

An Alternate Method for the Determination of Circular Dichroism

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A technique has been developed for determining the ellipticity, ψ (from which a circular dichroism plot can be made), of light emerging from a solution containing an optically active species, using a mica plate and a Rudolph spectropolarimeter. This technique has the advantage over previous procedures using a quarter-wave plate, in that precise orientation of the plate is not required. For ψ of less than one radian, $\psi = (\tau \cos \delta - \gamma \cos 2\tau)/\sin \delta$, where δ is the retardation of the plate, τ is the azimuth of the incident elliptical polarization, and γ is the azimuth of the resultant polarization with respect to the fast axis of the mica.

There are two general methods to measure circular dichroism, a direct and an indirect method. Since dichroism is a function of the differential absorption of right- and left-handed circularly polarized light, it can be measured directly by alternately passing right- and left-handed circularly polarized light through the solution and determining the difference in absorption. Several instruments have been designed which employ this method.²⁻⁴

The indirect method^{4,5} is to pass the elliptically polarized light from the optically active solution through an anisotropic crystal of known properties. If the axes of an elliptical vibration are oriented precisely parallel to the fast and slow axes of a mica compensator which is a quarter-wave plate at that wavelength, then the light emerges plane polarized. The azimuth of the plane-polarized light may be used to calculate the ellipticity. If the mica plate is not exactly a quarter-wave plate at the wavelength of the light used, there will also be a position of the mica axes where the elliptical polarization is converted to plane polarization. Measurements of ellipticities by these methods require precise orientation of the mica with respect to the axes of the ellipse. This is difficult to do.

Discussion

In the following method, the ellipticity is determined by interposing a mica plate between the optically active solution and the analyzing prism (Figure 1). The relation of the azimuth of the elliptically polarized light leaving the solution, τ , and the azimuth of the elliptically polarized light emerging from the mica, γ , with respect to the slow and fast axes of the mica is shown in Figure 2. The relation of the ellipticity to the measured angles is derived as follows.

From Figure 2 it can be seen that for elliptically polarized light of frequency ω incident on the mica, the major axis of the ellipse, whose vibration is $y' = d \sin$

ωt , is set at some small angle τ from the fast axes of the mica. The minor axis, c , whose vibration is $y'' = c \sin(\omega t - 90^\circ)$, is the same angle τ from the slow axis of the mica. The component vibrations of the major and minor axes of the ellipse along the fast axis of the mica are given by

$$f = d \cos \tau \sin \omega t \quad (1)$$

$$f = -c \sin \tau \sin(\omega t - 90^\circ) \quad (2)$$

and along the slow axes of the mica the vibrations are

$$s = d \sin \tau \sin \omega t \quad (3)$$

$$s = c \sin(\omega t - 90^\circ) \cos \tau \quad (4)$$

Each of these mica axes will have one resultant vibration, which is given by

$$f = A \sin(\omega t + \phi_I) \quad (5)$$

$$s = R \sin(\omega t + \phi_{II}) \quad (6)$$

where A and R are the amplitudes of the accelerated and retarded vibration directions in the mica and ϕ_I and ϕ_{II} are the relative phase constants. It is known that the amplitude is related to the phase constants in the following manner

$$A^2 = c^2 + d^2 + 2cd \cos(\phi_I - \phi_{II}) \quad (7)$$

Substituting $\phi = \phi_{II} - \phi_I$ and knowing also that

$$\tan \phi = \frac{d \sin \phi_I + c \sin \phi_{II}}{d \cos \phi_I + c \cos \phi_{II}} \quad (8)$$

a group of four parametric equations can be written which are known as Tuckerman's notation⁶ and which describe the resolution of any elliptically polarized light of ellipticity c/d , along axes oriented at an angle τ from the axes of the ellipse. These equations were derived by a route different from but equivalent to Skinner's original work. They are

$$(\sin 2\sigma_x)(d_x^2 - c_x^2)/2 = AR \cos(\phi + \delta_x) = K_x \quad (9)$$

$$c_x d_x = AR \sin(\phi + \delta_x) = S_x \quad (10)$$

$$(c_x^2 + d_x^2)/2 = (A^2 + R^2)/2 = P_x \quad (11)$$

$$(\cos 2\sigma_x)(d_x^2 - c_x^2)/2 = (A^2 - R^2)/2 = Q_x \quad (12)$$

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(3) S. F. Mason, *Mol. Phys.*, **5**, 343 (1962).

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(5) H. G. Jerrard, *J. Opt. Soc. Am.*, **38**, 35 (1948).

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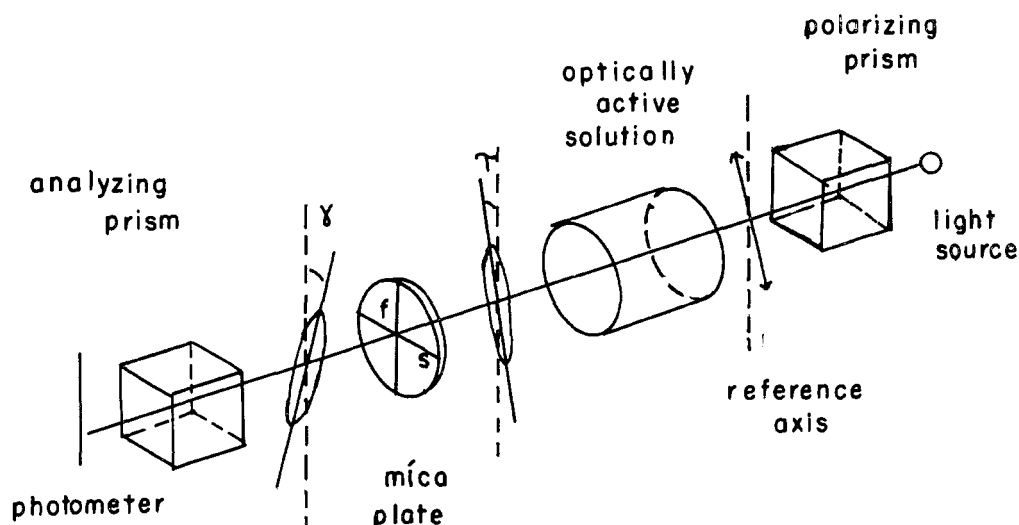


Figure 1.—Optical train for the determination of ellipticity using the Rudolph spectropolarimeter.

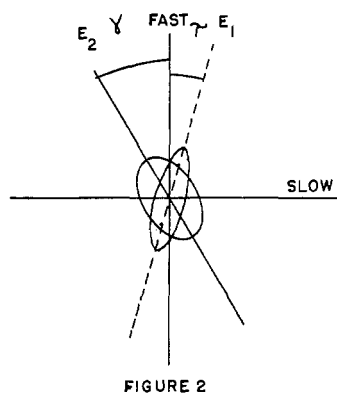


FIGURE 2

Figure 2.—The effect of a mica compensator on the incident elliptically polarized light to produce polarized light of a different ellipticity.

where for the incident polarized light $x = 1$, for the emergent polarized light $x = 2$, $\delta_1 = 0$ for the initial resolved vibration just as it enters the mica, and $\delta_2 =$ the experimentally determined value for the retardation. The angle σ_1 is τ , and the angle σ_2 is γ . A and R are the amplitudes of the resolved vibrations; c_1/d_1 , the ratio of the minor axis to the major axis, is the ellipticity, ψ ; and $\phi = \phi_{II} - \phi_I$ is the difference between the phase constants of the two vibrations. The relationship of ψ to τ , γ , and δ is derived as follows. Divide K_2/Q_2

$$\tan 2\gamma = \frac{2AR \cos \phi \cos \delta_2 - 2AR \sin \phi \sin \delta_2}{A^2 - R^2}$$

Substituting the equivalent of $2Q_1$, S_1 , and K_1

$$\tan 2\gamma = \frac{\sin 2\tau \cos \delta_2}{\cos 2\tau} - \frac{2c_1d_1 \sin \delta_2}{\cos 2\tau (d_1^2 - c_1^2)}$$

since

$$\psi = c_1/d_1$$

$$\tan 2\gamma = \tan 2\tau \cos \delta_2 - \frac{2\psi \sin \delta_2}{(1 - \psi^2) \cos 2\tau}$$

The ellipticity, ψ , expressed in radians, will be small compared to 1, and the equation reduces to

$$\tan 2\gamma = \tan 2\tau \cos \delta_2 - \frac{2\psi \sin \delta_2}{\cos 2\tau}$$

Solving for ψ gives

$$\psi = \frac{\sin 2\tau \cos \delta_2 - \tan 2\gamma \cos 2\tau}{2 \sin \delta_2}$$

The angles γ and τ are read from the polarimeter in degrees, but for the angles encountered here, $\tan x = x$ and $\sin x = x$ when the angles are expressed in radians. A further simplification therefore results

$$\psi = \frac{\tau \cos \delta_2 - \gamma \cos 2\tau}{\sin \delta_2} \quad (13)$$

Now upon reconvertting to degrees (multiplication by $180/\pi$), a fortuitous cancellation of this conversion factor occurs which allows the calculation of ψ in degrees directly from the polarimeter data also in degrees. The molecular ellipticity $[\theta]$ is related to ψ by the expression $[\theta] = \psi (10/cl)$, where c is the concentration in moles/liter and l is the length of the tube in decimeters. A 1-dm tube was used here.

The values of δ_2 also may be obtained from this relationship, since for plane-polarized light $\psi = 0$; then

$$\cos \delta_2 = \frac{\tan 2\gamma}{\tan 2\tau}$$

and again making the assumption that $\tan x = x$

$$\cos \delta_2 = \frac{\gamma}{\tau}$$

Data for the determination of the retardation are given in Table I. The retardation expressed in terms of path difference is converted to degrees at each wavelength by the relationship $\delta = (\delta_{m\mu}/\lambda_{m\mu})360$.

In order to test the precision of the method, the circular dichroism curves for two inorganic complexes

TABLE I
DATA FOR THE DETERMINATION OF RETARDATION OF MICA PLATE^a

| | $\lambda, m\mu$ | | | |
|-------------------------|-----------------|---------|---------|---------|
| | 450.0 | 440.0 | 430.0 | 425.0 |
| Mica zero, ^b | | | | |
| deg | 0.076 | 0.078 | 0.078 | 0.080 |
| P , deg | -1.572 | -1.490 | -1.516 | -1.476 |
| E , deg | 1.380 | 1.371 | 1.440 | 1.432 |
| γ , deg | 1.304 | 1.293 | 1.362 | 1.352 |
| τ , deg | -1.648 | -1.568 | -1.594 | -1.556 |
| $\cos \delta$ | -0.7913 | -0.8246 | -0.8545 | -0.8689 |
| δ , deg | 142.31 | 145.55 | 148.70 | 150.30 |
| $\delta_{m\mu}$ | 177.88 | 177.90 | 177.61 | 177.43 |

^a Average retardation in $m\mu = 177.7 (\pm 0.2)$. ^b The angle β , by which the mica axes deviate from coincidence with the midpoint of the polarizer oscillation. See eq xiii and Figure 6.

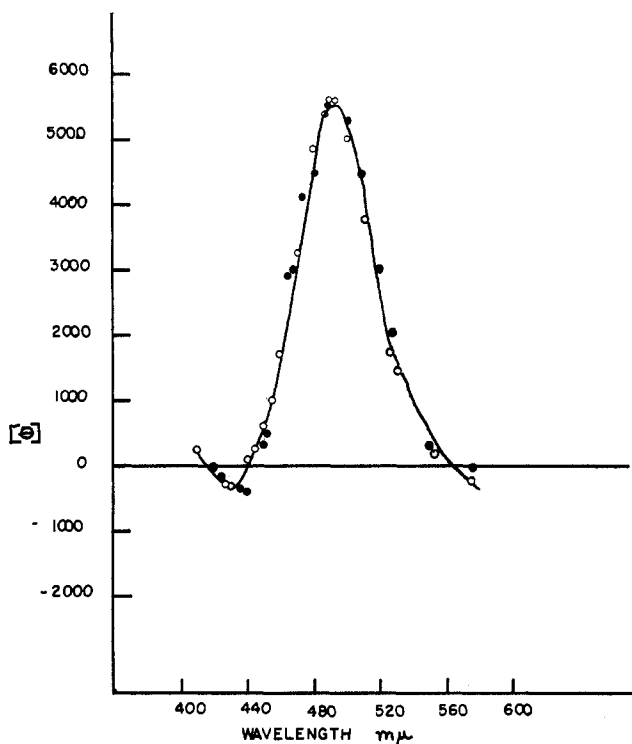


Figure 3.—The circular dichroism of Δ -(+)-tris(ethylenediamine)cobalt(III) iodide: O, this work; ●, Mathieu.

were determined. These two complexes were Δ -(+)-tris(ethylenediamine)cobalt(III) iodide and Δ -(+)-*cis*-dinitrobis(ethylenediamine)cobalt(III) bromide, whose circular dichroism curves were determined by Mathieu^{7,8} in 1936. The two experimental curves are shown in Figures 3 and 4. They agree closely with the curves published by Mathieu, including the small negative component around 420 $m\mu$ for the tris(ethylenediamine) complex. The molecular ellipticity of 5620 ± 20 at 490 $m\mu$ is close to Mathieu's value of 5650 for the bromide, but is low compared to the 5800 of Douglas⁹ for the bromide and Mason's¹⁰ value of 6230 for both the chloride and the perchlorate.

The dichroism curve for the *cis*-dinitrobis(ethylenediamine)cobalt(III) complex also agrees in general shape

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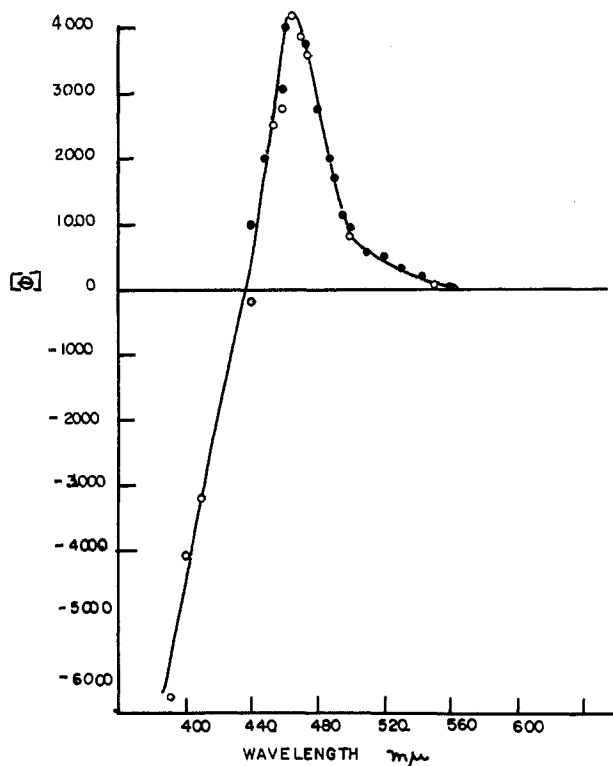


Figure 4.—The circular dichroism of Δ -(+)-*cis*-dinitrobis(ethylenediamine)cobalt(III) bromide: O, this work; ●, Mathieu.

with that of Mathieu except that he did not make measurements below 430 $m\mu$. The curve here shows an intense negative component as predicted by Douglas⁹ for compounds of the class $\text{Co}(\text{en})_2\text{XX}^+$. The molecular ellipticity of 4180 at 466 $m\mu$ is higher than the 3750 reported by Mathieu at the same wavelength, but lower than the 4620 reported by Mason¹¹ at 460 $m\mu$.

The data from which the curves in Figures 3 and 4 are plotted are given in Tables II and III. The values for the ellipticity have a standard deviation of $\pm 0.003^\circ$. It is felt that this represents the precision of the measurement at the present time. The wavelength range is limited on the low side by absorption of the mica which becomes serious at 340 $m\mu$. This can be improved slightly by using synthetic mica which cuts off at a slightly lower wavelength. The differences in molecular ellipticities obtained compared with the literature values probably reflect differences in optical purity of the separated isomers, rather than uncertainties in the technique. In general the shapes of the curves, and the location of minima and maxima, agree with curves obtained using other techniques.

Experimental Section

Equipment.—The polarimeter used was a Rudolph Model 200S photoelectric spectropolarimeter with a xenon source.

The anisotropic crystal used was a thin piece of mica of thickness 1.7×10^{-3} in., which made it a quarter-wave plate at about 520 $m\mu$. It was furnished in a small aluminum holder by the Asheville-Schoomaker Mica Co. of Newport News, Va. Since it is necessary that the mica plate be placed between the light to be analyzed and the analyzing prism, it was necessary to de-

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TABLE II
EXPERIMENTAL DATA FOR
Λ-(+)-TRIS(ETHYLENEDIAMINE)COBALT(III) IODIDE
($2.10 \times 10^{-3} M$)

| λ , m μ | Mica zero, deg $\times 10^3$ | E_2 , deg | $-E_1$, deg | γ , deg | $-\tau$, deg | ψ , deg | $[\theta]$, deg |
|---------------------|------------------------------|-------------|--------------|----------------|---------------|--------------|------------------|
| 575 | 6.7 | 0.714 | 1.611 | 0.647 | 1.678 | -0.042 | -199 |
| 550 | 8.6 | 0.540 | 1.080 | 0.454 | 1.166 | 0.069 | 330 |
| 530 | 7.9 | 0.442 | 1.149 | 0.363 | 1.228 | 0.306 | 1460 |
| 525 | 8.0 | 0.323 | 0.972 | 0.243 | 1.052 | 0.366 | 1740 |
| 510 | 7.8 | 0.156 | 1.173 | 0.078 | 1.251 | 0.795 | 3790 |
| 500 | 7.9 | 0.194 | 1.456 | 0.115 | 1.535 | 1.05 | 5000 |
| 492 | 6.5 | 0.527 | 2.062 | 0.462 | 2.127 | 1.18 | 5620 |
| 490 | 8.1 | 0.362 | 1.733 | 0.281 | 1.814 | 1.18 | 5620 |
| 488 | 8.1 | 0.430 | 1.777 | 0.349 | 1.858 | 1.16 | 5530 |
| 480 | 7.9 | 0.821 | 2.085 | 0.749 | 2.164 | 1.02 | 4860 |
| 470 | 7.3 | 1.500 | 2.565 | 1.427 | 2.638 | 0.690 | 3280 |
| 460 | 7.8 | 1.872 | 2.600 | 1.794 | 2.678 | 0.359 | 1710 |
| 455 | 6.1 | 2.182 | 2.848 | 2.121 | 2.909 | 0.219 | 1040 |
| 450 | 7.2 | 1.928 | 2.369 | 1.856 | 2.441 | 0.128 | 612 |
| 445 | 7.2 | 1.938 | 2.279 | 1.866 | 2.351 | 0.059 | 282 |
| 440 | 7.4 | 1.861 | 2.110 | 1.787 | 2.184 | 0.026 | 124 |
| 430 | 7.8 | 2.023 | 2.152 | 1.945 | 2.230 | -0.062 | -295 |
| 425 | 8.0 | 1.975 | 2.058 | 1.895 | 2.138 | -0.055 | -262 |
| 410 | 8.4 | 1.852 | 1.871 | 1.768 | 1.955 | 0.057 | 272 |

TABLE III
EXPERIMENTAL DATA FOR
Λ-(+)-*cis*-DINITROBIS(ETHYLENEDIAMINE)COBALT(III)
BROMIDE

| λ , m μ | Mica zero, deg $\times 10^3$ | $-E_2$, deg | E_1 , deg | $-\gamma$, deg | τ , deg | ψ , deg | $[\theta]$, deg |
|---------------------|------------------------------|--------------|-------------|-----------------|--------------|--------------|------------------|
| 550 ^a | 8.0 | 0.784 | 1.997 | 0.864 | 1.917 | 0.015 | 30 |
| 500 ^a | 8.8 | 1.865 | 2.744 | 1.953 | 2.656 | 0.395 | 783 |
| 475 ^b | 8.4 | 1.515 | 1.976 | 1.599 | 1.892 | 0.374 | 3600 |
| 470 ^b | 7.6 | 1.844 | 2.346 | 1.920 | 2.270 | 0.404 | 3880 |
| 465 ^b | 7.9 | 1.667 | 2.045 | 1.746 | 1.966 | 0.434 | 4180 |
| 460 ^c | 7.3 | 1.694 | 2.290 | 1.767 | 2.217 | 0.134 | 2770 |
| 455 ^c | 7.0 | 1.511 | 2.010 | 1.581 | 1.940 | 0.123 | 2540 |
| 440 ^c | 8.0 | 1.691 | 2.232 | 1.771 | 2.152 | -0.009 | -200 |
| 410 ^c | 8.3 | 1.791 | 2.197 | 1.874 | 2.114 | -0.157 | -3240 |
| 400 ^c | 7.5 | 1.919 | 2.264 | 1.994 | 2.189 | -0.195 | -4030 |
| 390 ^c | 8.1 | 2.435 | 2.775 | 2.516 | 2.694 | -0.302 | -6250 |

^a $5.04 \times 10^{-3} M$. ^b $1.04 \times 10^{-3} M$. ^c $4.96 \times 10^{-4} M$.

vide some sort of holder that would fit in the trough of the instrument, that would hold the mica steady, and that would permit the mica to be turned through 360° . The trough which holds the sample tube, and to which the analyzing and polarizing prism are firmly anchored, is bounded on one side by a constant-temperature chamber and the other by a light-tight door. A device to operate and hold the mica was developed, but in order to do so it was necessary to conduct all the measurements with the light-tight door open. All ellipticity measurements were conducted with the room in semidarkness. A drawing of the mica holder is shown in Figure 5. Attached to the aluminum disk holding the mica is a 60-tooth gear. A worm gear turns the gear attached to the mica. The pitch of the worm gear is such that the mica turns 6° for each revolution of the worm. The combination of the worm and the gear allowed the mica to be positioned. Although it was not necessary to orient the mica at a specific position, it was necessary to know precisely the position of the fast axes with respect to the reference axes. With the technique described in the following paragraphs the position of the mica could be determined to $\pm 0.001^\circ$.

Setting the Mica.—The Rudolph spectropolarimeter is built to measure the azimuth of polarized light. The measurement is made on plane-polarized light by orienting the analyzing prism

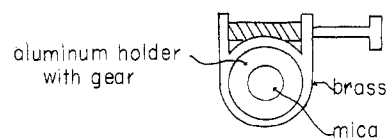


Figure 5.—Mica holder designed to fit into the Rudolph spectropolarimeter (view facing incoming light).

until a minimum of intensity registers on the photometer. The azimuth of the prism is then perpendicular to the vibration direction of the polarized light. The minimum of intensity with elliptically polarized light is registered when the azimuth of the prism is perpendicular to the vibration direction of the major axis of the ellipse. This minimum is not so low as in the case of the plane-polarized light, since there is a small component vibrating parallel to the transmission direction of the prism. If the mica and the prism are alternately adjusted until the lowest reading of the photometer is found, it can be assumed that the elliptically polarized light has been converted to plane-polarized light and its azimuth can be compared with the azimuth of the elliptically polarized light to determine the ellipticity. A few attempts to find this minimum quickly pointed out the impracticality of this technique. This method was too insensitive to reproduce the minimum with any significant precision.

However, with the polarizing prism oscillating through a symmetrical angle setting of about 2° at two equal photometer readings the sensitivity of the analyzing prism setting is $\pm 0.001^\circ$. If the analyzer is set in this position and the mica holder inserted, the mica can be rotated until the two photometer readings are again equal (the positions of the analyzer and the symmetrical angle are not changed) and one axis of the mica will be parallel to the middle position of the polarizer, perpendicular to the setting of the analyzer. As a standard procedure, the fast axis was the one oriented in this position. The direction of the fast axis was indicated on the aluminum holder for easy reference. If the two readings on the photometer are not exactly equal and the mica cannot be easily positioned to equalize them, the analyzer can be moved until the two readings are equal. The position of the mica can be determined from the small change in the position of the analyzer if the retardation is known to an approximate degree. The next paragraphs describe how this is done mathematically.

Figure 6 shows schematically the resolution of plane-polarized light by the mica and the analyzer in each of the two oscillating positions of the polarizer in the determination of the mica setting. With the oscillator in position no. 1, the reference axis Y is the midpoint of the polarizer oscillation, determined in the usual manner. Reference axis X is perpendicular to Y . The vibration plane of the plane-polarized light is P , represented by the equation $y = a \sin \omega t$. The axes f and s are the fast and slow axes of the mica, which are almost parallel to the axes Y and X , but differ from coincidence by a small angle β . The transmission direction of the analyzer is T , which has been rotated by a small angle θ from the reference axis. The angle α is the symmetrical angle and the angle η_1 is the angle between the plane of polarization and the slow axis of the mica.

The planar vibration is resolved into two components, one along each of the mica axes. These vibrations are: along s

$$y = a \cos \eta_1 \sin \omega t \quad (\text{i})$$

along f

$$y = a \sin \eta_1 \sin \omega t \quad (\text{ii})$$

After passing through the mica, the retardation δ has been imparted to the slow vibration and the resultant vibration is given by: along s

$$y = a \cos \eta_1 \sin (\omega t + \delta) \quad (\text{iii})$$

Each of these vibrations has a component which passes through the analyzer: from s

$$y = a \cos \eta_I \cos (\beta + \theta) \sin (\omega t + \delta) \quad (\text{iv})$$

from *f*

$$y = -a \sin \eta_I \sin (\beta + \theta) \sin \omega t \quad (\text{v})$$

These two vibrations are now vibrating in the same plane (along the transmission direction of the analyzer) and will interfere to produce single vibration according to eq 7 and 8. This light strikes the photomultiplier and its intensity registers on the photometer. Since the intensity is all that is measured, it is the only part of the new vibration that is necessary to describe. According to eq 7 the intensity is given by

$$I' \propto A^2 = a^2 \sin^2 \eta_I \sin^2 (\beta + \theta) + a^2 \cos^2 \eta_I \cos^2 (\beta + \theta) - 2a^2 \sin \eta_I \cos \eta_I \sin (\beta + \theta) \cos (\beta + \theta) \cos \delta \quad (\text{vi})$$

With the oscillator in position 2, all the parameters are the same except that the angle between the slow axis and the plane of polarization is η_{II} . An equation similar to (vi) can be written by using (iv) and (v) and taking into account the differences in signs. Since the analyzer is adjusted until the two intensities are equal ($I' = I''$), the following equation results after dividing through by a^2 and the constant of proportionality

$$\sin^2 \eta_I \sin^2 (\beta + \theta) + \cos^2 \eta_I \cos^2 (\beta + \theta) - 2 \sin \eta_I \cos \eta_I \sin (\beta + \theta) \cos (\beta + \theta) \cos \delta = \sin^2 \eta_{II} \sin^2 (\beta + \theta) + \cos^2 \eta_{II} \cos^2 (\beta + \theta) + 2 \sin \eta_{II} \cos \eta_{II} \sin (\beta + \theta) \cos (\beta + \theta) \cos \delta \quad (\text{vii})$$

Substituting the trigonometric identity $2 \sin x \cos x = \sin 2x$ in the third term of each side, using equations pertaining to sums and differences of sines and cosines, and finally dividing through by $\sin (\eta_I + \eta_{II})$, the equation is reduced to

$$\sin^2 (\beta + \theta) \sin (\eta_I - \eta_{II}) - \cos^2 (\beta + \theta) \sin (\eta_I - \eta_{II}) - 2 \sin (\beta + \theta) \cos (\beta + \theta) \cos \delta \cos (\eta_I - \eta_{II}) = 0 \quad (\text{viii})$$

the angles $\eta_I = (90^\circ - \alpha - \beta)$ and $\eta_{II} = (90^\circ - \alpha + \beta)$, and thus $\eta_I - \eta_{II} = -2\beta$. Equation viii then reduces to

$$\sin^2 (\beta + \theta) \sin (-2\beta) - \cos^2 (\beta + \theta) \sin (-2\beta) - 2 \sin (\beta + \theta) \cos (\beta + \theta) \cos \delta \cos (-2\beta) = 0 \quad (\text{ix})$$

Since the angles β and θ are very small, some approximations can be made. For small angles, $\sin x$ is about equal to x and $\cos x$ is about equal to 1. Using these approximations, eq ix reduces to

$$-(\beta + \theta)^2 (2\beta) + 2\beta - 2(\beta + \theta) \cos \delta = 0 \quad (\text{x})$$

The first term of this equation will be very small with respect to the other two terms since the values are less than 1 and very small. Thus

$$2\beta - 2(\beta + \theta) \cos \delta = 0 \quad (\text{xi})$$

Solving for β , the angle by which the mica axes deviate from coincidence with the midpoint of the polarizer oscillation

$$2\beta - 2\beta \cos \delta - 2\theta \cos \delta = 0 \quad (\text{xii})$$

$$\beta = \frac{\theta \cos \delta}{(1 - \cos \delta)} \quad (\text{xiii})$$

Syntheses.—The Λ -(+)-tris(ethylenediamine)cobalt(III) iodide (and the corresponding Δ isomer) was prepared and resolved according to the two methods of Broomhead, Dwyer, and Ho-

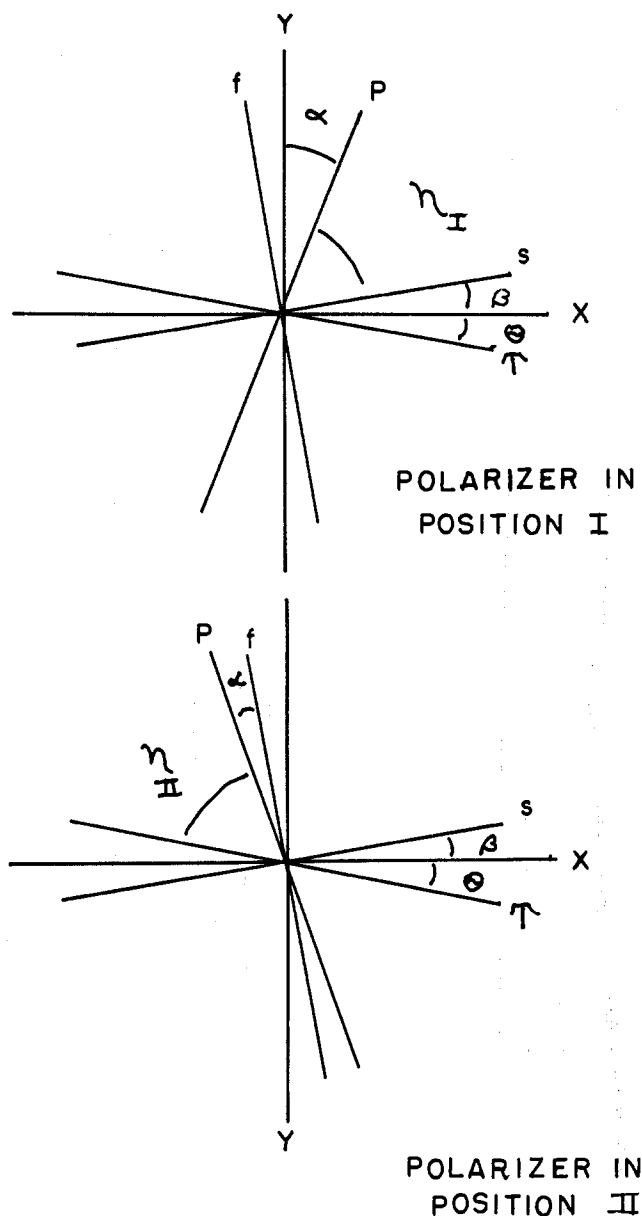


Figure 6.—Resolution of plane-polarized light by mica analyzer.

garth.¹² Three samples were prepared. The direct resolution yielded samples of both enantiomers and the partial asymmetric synthesis yielded the Δ enantiomer only. After two recrystallizations and drying under vacuum to give an anhydrous product, the specific rotation, $[\alpha]_D$, was $85.6 \pm 0.2^\circ$.

cis-Dinitrobis(ethylenediamine)cobalt(III) bromide was prepared according to the procedure of Holtzclaw, Sheetz, and McCarty¹³ and resolved according to Dwyer and Garvan.¹⁴ The specific rotation $[\alpha]_D$ was $42 \pm 2^\circ$.

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