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Solid-State Circular Dichroism Spectra of Tris(diamine)cobalt(III) Complexes: Decomposition into E and A_2 Components

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Solid-state circular dichroism spectra of some tris(diamine)cobalt(III) complexes were measured. Each CD band region was decomposed into E and A_2 components by combining the CD spectra in uniaxial single-crystals and in microcrystalline states. The observed values of R(E) and $R(A_2)$ were compared with the theoretical calculation of Mason and Seal based on dynamic coupling method. The agreements are generally good for those complexes with five-membered chelate rings, however, there are some discrepancies for six- and seven-membered chelate ring cases.

Tris(diamine) cobalt(III) complexes usually exhibit two circular dichroism bands with opposite signs in the first absorption region ($A_{1g}\rightarrow T_{1g}$). The two bands correspond to the E and A_2 components of O_h parentage in D_3 environment. However, they are considered to be residual wing absorption resulting from extensive cancellation of the rotatory strengths of the two transitions, since the trigonal splitting is small. Single-crystal CD spectra are generally attended by difficulty of double refraction. Uniaxial crystals are usually employed for the measurement of single-crystal CD spectra. With the aid of the known crystal structures, an attempt has been made to decompose the CD spectra into two components by combining the single-crystal and the microcrystalline CD spectra of uniaxial crystals.

Principle of the Method

Figure 1 illustrates the interaction of circularly polarized light with the complex ion in a uniaxial crystal. The light propagates along the optic axis OZ. The direction of a threefold axis of the complex ion is indicated by a small closed triangle. The threefold axis is inclined at an angle of α with respect to the optic axis. Let OY be a projection of the threefold axis on a plane perpendicular to OZ. OX is chosen in such a way that OX, OY and OZ form a right-handed Cartesian coordinate system. When the circularly polarized light propagates along OZ, its electric vector $\boldsymbol{E}$ rotates on the XY plane. E component can be excited with the light whose electric vector is perpendicular to the threefold axis of the complex ion, whereas A_2 component can be excited when the electric vector is parallel to the threefold axis. At a given moment, let the electric vector $\boldsymbol{E}$ make an angle of φ with OX. The intensities of E and A_2 components excited at this moment will be proportional to

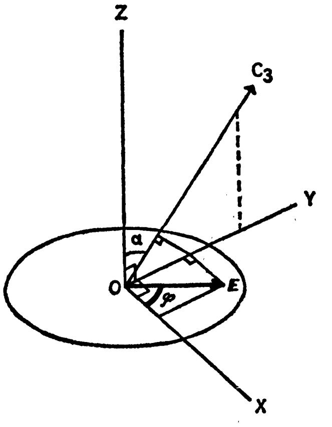

Fig. 1. Illustrating the interaction of circularly polarized light with the complex ion in a uniaxial crystal.

$$E^2\cos^2\alpha\sin^2\varphi + E^2\cos^2\varphi \quad \text{for E} \qquad (1)$$

and

$$E^2\sin^2\alpha\sin^2\varphi \quad \text{for } A_2 \qquad (2)$$

respectively. The averaged intensity over a period of rotation of the $\boldsymbol{E}$ vector will be obtained as follows:

$$1/2\pi\int_0^{2\pi}(E^2\cos^2\alpha\sin^2\varphi + E^2\cos^2\varphi)\mathrm{d}\varphi = E^2(1+\cos^2\alpha)/2 \quad \text{for E} \qquad (3)$$

and

$$1/2\pi\int_0^{2\pi}(E^2\sin^2\alpha\sin^2\varphi)\mathrm{d}\varphi = E^2(\sin^2\alpha)/2 \quad \text{for } A_2 \qquad (4)$$

Since E level is doubly degenerate, the difference between ε_l and ε_r of the single crystal, $\Delta\varepsilon_s$, can be written as a sum of the $\Delta\varepsilon(E_X)$, $\Delta\varepsilon(E_Y)$ and $\Delta\varepsilon(A_2)$ as follows:

$$\Delta\varepsilon_s = (1+\cos^2\alpha)/4\Delta\varepsilon(E_X) + (1+\cos^2\alpha)/4\Delta\varepsilon(E_Y) + (\sin^2\alpha)/2\Delta\varepsilon(A_2) \qquad (5)$$

On the other hand, in microcrystalline state the threefold axes of the complex ions are randomly oriented, hence $\Delta\varepsilon$ in microcrystalline state, $\Delta\varepsilon_m$, can be written as

$$\Delta\varepsilon_m = 1/3\Delta\varepsilon(E_X) + 1/3\Delta\varepsilon(E_Y) + 1/3\Delta\varepsilon(A_2) \qquad (6)$$

where 1/3 is a random orientation factor.
Since $\Delta\varepsilon(E_X) = \Delta\varepsilon(E_Y)$, Eqs. (5) and (6) become

$$\Delta\varepsilon_s = (1+\cos^2\alpha)/2\Delta\varepsilon(E_X) + (\sin^2\alpha)/2\Delta\varepsilon(A_2) \qquad (7)$$

and

$$\Delta\varepsilon_m = 2/3\Delta\varepsilon(E_X) + 1/3\Delta\varepsilon(A_2) \qquad (8)$$

Now we obtain the two simultaneous Eqs. (7) and (8) involving $\Delta\varepsilon(E_X)$ and $\Delta\varepsilon(A_2)$ as two unknowns. Using $\Delta\varepsilon_s$ and $\Delta\varepsilon_m$ measured at an arbitrary wavelength, $\Delta\varepsilon(E_X)$ and $\Delta\varepsilon(A_2)$ can be easily calculated by Eqs. (7) and (8). In this way the observed CD spectra can be decomposed into E and A_2 components.

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Experimental

By the procedure described above, CD spectra of the following seven tris(diamine)cobalt(III) complexes of known crystal structures were decomposed.

Five-membered chelate rings	α	Ref.
Λ-2[Co(en)$_3$]Cl$_3$·NaCl·6H$_2$O	0°	1
Λ-[Co(en)$_3$]Br$_3$·H$_2$O	0	2
Δ-[Co(*R*-pn)$_3$]Br$_3$	0	3
Λ-[Co(*S*,*S*-chxn)$_3$]Cl$_3$·5H$_2$O	8	4
Δ-[Co(*R*,*R*-cptn)$_3$]Cl$_3$·4H$_2$O	22	5
Six-membered chelate rings		
Δ-[Co(*R*,*R*-ptn)$_3$]Cl$_3$·2H$_2$O	69.5	6
Seven-membered chelate rings		
Δ-[Co(tmd)$_3$]Br$_3$	0	7

Abbreviations: en ethylenediamine; pn propylenediamine; chxn *trans*-1,2-diaminocyclohexane; cptn *trans*-1,2-diaminocyclopentane; ptn 2,4-diaminopentane; tmd 1,4-diaminobutane.

These are all uniaxial crystals and the values of α are also shown.

The CD spectra of these D$_3$ complexes were measured for single-crystal and microcrystalline states except those of Δ-[Co(*R*,*R*-cptn)$_3$]Cl$_3$·4H$_2$O. For this complex Toftlund and Pedersen[8] measured the single-crystal CD spectra by diluting the complex ion in Δ-[Rh(*R*,*R*-chxn)$_3$]Cl$_3$·4H$_2$O. Though the crystal structure of this Rh(III) complex is not yet known, it is highly probable that the compound is isostructural with Δ-[Co(*R*,*R*-cptn)$_3$]Cl$_3$·4H$_2$O, in view of the fact that they belong to the same space group P6$_1$22 and form mixed crystals. Accordingly α was assumed to be 22° based on the known crystal structure of the cobalt complex[5].

The crystals of Λ-2[Co(en)$_3$]Cl$_3$·NaCl·6H$_2$O, Λ-[Co(en)$_3$]Br$_3$·H$_2$O, Δ-[Co(*R*-pn)$_3$]Br$_3$ and Λ-[Co(*S*,*S*-chxn)$_3$]Cl$_3$·5H$_2$O were prepared according to the method described by Nakatsu, Shiro, Saito and Kuroya[9], Werner[10], Iwasaki and Saito[3] and Jaeger and Bijkerk[11], respectively. The crystals of Δ-[Co(*R*,*R*-ptn)$_3$]Cl$_3$·2H$_2$O and Δ-[Co(tmd)$_3$]Br$_3$ were kindly supplied by Professor J. Fujita of Nagoya University.

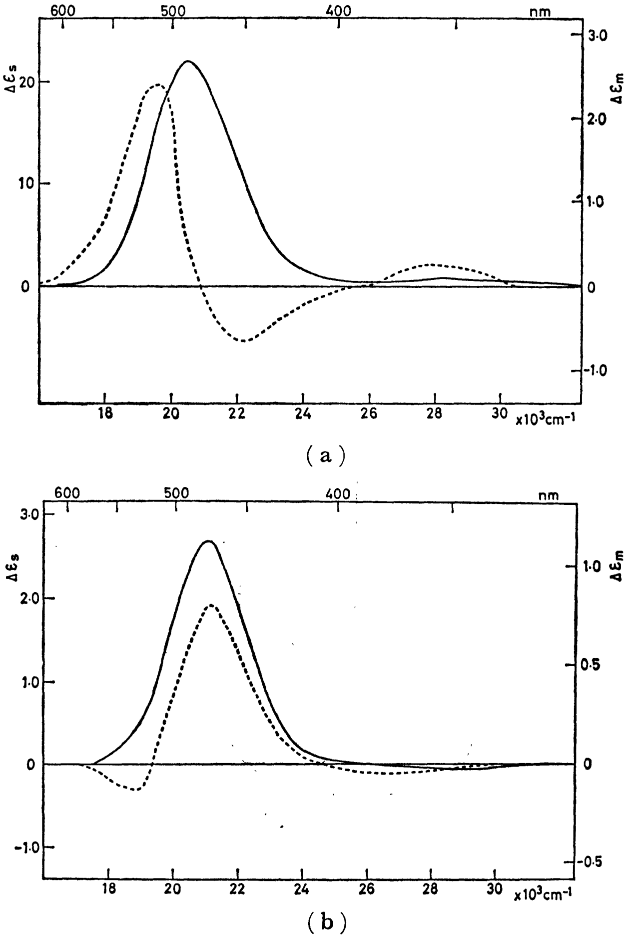
CD Spectra. *a) Single-crystal CD Spectra*: Crystals were cut with a thin razor blade perpendicular to the optic axis and then they were polished on a filter paper moistened with water to the required thickness (0.01—0.08 mm). The thickness was measured by using a microscope fitted with a microscale. Direction of the optic axis for each specimen was checked by observing conoscopic figure under a polarizing microscope. The single-crystal CD spectra were measured over the range 300—650 nm by means of JASCO J-20 and partly by J-40, with the light beam parallel to the optic axis of the crystal. The measurements were repeated at least twice by employing different specimen in order to check the reproducibility except for Δ-[Co(tmd)$_3$]Br$_3$. For the latter case, the crystal was brittle and hard to manipulate. A specimen with suitable thickness for the measurement could not be obtained.

b) Preparation of KBr Disk and Measurement of CD Spectra in Microcrystalline State: About 180 mg of dry KBr and the required amount of complexes(*ca*. 1 mg) were weighed and powdered in a dental amalgam mill (Amalgamator) together with a stainless steel ball for about 150 s. In order to prevent from diffused reflections at grain boundaries, samples must be powdered elaborately. Dependence of CD spectra on duration of grinding was examined. $\Delta\varepsilon$ increases with the duration of grinding and tends to a constant value. The optimum duration of grinding was determined. The powdered samples were pressed in a standard KBr press at 9 t/cm^2 for five to ten minutes. The pellet was, after weighing, mounted on a KBr disk holder and placed normal to the light beam. CD spectra were measured over the range 300—650 nm by JASCO J-20. It was established that there exists a linear relationship between the circular dichroism deflection and the sample concentration, if the latter is less than 1% by weight.[12] Accordingly $\Delta\varepsilon$ values were calculated in the usual way.

The CD spectra under the second absorption band were recorded for those complexes containing chloride ions. The intensities were very weak, since the involved transitions are magnetically forbidden. The results are less reliable as compared to those under the first absorption band.

Results and Discussion

Figure 2 represents two typical CD spectra in single crystal and in microcrystalline state: Λ-[Co(*S*,*S*-chxn$_3$]-Cl$_3$·5H$_2$O and Δ-[Co(*R*,*R*-ptn)$_3$]Cl$_3$·2H$_2$O. Table 1 gives the observed $\Delta\varepsilon_{\max}$ and the peak positions for Λ-2[Co(en)$_3$]Cl$_3$·NaCl·6H$_2$O, Λ-[Co(*S*,*S*-chxn)$_3$]Cl$_3$·5H$_2$O and Δ-[Co(*R*,*R*-ptn)$_3$]Cl$_3$·2H$_2$O. In Fig. 3 are shown the results of decomposition into E and A$_2$ components of the CD spectra shown in Fig. 2. Table 2 summarizes the peak positions and $\Delta\varepsilon_{\max}$ of the decomposed E and A$_2$ components in the first absorption region for all the seven D$_3$ complexes. Trigonal splitting param-

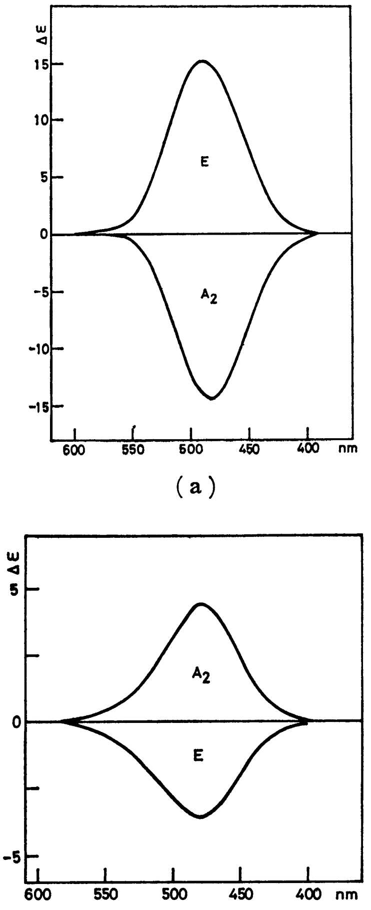


(a)

(b)

Fig. 2. The circular dichroism spectrum of a single-crystal (——) and that in KBr matrix (----).
(a) Λ-[Co(*S*,*S*-chxn)$_3$]Cl$_3$·5H$_2$O
(b) Δ-[Co(*R*,*R*-ptn)$_3$]Cl$_3$·2H$_2$O

eters $K(\equiv 2/3(\tilde{\nu}_E-\tilde{\nu}_{A_2}))$ are also included. Single-crystal CD spectra of some D_3 complexes with $\alpha=0°$ were reported by McCaffery and Mason[13] and Judkins and Royer[14]. General features of the spectra and peak positions obtained by these authors agree well with those of the present study. However, the $\Delta\varepsilon$ values are somewhat different, reflecting the experimental difficulties of this kind of measurement. The CD spectra of Λ-[Co(S,S-chxn)$_3$Cl$_3\cdot$5H$_2$O are broadly similar to those of Λ-2[Co(en)$_3$]Cl$_3\cdot$NaCl$\cdot$6H$_2$O. The CD spectra in KBr matrix of Λ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(S,S-chxn)]$_3{}^{3+}$ are not so much different from their solution CD spectra. However, it is not true for Δ-[Co(R,R-ptn)$_3$]Cl$_3\cdot$2H$_2$O: in its microcrystalline state, it gives a weak negative peak at a longer wavelength side and a large positive peak at shorter wavelength side of the first absorption band and a very weak negative peak in the second absorption region, whereas in solution the peak heights in the first absorption region are inverted, suggesting a conformational change in solution.[15] From Table 2, it can be easily seen that R(E) is positive and $R(A_2)$ is negative for the absolute configuration Λ, while R(E) is negative and $R(A_2)$ is positive for Δ configuration, in agreement with the well-known empirical rule for the solution CD spectra. The sign of K is always negative throughout the series of the complexes. For the complexes with five-membered chelate rings, K ranges from -250 to $-130\ \text{cm}^{-1}$, while $\tilde{\nu}_{\text{max}}$ of the two bands nearly coincide and the sign of K is



(a)

(b)

Fig. 3. The E and A_2 components obtained from the spectra shown in Fig. 2.
(a) Λ-[Co(S,S-chxn)$_3$]Cl$_3\cdot$5H$_2$O
(b) Δ-[Co(R,R-ptn)$_3$]Cl$_3\cdot$2H$_2$O

TABLE 1. CD SPECTRA OF SINGLE-CRYSTAL AND IN KBr MATRIX

		$\Delta\varepsilon_{\text{max}}$	λ_{max}
Λ-2[Co(en)$_3$]Cl$_3\cdot$ NaCl$\cdot$6H$_2$O	single-crystal	+24.4 +0.74	489 nm 349
	KBr matrix	+2.0 −0.59 +0.19	505.5 445.5 352
Λ-[Co(S,S-chxn)$_3$]$\cdot$ 5H$_2$O	single-crystal	+22.17 +0.58	488 350
	KBr matrix	+2.38 −0.61 +0.24	512.2 449.5 360
Δ-[Co(R,R-ptn)$_3$]Cl$_3\cdot$ 2H$_2$O	single-crystal	+2.7 −0.064	478 345
	KBr matrix	−0.13 +0.79 −0.046	533.2 476.8 375

TABLE 2. E AND A_2 COMPONENTS OF SOLID-STATE CD SPECTRA
The values of $\Delta\varepsilon$(E) and $\Delta\varepsilon(A_2)$ are corrected by the fixed-orientation factors of 2/3 and 1/3 respectively.

Complex	E		A_2		K
	$\tilde{\nu}_{\text{max}}$	$\Delta\varepsilon_{\text{max}}$	$\tilde{\nu}_{\text{max}}$	$\Delta\varepsilon_{\text{max}}$	
Five-membered chelate rings	$\times 10^3\ \text{cm}^{-1}$		$\times 10^3\ \text{cm}^{-1}$		cm^{-1}
Λ-2[Co(en)$_3$]Cl$_3\cdot$NaCl$\cdot$6H$_2$O	20.75	+15.9	20.97	−15.3	−150
Λ-[Co(en)$_3$]Br$_3\cdot$H$_2$O	20.76	+15.7	20.99	−15.1	−150
Δ-[Co(R-pn)$_3$]Br$_3$	20.45	−10.9	20.83	+9.8	−253
Λ-[Co(S,S-chxn)$_3$]Cl$_3\cdot$5H$_2$O	20.45	+14.6	20.75	−13.7	−197
Δ-[Co(R,R-cptn)$_3$]Cl$_3\cdot$4H$_2$O[a]	19.6	−15.6	19.8	+14.3	−127
Six-membered chelate rings					
Δ-[Co(R,R-ptn)$_3$]Cl$_3\cdot$2H$_2$O	20.92	−3.6	20.94	+4.4	−13
Seven-membered chelate rings					
Δ-[Co(tmd)$_3$]Br$_3$	18.8[b]	−8.6[b]	19.3[b]	+10.2[b]	−333[b]

a) The decomposition was based on the CD spectra reported by Toftlund and Pedersen.[8] b) These values are not reliable. See text.

TABLE 3. ROTATORY STRENGTHS OF TRIS(DIAMINE)COBALT(III) COMPLEXES (10^{-40} c.g.s.)
Crystal values of R(E) and $R(A_2)$ are corrected by the fixed-orientation factors of 2/3 and 1/3 respectively.

	Observed			Calculated by Mason and Seal[16,17]			$R(T_1)_{expt}$
	R(E)	$R(A_2)$	$R(T_1)$	R(E)	$R(A_2)$	$R(T_1)$	
Λ-2[Co(en)$_3$]Cl$_3$·NaCl·6H$_2$O	+62.9	−58.6	+4.3	+63.8	−59.8	+4.0	+4.4
Λ-[Co(en)$_3$]Br$_3$·H$_2$O	+59.9	−55.7	+4.2	+63.8	−59.8	+4.0	+4.4
Λ-[Co(S-pn)$_3$]Br$_3$[a]	+38.1	−36.6	+1.5	+65.1	−61.3	+3.8	+4.2
Λ-[Co(S,S-chxn)$_3$]Cl$_3$·5H$_2$O	+56.5	−51.1	+5.4	+78.1	−74.0	+4.1	+3.9
Λ-[Co(S,S-cptn)$_3$]Cl$_3$·4H$_2$O[b]	+57.3	−54.5	+2.8	+69.3	−65.4	+3.9	−4.3
Λ-[Co(S,S-ptn)$_3$]Cl$_3$·2H$_2$O[a]	+12.5	−14.5	−2.0	+57.7	−55.3	+2.4	+1.9
Λ-[Co(tmd)$_3$]Br$_3$[a]	+31.1	−38.7	−7.6	+93.0	−89.3	+3.7	−4.9

a) Experiments were carried out for the enantiomers. b) These values are based on the CD spectra measured by Toftlund and Petersen[8]. $R(T_1)=R(E)+R(A_2)$. $R(T_1)_{expt}$ are values observed for solution CD spectra.[16].

ambiguous in the six-membered chelate ring case. The K value for Δ-[Co(tmd)$_3$]$^{3+}$ was not so reliable and it may not be practicable to discuss further. Rotatory strengths of each component under the first absorption band were obtained from the band areas of the CD spectrum. Table 3 lists the values of R(E) and $R(A_2)$. The net rotatory strengths, $R(T_1)=R(E)+R(A_2)$ are also included. The net rotatory strengths obtained from solution CD spectra are also included in Table 3 under the heading $R(T_1)_{expt}$.[16] For R(E) of Λ-2[Co(en)$_3$]Cl$_3$·NaCl·6H$_2$O values of +52.6[13] and +50.9[14] are reported. +45.3 is given for R(E) of Λ-[Co(en)$_3$]Br$_3$·H$_2$O.[13] All these values are somewhat smaller than those of the present study. R(E) of −41.5 for Δ-[Co(R-pn)$_3$]Br$_3$ by Judkins and Royer[14] agrees well with −38.1 of the present study. As can be seen from Table 3, the absolute values of the observed rotatory strengths of the E and A_2 bands possess nearly the same magnitudes and opposite signs in conformity with the theoretical prediction. R(E) and $R(A_2)$ are unequal: $|R(E)|>|R(A_2)|$ for the complexes with five-membered chelate rings, whereas $|R(E)|<|R(A_2)|$ for the complexes with six- and seven-membered chelate rings. $R(T_1)$'s obtained from solid state CD spectra generally agree well in magnitude and sign with those obtained from solution CD spectra except for Λ-[Co(S,S-cptn)$_3$]$^{3+}$, Λ-[Co(S,S-ptn)$_3$]$^{3+}$ and Λ-[Co(tmd)$_3$]$^{3+}$. For the latter three cases, some change in the conformation of the complex ion or in the mode of ion association may be expected in solution.[8,15]

Recently Mason and Seal calculated the d-electron optical activity of tris(diamine) cobalt(III) complex ions based on dipole-coupling ligand-polarization model.[16,17] All the computations are based on the crystal structures determined by us.[1–7] The results are listed in Table 3. The theoretical calculations correctly predict all the signs of R(E) and $R(A_2)$. Moreover, theoretical values of $R(T_1)$ agree well in sign and magnitudes with those observed in solid-states for the complexes with five-membered chelate rings. Theoretical values of R(E) and $R(A_2)$ for Λ-[Co(en)$_3$]$^{3+}$ agree satisfactorily with the observed values. For five-membered ring cases R(E) and $R(A_2)$ agree pretty well with the observation. For the six- and seven-membered chelate ring cases, the agreement is less satisfactory. No explanation can be offered at present.

Unlike solution CD spectra, crystal CD spectra are free from the effect of conformational change which sometimes occurs in solution, on the other hand the effect of neighboring anion in the crystal cannot be ignored. This latter effect might not be of a primary importance, as can be seen from Table 3.

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