Determination of Circular Dichroism in Multiple Scattering Systems

Yutaka TANIGUCHI* and Yoichi SHIMURA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received June 12, 1981)

In a thick suspension circular dichroism cannot be directly determined by the Grosjean-Legrand type CD instrument, because Lambert's law does not hold in it. The transfer of light intensity is discussed when polarized light is incident on a plane-parallel scattering medium containing randomly oriented, optically active particles. This problem is analyzed based on a two-beam radiative transfer model. We provide a method to determine the molar CD in a multiple scattering system. The measurements of ellipticity and transmittance with conventional instruments is served for our method by using a plate of opal glass. The molar CD is determined in Nujol mulls of Λ-$[Co(en)_3]Br_3\cdot H_2O$ and $[Co(NH_3)_6](d\text{-tart})_{1.5}\cdot 5H_2O$. The results are reproducible and reliable.

The measurement of circular dichroism (CD) spectrum is a useful method in the study of molecular structure in solution. The CD spectrum is easily measured by the Grosjean-Legrand method.$^{1)}$ Because the intensity of incident light decreases in a transparent material exponentially following Lambert's law, the ellipticity of the transmitted light is given by the familiar equations

$$\Theta = (1/4)(k_L - k_R), \tag{1}$$

and

$$\Theta = (1/4)\ln(I_{t,R}/I_{t,L}), \tag{2}$$

where Θ is the ellipticity in radians, k the absorption coefficient, I_t the light intensity transmitted by a sample, and the subscripts L and R denote the left and right circular polarization, respectively. Actually, Θ can be adequately approximated by

$$\Theta = (1/4)(I_{ac}/I_{dc}), \tag{3}$$

where $I_{ac} = I_{t,R} - I_{t,L}$ and $I_{dc} = (I_{t,R} + I_{t,L})/2$. Therefore, Θ is obtained electronically by detecting I_{ac} and I_{dc} as the alternating and direct current signals, respectively, in the photomultiplier of a Grosjean-Legrand type CD instrument.

The CD measurement has recently been extended to suspensions of biological materials.$^{2,3)}$ The decrease in light intensity transmitted by a dilute suspension also follows Lambert's law. The CD of a suspension, which contains a scattering contribution, is also measured by the conventional Grosjean-Legrand type CD instrument. However, on account of unequal scattering of left and right circularly polarized light by optically active particles, the interpretation of the resulting CD spectra is very complicated. A few investigations based on classical scattering theory were made to analyze the scattering effect on CD spectra,$^{4)}$ but general approaches to this problem have not been confirmed yet.

In the previous studies suspensions were always assumed to be dilute, where multiple scattering effects were neglected. However, multiple scattering effects are no longer negligible in a somewhat thick suspension. Lambert's law does not hold in it, and hence the Θ measured by the Grosjean-Legrand type CD instrument is not the direct information of CD.

In this paper, we propose a method to determine the molar CD of a thick suspension, a Nujol mull of solid-state complex salt, by the Grosjean-Legrand type CD instrument. The reproducibility of CD data obtained by our method will be shown too.

Principles and Practical Method

Stokes Vector. The light beams suffered multiple scattering have randomly different phases from one another, and hence the scattered beams are incoherent. The polarization state of an incoherent light beam is conveniently expressed by a Stokes vector$^{5)}$ with four components having the dimensions of light intensity. In this study, the representation based on the left and right circular polarizations$^{6)}$ will be used instead of the original Stokes vector. It is defined as

$$\boldsymbol{I} = \begin{bmatrix} I_1 \\ I_R \\ I_L \\ I_4 \end{bmatrix} = \begin{bmatrix} \langle E_R E_L^* \rangle \\ \langle E_R E_R^* \rangle \\ \langle E_L E_L^* \rangle \\ \langle E_L E_R^* \rangle \end{bmatrix}, \tag{4}$$

where E is the amplitude of electric field vector, the brackets denote time averages, and the asterisks complex conjugates. In the Grosjean-Legrand type CD instrument, the Stokes vector of the incident beam $\boldsymbol{I}_o$ (total intensity$=I_o$) is

$$\boldsymbol{I}_o = (I_o/2) \begin{bmatrix} \cos(\delta \sin \omega t) \\ 1 - \sin(\delta \sin \omega t) \\ 1 + \sin(\delta \sin \omega t) \\ \cos(\delta \sin \omega t) \end{bmatrix}, \tag{5}$$

where δ is the maximum phase difference produced in the modulator and ω the modulation frequency.

Equation of Radiative Transfer. The problem of radiative transfer in a scattering medium has been well investigated by Chandrasekhar.$^{7,8)}$ It is assumed in this paper that a homogeneous scattering medium consisting of randomly oriented particles is bounded by two parallel planes and extends over a region very large compared to its thickness. In such a plane-parallel scattering medium, the radiation field is characterized by the coordinate z on the axis normal to the boundary planes, the polar angle θ with respect to the z-axis, and the azimuthal angle ϕ referred to a suitably chosen x-axis (see Fig. 1). The variation of a light flux travelling through a layer dz in the direction (θ,ϕ) is given by

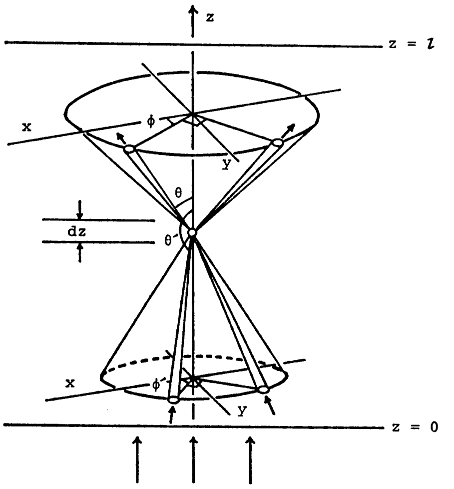

Fig. 1. Coordinate system and the directions of the incident and scattered beams.

$$(\cos\theta/\mathrm{d}z)\mathrm{d}\boldsymbol{I}(z,\theta,\phi) = -(k+s)\boldsymbol{I}(z,\theta,\phi) + (s/4\pi)\int_0^{\pi}\int_0^{2\pi} P(\theta,\phi;\theta',\phi')\boldsymbol{I}(z,\theta',\phi')\sin\theta'\mathrm{d}\theta'\mathrm{d}\phi', \tag{6}$$

where k and s are the absorption and scattering coefficients, respectively, and $P(\theta,\phi;\theta',\phi')$ is the normalized phase matrix defining the angular distribution of the scattered light incident from a direction (θ',ϕ') into the direction (θ,ϕ). The phase matrix is represented by a 4×4 matrix. When scattering particles are optically active, k and s are rewritten by the diagonal matrices, *viz.*,

$$K = \mathrm{diag}(k_1, k_\mathrm{R}, k_\mathrm{L}, k_4) \text{ and } S = \mathrm{diag}(s_1, s_\mathrm{R}, s_\mathrm{L}, s_4). \tag{7}$$

For the problem in a plane-parallel scattering medium, the Stokes vector is customarily referred to the directions parallel and perpendicular to the meridian plane,[9] which is defined by the z-axis and the propagation direction of a light beam.

We shall now consider the nature of the radiation scattered from the direction (θ',ϕ') into the direction (θ,ϕ), and that of the radiation from the direction $(\theta',\phi'+\chi)$ into the direction $(\theta,\phi+\chi)$; so the azimuthal angles of both beams are greater for the latter than for the former by an angle χ. The phase matrix depends only on the characteristics of the scattering medium. The phase matrix $P(\theta,\phi+\chi;\theta',\phi'+\chi)$ is identical with the matrix $P(\theta,\phi;\theta',\phi')$ because the scattering medium containing particles with random orientation has, on the whole, an axial symmetry about the z-axis.

When a parallel beam of light is incident into a scattering medium perpendicularly to the boundary plane (parallel to the z-axis), the relation between $\boldsymbol{I}(z,\theta',\phi')$ and $\boldsymbol{I}(z,\theta',\phi'+\chi)$ can be derived as follows. The Stokes vector $\boldsymbol{I}(z,\theta',\phi'+\chi)$ is identical with the new vector which should be yielded in the direction (θ',ϕ') when the reference axes of the original parallel beam are rotated around its propagation axis by the angle χ in the clockwise direction, as viewed in the direction of propagation. The rotation matrix $R(\chi)$ for the Stokes vector $\boldsymbol{I}=(I_1,I_\mathrm{R},I_\mathrm{L},I_4)$ is a diagonal matrix with the elements $(\mathrm{e}^{2\mathrm{i}\chi}, 1, 1, \mathrm{e}^{-2\mathrm{i}\chi})$.[6] The components I_R and I_L are invarient for the rotation of the axes. But the other components I_1 and I_4 change with such a rotation. When $\chi=\pi/2$, each of I_1 and I_4 has the value equal in magnitude but opposite in sign to the original value before the rotation.

In the CD measurements, any of the four components of the Stokes vector, $(I_1,I_\mathrm{R},I_\mathrm{L},I_4)$, is not separately detected by our instrument. The CD signals are obtained by measuring the ac and dc components of the total intensity, $I_\mathrm{R}+I_\mathrm{L}$, emitted in the forward direction. The total intensities, even in different directions, can be added arithmetically. From the above discussion it is found that the scattering contributions to the total intensity of $\boldsymbol{I}(z,\theta,\phi)$ by the I_1 and I_4 components of $\boldsymbol{I}(z,\theta',\phi')$, and those to the total intensity of $\boldsymbol{I}(z,\theta,\phi+\pi/2)$ by the corresponding components of $\boldsymbol{I}(z,\theta',\phi'+\pi/2)$ are cancelled out each other. The same argument applies to any couple of scatterings having such a directional relation. The azimuthal angles ϕ and ϕ' can be chosen arbitrarily. Therefore, when light beams scattered in the directions with the polar angle θ are all accepted simultaneously, the total intensity is, on the whole, not contributed by the components I_1 and I_4 of the incident beams from the directions with another polar angle θ'. Then the transfer equation of the total intensity is written by a 2-vector with the components I_R and I_L. The matrices P, K, and S are, of course, rewritten by 2×2 matrices.

Two-beam Model. The exact solution of the transfer equation is rarely obtained, because in most cases the phase matrix is seldom known. To a fairly good approximation, a two-beam model, dividing the radiation field into the two streams in the forward and backward directions, has been employed to solve the practical problems of radiative transfer. The scattering particles dealt with in previous papers were always optically inactive. We now extend the two-beam model to an optically active case.

Let $\boldsymbol{I}=(I_\mathrm{R},I_\mathrm{L})^\mathrm{t}$ and $\boldsymbol{J}=(J_\mathrm{R},J_\mathrm{L})^\mathrm{t}$ represent the streams propagating in the forward and backward directions, respectively (see Fig. 2). The superscript t denotes the transposed matrix. Assuming that the optical activity (circular birefringence and circular dichroism) of a particle is small, we may, as a first approximation, let the elements of the phase matrix be

$$p_\mathrm{RR} = p_\mathrm{LL} = 1 \text{ and } p_\mathrm{RL} = p_\mathrm{LR} = 0. \tag{8}$$

Within the limits, the transfer equation 6 can be replaced by the two equations of Schuster[10] or Kubelka-

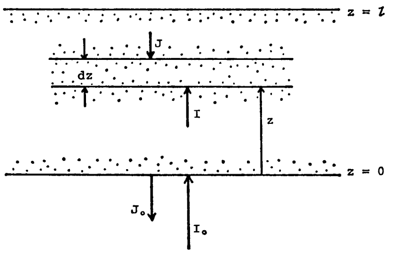

Fig. 2. Directions of the light streams used in the two-beam model.

Munk:[11]

$$\mathrm{d}\boldsymbol{I}/\mathrm{d}z = -(K+S)\boldsymbol{I}+S\boldsymbol{J}, \tag{9}$$

$$\mathrm{d}\boldsymbol{J}/\mathrm{d}z = (K+S)\boldsymbol{J}-S\boldsymbol{I}, \tag{10}$$

where $K=\mathrm{diag}(k_\mathrm{R},k_\mathrm{L})$ and $S=\mathrm{diag}(s_\mathrm{R},s_\mathrm{L})$. The general solutions of the Eqs. 9 and 10 are

$$I_\mathrm{i} = A_\mathrm{i}(1-\beta_\mathrm{i})\mathrm{e}^{\alpha_\mathrm{i}z} + B_\mathrm{i}(1+\beta_\mathrm{i})\mathrm{e}^{-\alpha_\mathrm{i}z};\ \mathrm{i} = \mathrm{R, L}, \tag{11}$$

$$J_\mathrm{i} = A_\mathrm{i}(1+\beta_\mathrm{i})\mathrm{e}^{\alpha_\mathrm{i}z} + B_\mathrm{i}(1-\beta_\mathrm{i})\mathrm{e}^{-\alpha_\mathrm{i}z};\ \mathrm{i} = \mathrm{R, L}, \tag{12}$$

where A_i and B_i are arbitrary constants to be determined by the boundary conditions, α_i and β_i are constants, given by

$$\alpha_\mathrm{i} = [k_\mathrm{i}(k_\mathrm{i}+2s_\mathrm{i})]^{1/2}, \tag{13}$$

$$\beta_\mathrm{i} = [k_\mathrm{i}/(k_\mathrm{i}+2s_\mathrm{i})]^{1/2}. \tag{14}$$

If

$$I_\mathrm{i} = (I_\mathrm{o})_\mathrm{i};\ \mathrm{i} = \mathrm{R, L} \tag{15}$$

at the illuminated surface ($z=0$), and

$$I_\mathrm{i} = (I_l)_\mathrm{i},\ J_\mathrm{i} = 0;\ \mathrm{i} = \mathrm{R, L} \tag{16}$$

at the back surface ($z=l$), we have

$$A_\mathrm{i} = -(1-\beta_\mathrm{i})\mathrm{e}^{-\alpha_\mathrm{i}l}(I_\mathrm{o})_\mathrm{i}/[(1+\beta_\mathrm{i})^2\mathrm{e}^{\alpha_\mathrm{i}l}-(1-\beta_\mathrm{i})^2\mathrm{e}^{-\alpha_\mathrm{i}l}], \tag{17}$$

$$B_\mathrm{i} = (1+\beta_\mathrm{i})\mathrm{e}^{\alpha_\mathrm{i}l}(I_\mathrm{o})_\mathrm{i}/[(1+\beta_\mathrm{i})^2\mathrm{e}^{\alpha_\mathrm{i}l}-(1-\beta_\mathrm{i})^2\mathrm{e}^{-\alpha_\mathrm{i}l}]. \tag{18}$$

Therefore, the transmittance of the i component is given by

$$T_\mathrm{i} = 4\beta_\mathrm{i}(I_\mathrm{o})_\mathrm{i}/[(1+\beta_\mathrm{i})^2\mathrm{e}^{\alpha_\mathrm{i}l}-(1-\beta_\mathrm{i})^2\mathrm{e}^{-\alpha_\mathrm{i}l}]I_\mathrm{o}, \tag{19}$$

when

$$I_\mathrm{o} = \Sigma_\mathrm{i}(I_\mathrm{o})_\mathrm{i}. \tag{20}$$

Determination of Δk. The Eq. 1 between the ellipticity Θ and the circular dichroism $\Delta k=k_\mathrm{L}-k_\mathrm{R}$ is not valid for a multiple scattering system, because Lambert's law does not hold in it. The Θ measured in such a system only gives the ratio of the ac and dc components of the light intensity transmitted, as indicated in Eq. 3.

The Eq. 3 can be rewritten by the transmittances for the left and right circular polarizations:

$$\Theta = -(1/4)\Delta T/T, \tag{21}$$

where

$$\Delta T = T_\mathrm{L} - T_\mathrm{R}, \tag{22}$$

and

$$T = (T_\mathrm{R}+T_\mathrm{L})/2. \tag{23}$$

From Eqs. 21, 22, and 23 it follows that

$$T_\mathrm{R} = T-\Delta T/2 = (1+2\Theta)T, \tag{24}$$

and

$$T_\mathrm{L} = T + \Delta T/2 = (1-2\Theta)T. \tag{25}$$

According to Eqs. 13, 14, and 19, k_R and k_L can be calculated from the values of T_R, T_L, s_R, and s_L. The T_R and T_L are evaluated from the Θ and T which are measurable by conventional spectrometers. If the values of s_R and s_L are known, we can determine $k_\mathrm{L}-k_\mathrm{R}$, *viz.*, Δk, even in a multiple scattering system.

Estimation of Scattering Coefficients. In the Kubelka-Munk equations, s is the back-scattering coefficient. When scatterers are optically active, the scattering coefficients for left- and right-circularly polarized light are, in general, different from each other. The angular dependence of the difference between scattering of left- and right-circularly polarized light by optically active spheres has been discussed recently.[12,13] It has been indicated that the difference is virtually significant in the forward scattering directions. Therefore, the back-scattering coefficients s_R and s_L may be taken as equal, and hence their values are equal to that for natural light:

$$s_\mathrm{R} = s_\mathrm{L} = s. \tag{26}$$

In Eq. 19, if k approaches zero, the equation of transmittance becomes the simplified expression

$$\lim_{k\to 0}T = 1/(1+sl). \tag{27}$$

At a wavelength where scattering particles have no absorption, the scattering coefficient s can be calculated by substituting the value of transmittance in Eq. 27.

While the scattering coefficient in an absorption band region cannot be determined directly. The scattering coefficient generally varies with wavelength; it's value normally increases with decreasing wavelength. Kortüm and Oelkrug[14] showed that for the powder samples having no absorption, there exists the empirical relation between s and λ:

$$\log s \propto \log \lambda^{-1}, \tag{28}$$

where λ is wavelength. At any wavelength in an absorption band region, we now estimate the value of the scattering coefficient by extrapolating the linearity between $\log s$ and $\log \lambda^{-1}$ in the wavelength region having no absorption to a desired wavelength (see Fig. 3).

Molar Circular Dichroism. The present paper is concerned with Nujol mulls of complex salts. The Nujol mull is composed of particles of different shapes and sizes. Because the shape and size distributions are different in every mull, neither absorption nor scattering coefficient is identical for every mull, even if it may have the same concentration. Then the values of k and s are not characteristic of a material. Nevertheless, the ratio of Δk to k should be characteristic of a material, even if it is in different mulls. Then we have

$$\Delta k/k = \Delta\varepsilon(\mathrm{cryst})/\varepsilon(\mathrm{cryst}), \tag{29}$$

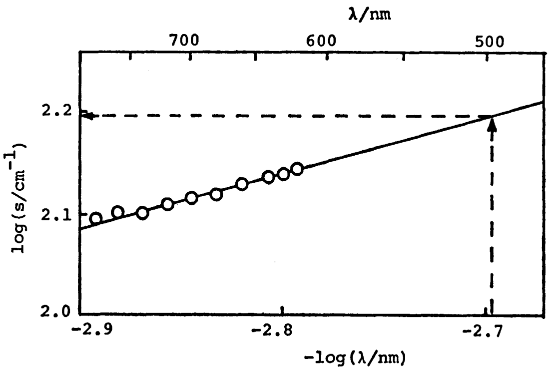

Fig. 3. Extrapolation of the scattering coefficient to a desired wavelength.
This figure is drawn based on the transmittance data in a Nujol mull of Λ-[Co(en)$_3$]Br$_3$·H$_2$O.

where $\Delta\varepsilon$(cryst) is the molar circular dichroism and ε(cryst) the molar absorption coefficient in crystalline state.

By using a microspectrophotometer Kondo measured the absorption spectra of nine crystalline hexaamminecobalt(III) complex salts in the d-d transition band region.[15] The spectrum in crystal is not much different from that in aqueous solution, *e.g.*, the molar absorption coefficients of hexaamminecobalt(III) chloride are $\varepsilon_{\max}(\text{cryst}) = 59.7$ and $\varepsilon_{\max}(\text{soln}) = 57.6\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$ for the first absorption band. We now assume that the molar absorption coefficient in crystal is equal to that in solution in the d-d transition band region:

$$\varepsilon(\text{cryst}) = \varepsilon(\text{soln}). \tag{30}$$

From Eqs. 29 and 30 the molar CD is given by

$$\Delta\varepsilon(\text{cryst}) = \varepsilon(\text{soln})\Delta k/k. \tag{31}$$

The value of k is, of course, calculated from the values of T and s for natural light.

Experimental

Measurements. In the Kubelka-Munk model the radiation field is divided into two streams in the forward and backward directions. Therefore, the light transmitted in the forward directions ($0 \leqq \theta < \pi/2$) has to be all detected in order to obtain the transmittance based on the Kubelka-Munk model. In a usual measurement parallel light, which passes through the space among suspended particles and hence contains no information from the particles, is more effectively detected by a photomultiplier than scattered light. By setting a plate of opal glass[16] on the unilluminated side of a sample cell, both of the parallel and the scattered light passing through the sample cell are accepted and transformed into diffused light at the plate of opal glass. If the diffused light emerging from the plate of opal glass has the same angular distribution for the incidence of parallel and scattered light, the transmittance is measured by detecting the diffused light on a photomultiplier of a conventional spectrophotometer. The plate of opal glass needs to be much larger than the cross section of light-path in order to prevent missing any of light scattered in the forward directions.

A mull between two parallel plates of quartz may be regarded as a plane-parallel scattering medium. When all of the light scattered into a cone, whose axis is colinear with the z-axis, is accepted simultaneously, the scattering contribution of the Stokes parameters I_1 and I_4 is eliminated from the transfer equation of light intensity. Then the opal glass method is served for the measurement of Θ.

The transmittance was measured with a Shimadzu UV-200 spectrophotometer, and the measurements of Θ were carried out on a JASCO MOE-1 spectropolarimeter at room temperature.

The measurements on Nujol mulls were made by using a quartz cell with demountable window (path length 9.15×10^{-3} cm). The blank values were also obtained by setting the plate of opal glass on the unilluminated side of the blank cell containing the mulling agent Nujol only.

A mull was prepared by adding Nujol (40—50 mg) to a sample complex salt (5—30 mg) in an agate mortar, and good grinding and mixing it.

Materials. The preparation of Λ-[Co(en)$_3$]Br$_3\cdot$H$_2$O was performed by well-known procedures.[17]

Hexaamminecobalt(III) tartrate was obtained by treating the solution of its chloride salt with an equivalent amount of freshly prepared silver *d*-tartrate. Silver chloride was precipitated and filtered off; the tartrate salt was crystallized from the filtrate. Found: C, 15.00; H, 7.24; N, 17.66%. Calcd for [Co(NH$_3$)$_6$](*d*-tart)$_{1.5}$5H$_2$O: C, 15.23; H, 7.24; N, 17.76%.

Results and Discussion

In a scattering system, the ellipticity Θ recorded in a usual manner without a plate of opal glass was always smaller than that recorded by the opal glass method. This is because the parallel light, which contributes not to the numerator I_{ac} but to the denominator I_{dc} in Eq. 3, is more effectively detected by the photomultiplier when a plate of opal glass is absent.

When the CD spectrum was measured on mulls in a conventional manner, no reproducibility was found in the intensity and shape of the spectrum. By using a plate of opal glass, the reproducibility of the CD data was obtained. Especially the shape of recorded CD curves was well reproducible on repeated runs. For two complex salts the values of $\Delta\varepsilon$(cryst) at the maximum or the minimum in the first absorption region, which were measured on the samples having various concentrations of the salts, are shown in Table 1. As can be seen from the table, the deviations from the average value of $\Delta\varepsilon$(cryst) are, at most, 5% for Λ-[Co(en)$_3$]Br$_3\cdot$H$_2$O and 4% for [Co(NH$_3$)$_6$](*d*-tart)$_{1.5}\cdot$5H$_2$O. Particles in every mull have different shape and size distributions, so that the values of absorption and scattering coefficients

TABLE 1. CONCENTRATIONS AND THE MOLAR CD IN NUJOL MULLS

Complex	Concentration	$\Delta\varepsilon$(cryst)[a]
Λ-[Co(en)$_3$]Br$_3\cdot$H$_2$O	10.6%	+1.79
	12.3	+1.91
	12.7	+1.86
	14.2	+1.86
	14.6	+1.83
	15.8	+1.84
	15.9	+1.73
	18.3	+1.79
	19.0	+1.81
	av.	+1.82
[Co(NH$_3$)$_6$](*d*-tart)$_{1.5}\cdot$5H$_2$O	14.6%	−0.61
	24.6	−0.62
	25.0	−0.61
	31.9	−0.65
	33.6	−0.64
	39.2	−0.66
	39.8	−0.65
	40.2	−0.65
	av.	−0.64

a) The values are observed at 496 nm for Λ-[Co(en)$_3$]Br$_3\cdot$H$_2$O, and at 478 nm for [Co(NH$_3$)$_6$](*d*-tart)$_{1.5}\cdot$5H$_2$O.

are characteristic not of materials but of every mull. Taking this fact into account, the magnitudes of the deviations are not so large; rather good reproducibility can be attained in the CD intensity regardless of the sample concentrations.

The CD spectrum of Λ-$[Co(en)_3]Br_3 \cdot H_2O$ in Nujol, which will be given elsewhere,[18] resembles that in aqueous solution. We have observed $\Delta\varepsilon(\mathrm{cryst}) = +1.83$ at 496 nm, −0.26 at 435 nm, and +0.24 at 346 nm in a Nujol mull, and $\Delta\varepsilon(\mathrm{soln}) = +1.89$ at 491 nm, −0.14 at 430 nm and +0.24 at 347 nm in an aqueous solution. Since the spectroscopic discrepancy is small, we suppose that the chirality around the central cobalt ion in crystal is not so different from that in solution. Kuroda and Saito have reported the CD data of some cobalt(III) complexes in KBr matrices.[19] For Λ-$[Co(en)_3]Cl_3 \cdot (1/2)NaCl \cdot 3H_2O$ the values of $\Delta\varepsilon = +2.0$ at 505.5 nm, −0.59 at 445.5 nm and +0.19 at 352 nm have been obtained. These values are appreciably different from the solid-state CD data obtained for Λ-$[Co(en)_3]Br_3 \cdot H_2O$ in this study. However, this is supposed to be caused by the influence of outer-sphere configuration.[20] Thus the value of $\Delta\varepsilon$(cryst) in our method is regarded as the value of the molar CD in crystal, which seems free from the effects of crystal anisotropies.[21]

On the other hand, the induced CD of $[Co(NH_3)_6](d\text{-tart})_{1.5} \cdot 5H_2O$ in crystal is more intensive than that in aqueous solution, *i.e.*, the value of $\Delta\varepsilon$(cryst), −0.64, is about 65 times that of $\Delta\varepsilon$(soln), −0.0098, in the first absorption band. It is because the chirality is induced in the achiral complex ion by surrounding tartrate ions more effectively in crystal than in solution.

At present our method is the only approach to determine the molar CD in multiple scattering systems. In the study of solid-state CD, the advantage of our method is that the isotropic solid-state CD, likewise the CD in solution, is obtained by easy experimental procedures, even if a minor error may exist.

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