator is used which is itself an acid that is at least one hundred times weaker than the acid being titrated. During the titration, which is followed spectropolarimetrically at the wavelength giving the most suitable rotation changes per unit volume of titrant, the rotation of the indicator remains essentially constant. After the endpoint, the indicator itself is being titrated, and this results in measurable rotation changes (Fig. 20). Metal ions may be titrated with optically active ligands (whose rotation changes upon coordination) or with optically inactive ligands provided an optically active ligand is added as an indicator. The indicator ligand is one which changes rotation upon coordination and which forms a significantly weaker complex with the metal ion than the optically inactive ligand (Fig. 21). Pecsok and Juvet[160] have studied the change in optical rotation with changing pH of some lead complexes with an optically active ligand. They call these studies "rotometric titrations".

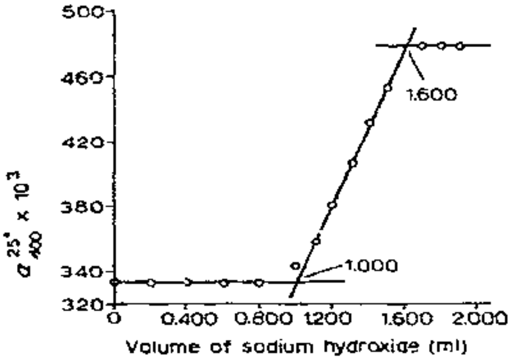


Fig. 20. Spectropolarimetric titration of HCl and *d*-tartaric acid with aqueous NaOH at 400 mμ.

(ii) Determination of coordination

Kirschner and co-workers[161] have also applied ORD techniques to the determination of whether or not optically active ligands are coordinated. In these studies they determined that it is feasible to compare the ORD curves of complexes containing an optically active ligand inside the coordination sphere (*e.g.*, $[Co(NH_3)_4(d\text{-tart})]^+$ or $[Co(NH_3)_5(d\text{-tart})]^+$) with the ORD curves of similar complexes containing the ligand as a free ion only (*e.g.*, $[Co(NH_3)_6]_2(d\text{-tart})_3]$). The ORD curve of the latter is essentially identical to the ORD curve for the ligand anion alone (indicating non-coordination of this anion), and the ORD curves of the former complexes show Cotton effect peaks in the region of visible absorption–indicating coordination of the ligand in these cases.

(iii) Stereoselectivity and spectroscopic assignments

Gillard and co-workers[162] have described some interesting work in the stereoselectivity of coordination compounds, with particular reference to optically active complexes and their ORD and CD properties. Mason and co-workers[163] have done a substantial quantity of excellent work in the area of spectroscopic and configurational assignments in coordination compounds utilizing CD and other spectroscopic data. Sargeson and co-workers[164] have studied the stereospecific coordination of sarcosine as well as several rearrangement reactions using ORD techniques.

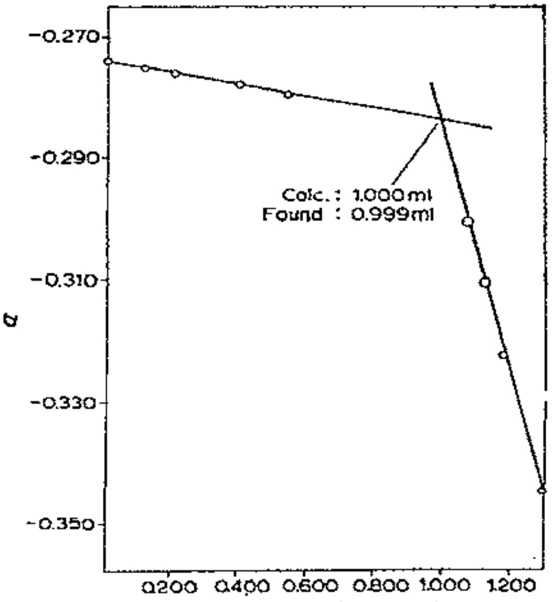


Fig. 21. Spectropolarimetric titration of disodium dihydrogen ethylenediaminetetraacetate and aqueous zinc (II) nitrate at 350 mμ with *levo*-histidine as indicator.

Douglas and co-workers[165] have studied the ORD and CD of many compounds, and have shown that the *configurational effects* (contributions to the optical activity from the right or left spiral of chelate rings) and the *vicinal effect* (contribution to the optical activity of a complex from an optically active ligand) can be separated and are additive for complexes of the type $[Co(en)_2(alanine)]^{2+}$. They have done excellent work in analyzing the composite ORD and CD curves obtained from complex systems, and the application of ORD and CD techniques to the prediction of absolute configuration[166]. Bürer[167] has also done interesting work on spectroscopic assignments and absolute configuration using ORD and CD, as have Hawkins and Larsen and co-workers[168]. Several research groups in Japan have done significant work in ORD and CD studies of complexes, including those by Yasui and his co-workers[169], Misumi and co-workers[170], Shibata and co-workers[171], and Shimura and co-workers[172].

(iv) *Optical inversions and other phenomena*

Bailar and his co-workers[173] have applied ORD techniques to the study of optical inversions in coordination compounds and have described the criteria necessary for such inversions of configuration to occur.

Two important topics which have been omitted from this review pertain to the ORD and CD of biologically active coordination compounds, and magnetic ORD and CD. Each of these should be subjects for reviews in their own right, especially since there has been a renewed interest in them in recent years. One excellent recent review by Blout[174] on the ORD of polypeptides and proteins discusses some aspects of the former subject and, in several recent interesting papers, Schatz and co-workers[175], Foss and co-workers[175a], Shashoua[176], and Stephens[177] discuss the latter.

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