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SOLID-STATE CIRCULAR DICHROISM SPECTRA OF COBALT(III) COMPLEXES MEASURED BY A NUJOL MULL METHOD

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Circular dichroism spectra of cobalt(III) complexes in microcrystalline states were measured by a Nujol mull method. The principle of this method was briefly outlined. The reproducibility and features of the spectra obtained were discussed.

The usefulness of CD measurements for studies on stereochemistry of metal complexes has been confirmed in a number of previous studies, but there remain some questions about CD changes in solution effected by decomposition of the complexes, shift of conformational equilibrium, association with counter ions, and especially solvation. In such cases it becomes important to measure the CD spectra of complex compounds in crystalline state. But it is rather difficult to obtain an appropriate single crystal, and it being obtained, the measurement will be attended with much difficulty in most cases because of double refraction of the crystal. The CD spectra in KBr disks are readily obtained, but it was found in our studies that the anions of the compound were often substituted by bromide ions. Then the Nujol mull method seems to be effective; especially for the cases where CD is sensitive to the counter ions or is induced by the optically active counter ions. In the present work we provide a semi-quantitative method for CD measurements in a Nujol mull and some CD spectra resulting from this method are reported.

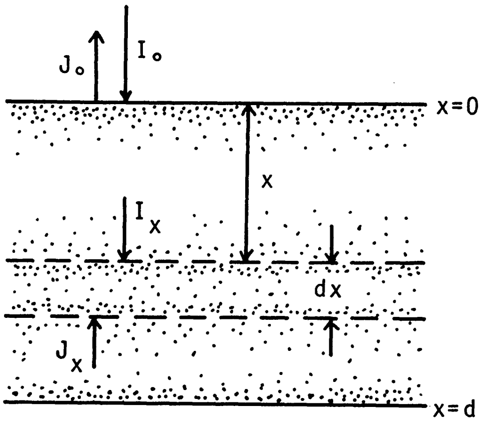

Fig. 1. Schematic diagram of the slab of particles and coordinate system used in Kubelka-Munk equations.

Since the cloud of particles in our Nujol mulls is too thick, the effect of multiple scattering cannot be neglected and the intensity of light does not decrease exponentially in it. In such case the attenuation of light intensity is usually described by the so-called Kubelka-Munk equations:[1)]

$$dI = -(K + S)Idx + SJdx, \qquad (1)$$

$$dJ = (K + S)Jdx - SIdx, \qquad (2)$$

where x is the coordinate perpendicular to the boundary planes of a particle slab (see Fig. 1), I and J are the intensities of light passing in the forward and backward directions, and K and S are absorption and back-scattering coefficients, respectively. Under the following boundary conditions:

$$I = I_o \qquad \text{for} \quad x = 0,$$

$$I = I_{x=d} \quad \text{and} \quad J = 0 \qquad \text{for} \quad x = d,$$

where d is the thickness of the particle slab, the differential equations are easily integrated. The transmittance is then given by

$$T = \frac{I_{x=d}}{I_o} = \frac{4\beta}{(1+\beta)^2 e^{\alpha d} - (1-\beta)^2 e^{-\alpha d}} , \tag{3}$$

where $\alpha = \sqrt{K(K+2S)}$ and $\beta = \sqrt{K/(K+2S)}$.

Now it is assumed that these equations hold when the light incident on a slab of optically active particles is left (L) or right (R) circularly polarized. If S and T for left and right circularly polarized light are determined at a certain wavelength, K_L and K_R are calculated by the Eq. (3).

In our CD instrument (Jasco MOE-1) CD is measured by the Grosjean-Legrand method,2) where experimentally observed ellipticity (θ) is correlated with light intensities I_L and I_R, which are observed after passing a sample, that is,

$$\theta = \frac{33}{\ln 10} \cdot \frac{I_R - I_L}{\frac{1}{2}(I_R + I_L)} . \tag{4}$$

Then

$$T_R - T_L = \frac{\ln 10}{33} \theta T , \tag{5}$$

where

$$T = \frac{1}{2}(T_R + T_L) . \tag{6}$$

The average transmittance T is equal to that for natural light, and is measured by a usual spectrophotometer. From Eqs. (5) and (6) the two components of transmittance are obtained as follows:

$$T_R = T + \frac{1}{2}(T_R - T_L) = T + \frac{\ln 10}{66} \theta T , \tag{7}$$

and

$$T_L = T - \frac{1}{2}(T_R - T_L) = T - \frac{\ln 10}{66} \theta T , \tag{8}$$

where θ and T are easily observable values.

If, in experimental measurements, the light scattered into the forward directions were missed by the detectors of conventional spectrophotometer or circular dichrograph, K may contain some error due to the scattering. Therefore, in our studies, almost all of the light scattered into the forward directions is accepted by a sheet of opal glass3) so that the true value of K is obtained. The scattering coefficients for left and right circularly polarized light are, in general, not equal for an optically active particle. On the basis of the electromagnetic theory Bohren4) showed that the difference in scattering between left and right circularly polarized light by optically active spheres is significant only for the forward directions. Then the back-scattering coefficients S_L and S_R might be considered equal, i.e., $S_L \simeq S_R = S$. When K = 0,

Table 1. The concentration of $[Co(NH_3)_6](d\text{-}C_4H_4O_6)_{3/2}\cdot 5H_2O$ in Nujol mulls and CD intensity at the peak position.

Complex	Nujol	Concentration	$\Delta\varepsilon'_{max}$
7.3 mg	42.8 mg	14.6 %	-0.61
14.3	43.8	24.6	-0.62
14.2	42.5	25.0	-0.61
21.0	44.8	31.9	-0.65
21.4	42.2	33.6	-0.64
28.3	43.9	39.2	-0.66
28.4	42.9	39.8	-0.65
28.4	42.3	40.2	-0.65

namely for non-absorbing particles, S is easily determined by the equation

$$T = \frac{1}{1 + Sd}\,, \tag{9}$$

which is derived from Eq. (3). But at a certain wavelength in the absorption band region of a complex $K \neq 0$, and S cannot be obtained directly. The scattering coefficient S generally depends upon the wavelength. Its exact relationship is not simple, but, to a fairly good approximation, it is described by a simple empirical equation:[5)]

$$S = \text{const.}\ \lambda^{-n}. \tag{10}$$

Then S at any wavelength in the absorption band region is obtained by the extrapolation of a linear log S vs. log λ plot obtained for K = 0. Here K_L and K_R, and hence ΔK (= $K_L - K_R$) at a desired wavelength are evaluated for the microcrystalline sample in Nujol.

The CD values ($\Delta\varepsilon'$) in Figs. 2 and 3, and Table 1 are based on the assumption that the molar absorption coefficient (ε') in crystal is equal to that (ε) in aqueous solution.[6)] The CD spectra were not modified by varying contents of each complex in Nujol mulls. The intensities of CD peak measured for eight runs having variable contents of $[Co(NH_3)_6](d\text{-}C_4H_4O_6)_{3/2}\cdot 5H_2O$ are shown in Table 1. Taking into account that the shapes and sizes of particles are all different for the eight runs, the reproducibility of the CD intensity seems to be in a permissible range.

As shown in Fig. 2, the bromide salt of Λ-tris(ethylenediamine)cobalt(III) complex has almost the same CD intensity and pattern in the microcrystalline state and in aqueous solution. Closer comparison, however, reveals that the component E_a tends to decrease in intensity and A_2, inversely, to increase in the microcrystalline

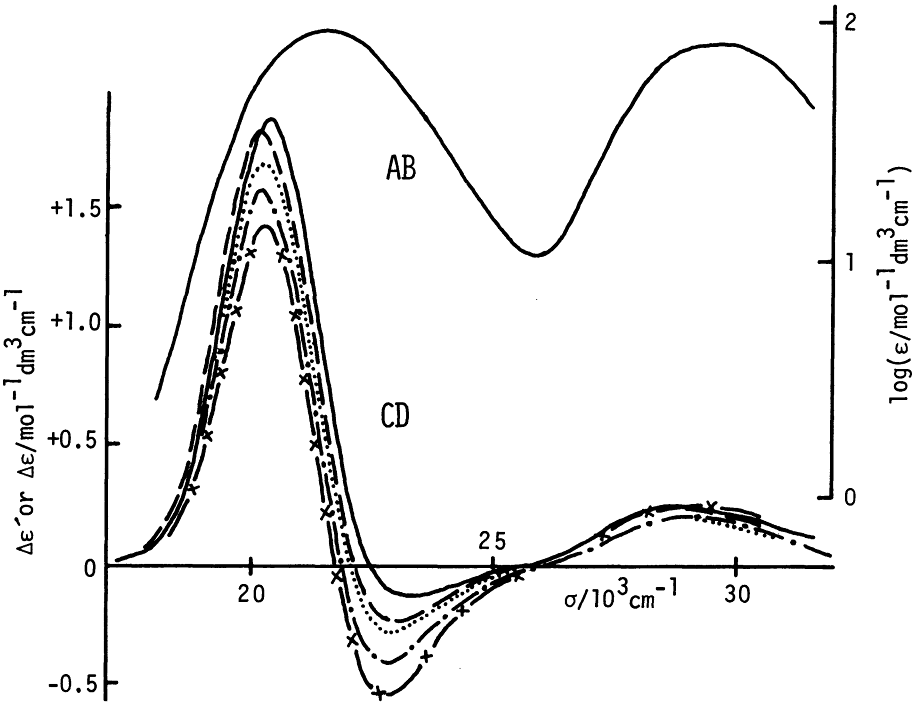

Fig. 2. CD spectra of Λ-$[Co(en)_3]X$, where X = $Br_3\cdot H_2O$ (— — —), $Cl_3\cdot H_2O$ (·····), $Cl_3\cdot\frac{1}{2}NaCl\cdot 3H_2O$ (—·—), and $Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$ (—×—) in Nujol, and absorption (AB) and CD spectra of the bromide (X = Br_3) in water (———).

state. This phenomenon is analogous to that caused by ion-pairing in solution.[7)] Smith and Douglas[8)] showed that chloride ion has not larger effect on the CD of the same complex ion in solution. However, it is found that the Cl^- has somewhat larger effect in crystal. The $(+)_{589}$-tartrate ion produces a larger change than Cl^- and Br^-. The strong interaction between Λ-$[Co(en)_3]^{3+}$ and $(+)_{589}$-tartrate ion has been suggested from X-ray analysis of the Λ-$[Co(en)_3]Br(d\text{-}C_4H_4O_6)\cdot 5H_2O$ crystal.[9)]

Although the hexaamminecobalt(III) complex ion is achiral, CD is observed for the d-tartrate salt in the first absorption band region, as shown in Fig. 3. The induced CD is weak in aqueous solution (7.86×10^{-3} mol dm^{-3}). On the other hand, the CD peak intensity is about sixty times as large in a Nujol mull as in aqueous solution. It seems that the direct interaction between the complex cations and tartrate anions in the crystal lattice is responsible for this intense CD. On the other hand, any CD could not be observed for this complex salt in KBr disks. This fact indicates that the tartrate ion is substituted by bromide ion in KBr disks. Thus the Nujol mull method is particularly useful to investigate the CD induced by an optically active counter ion.

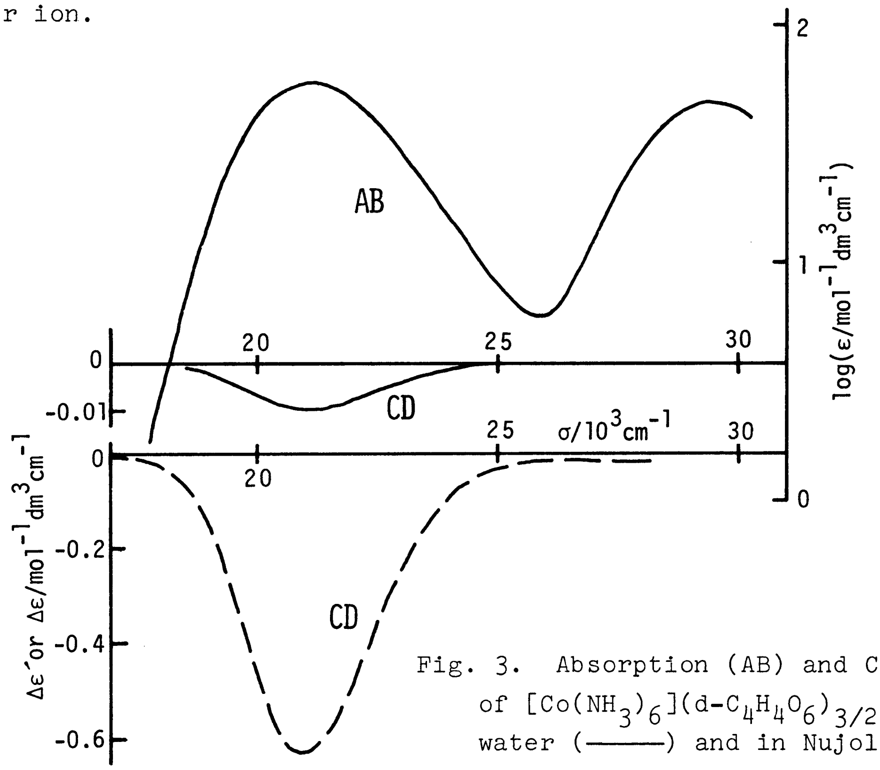

Fig. 3. Absorption (AB) and CD spectra of $[Co(NH_3)_6](d\text{-}C_4H_4O_6)_{3/2}\cdot 5H_2O$ in water (———) and in Nujol (– – –).

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