August, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *2383—2389 (1982)* 2383

Theoretical Prediction of Cotton Signs in CD Spectra of Λ-$[Co(N)_2(O)_4]^-$- and Λ-$[Co(N)_4(O)_2]^+$-type Complexes

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(Recieved December 11, 1981)

The crystal field model of d-d optical activity has been applied to complexes with *cis*(*N*)-$[Co(N)_2(O)_4]^-$ and *cis*(*O*)-$[Co(N)_4(O)_2]^+$ chromophores, and the Cotton signs of these complexes have been predicted. The model has shown that the Cotton signs in CD spectra of the complexes depend upon: 1) the energy difference between E_g^a and A_{2g} states, 2) the coordination angle in a bidentate chelate, and 3) the effective charge of the ligating atoms. The CD spectral difference between an optically active carbonato complex and the corresponding diaqua complex derived from the carbonato complex has been understood in terms of the effective charge of the ligating O atoms.

In our laboratory, we have been investigating CD spectra in the ligand-field transition region of complexes with *cis*(*N*)-$[Co(N)_2(O)_4]$ and *cis*(*O*)-$[Co(N)_4(O)_2]$ chromophores.[1–3] A method of assigning a transition component of a given Cotton peak was proposed on the basis of a regular CD spectral change due to a change of chelate ring size of bidentate OO ligand.[1] The CD spectrum of a diaqua complex, which had been derived from an optically active carbonato complex by an acid-hydrolysis, was found to be remarkably different from that of the parent carbonato complex.[1,3] For examples, $(-)_{589}[Co(CO_3)(ox)(en)]^-$ exhibits a single positive Cotton peak in the first absorption band region, which is assignable to the $A_{1g}\rightarrow E_g^a(D_{4h})$ transition component. On the other hand, $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$ complex derived from the $(-)_{589}$ carbonato complex exhibits negative and positive Cotton peaks from the lower-frequency side in the region, the negative peak being assigned to the same transition component. That is to say, the Cotton sign in the diaqua complex is opposite to that in the parent carbonato complex.

The optical activity associated with the d-d transition of *cis*-$[Co(a)_2(en)_2]^{n+}$ (a represents unidentate ligands such as H_2O, Cl^-, *etc.*) has been discussed by McCaffery *et al.*[4] They attempted to relate the Cotton signs in the bis(ethylenediamine) complexes with those in the tris(ethylenediamine)cobalt(III) complex with D_3 symmetry, and found a rule that the Cotton peak of the $A_{1g}\rightarrow E_g$ transition component in the Λ-$[Co(a)_2(en)_2]^{n+}$ complexes has a positive sign, as does that in the Λ-$[Co(en)_3]^{3+}$ complex. However, an exception to the rule was reported, that is, the Cotton peak assignable to $A_{1g}\rightarrow E_g$ transition in Λ-$[Co(N_3)_2(en)_2]^+$ has a negative sign.[5] The rule is not useful for an understanding of the CD spectrum of $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$.

There are two types of theoretical treatments of optical activity; one is called a crystal field model (or static coupling model), developed by Piper *et al.*,[6] and the other is called a dynamic coupling model, developed by Mason *et al.*[7] The former is based upon the crystal field theory, and optical activity of a metal complex is explained by anadmixture of d-orbitals with p- or f-orbitals in a central metal ion. In the latter, the optical activity is explained by an interaction of the hexadecapole moment at a central metal ion with transient electric dipole moments at ligands. However, the application of these models is mostly limited to the tris(diamine) complex with D_3 symmetry.

In this paper, a crystal field model for mixed complexes with lower symmetry than D_3 is proposed, in which the signs of rotatory strength of $A_{1g}\rightarrow A_{2g}(D_{4h})$ transition component are predicted in Λ-$[Co(NN)(OO)_2]^{n-}$ and Λ-$[Co(NN)_2(OO)]^{n+}$ complexes ($OO=CO_3^{2-}$, ox^{2-}, mal^{2-}, or $2H_2O$; NN=en or tn). The proposed model is useful for the understanding of the CD spectrum of the appropriate diaqua complex.

General Theory

The Hamiltonian for the octahedral coordination system may be written as

$$\boldsymbol{H}=\boldsymbol{H}_0+\boldsymbol{V}_g+\boldsymbol{V}_u \tag{1}$$

where $\boldsymbol{H}_0$ represents the unperturbed Hamiltonian in the regular octahedron, and $\boldsymbol{V}_g$ and $\boldsymbol{V}_u$ represent the potentials with even and odd parity, respectively. The eigenstates of $\boldsymbol{H}_0$ in cobalt(III) complexes are classified as

$|A_{1g}\rangle$ =nondegenerate ground state with even parity,

$|T_{1g}i\rangle$ =octahedral components (i=α, β, γ) of the first excited state with even parity,

$|T_{2g}j\rangle$ =octahedral components (j=ξ, η, ζ) of the second excited state with even parity,

$|M_uk\rangle$=octahedral components of higher excited states with odd parity.

The first-order perturbed wavefunctions for the ligand field excited states can be written in terms of the perturbation theory as follows:

$$\begin{aligned}|A_{1g}) = {} & |A_{1g}\rangle \\ & + \sum_k |M_uk\rangle\langle M_uk|\boldsymbol{V}_u|A_{1g}\rangle\{E(M_uk)-E(A_{1g})\}^{-1} \\ & + \sum_i |T_{1g}i\rangle\langle T_{1g}i|\boldsymbol{V}_g|A_{1g}\rangle\{E(T_{1g}i)-E(A_{1g})\}^{-1} \\ & + \sum_j |T_{2g}j\rangle\langle T_{2g}j|\boldsymbol{V}_g|A_{1g}\rangle\{E(T_{2g}j)-E(A_{1g})\}^{-1}\end{aligned} \tag{2}$$

$$\begin{aligned}|T_{1g}i) = {} & |T_{1g}i\rangle \\ & + \sum_k |M_uk\rangle\langle M_uk|\boldsymbol{V}_u|T_{1g}i\rangle\{E(M_uk)-E(T_{1g}i)\}^{-1} \\ & + \sum_{i'\neq i} |T_{1g}i'\rangle\langle T_{1g}i'|\boldsymbol{V}_g|T_{1g}i\rangle\{E(T_{1g}i')-E(T_{1g}i)\}^{-1} \\ & + \sum_j |T_{2g}j\rangle\langle T_{2g}j|\boldsymbol{V}_g|T_{2g}j\rangle\{E(T_{2g}j)-E(T_{1g}i)\}^{-1},\end{aligned} \tag{3}$$

where $E(M_uk)$, *etc.* denote the energy of the unperturbed states.

The rotatory strength associated with a $A_{1g}\rightarrow T_{1g}i$ transition, $R(T_{1g}i)$, is expressed by

$$R(\mathrm{T_{1g}i}) = \mathrm{Im}\{(\mathrm{A_{1g}}|\boldsymbol{P}|\mathrm{T_{1g}i})\cdot(\mathrm{T_{1g}i}|\boldsymbol{M}|\mathrm{A_{1g}})\}, \tag{4}$$

where $\boldsymbol{P}$ and $\boldsymbol{M}$ are the electric and magnetic dipole operators, respectively. If we neglect higher terms of the energy differences, the rotatory strength $R(\mathrm{T_{1g}i})$ can be expressed by using the first-order wavefunctions given in Eqs. 2 and 3.

A Crystal Field Model for Mixed Complexes

We deal with cobalt(III) complexes with *cis*(*N*)-$[\mathrm{Co(N)_2(O)_4}]$ or *cis*(*O*)-$[\mathrm{Co(N)_4(O)_2}]$ chromophore. Since the holohedrized symmetry[8] of those complexes is $\mathrm{D_{4h}}$, the electronic states can be approximated by a treatment in $\mathrm{D_{4h}}$ symmetry. Therefore, we use tetragonal basis sets of 3d and 4p orbitals as zero-order wavefunctions. The wavefunction of the ground state is written in determinant form as follows:

$$|\mathrm{A_{1g}}) = |\overset{+}{(\mathrm{yz})}\overset{-}{(\mathrm{yz})}\overset{+}{(\mathrm{zx})}\overset{-}{(\mathrm{zx})}\overset{+}{(\mathrm{xy})}\overset{-}{(\mathrm{xy})}|.$$

As for the excited states, $\mathrm{T_{1g}}$ state in octahedral symmetry splits into $\mathrm{A_{2g}}$ and $\mathrm{E_g^a}$ states in tetragonal symmetry, while $\mathrm{T_{2g}}$ state splits into $\mathrm{B_{2g}}$ and $\mathrm{E_g^b}$ states. The wavefunctions of the excited states are listed in Table 1, in which the wavefunctions are represented by a d- or p-orbital component of the occupied orbital and a d-orbital component of the hole orbital. Thus, the wavefunction for $|\mathrm{A_{2g}})$ is:

$$|(\mathrm{xy})(\mathrm{x^2-y^2})| = \{|\cdots\overset{+}{(\mathrm{yz})}\overset{-}{(\mathrm{yz})}\overset{+}{(\mathrm{zx})}\overset{-}{(\mathrm{zx})}\overset{+}{(\mathrm{xy})}\overset{-}{(\mathrm{x^2-y^2})}| + |\cdots\overset{+}{(\mathrm{x^2-y^2})}\overset{-}{(\mathrm{xy})}|\}/\sqrt{2}.$$

Non-vanishing matrix elements of $\boldsymbol{P}$ and $\boldsymbol{M}$ are gathered in Tables 2 and 3. Using the wavefunctions in Table 1, the rotatory strength of $R(\mathrm{A_{2g}})$, which arises from d-p and d-d mixings, can be expressed as follows:

$$\begin{aligned}
R(\mathrm{A_{2g}}) = {} & (\sqrt{3}/4)[\langle \mathrm{x}|\boldsymbol{V}_\mathrm{u}|\mathrm{x^2-y^2}\rangle \Delta E_\mathrm{u2}^{-1} \\
& - \langle \mathrm{y}|\boldsymbol{V}_\mathrm{u}|\mathrm{xy}\rangle \Delta E_\mathrm{u1}^{-1}] \\
& \times [\{\langle \mathrm{x^2-y^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle - \sqrt{3}\langle \mathrm{z^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle\}\Delta E_1^{-1} \\
& - 2\langle \mathrm{xy}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle \Delta E_2^{-1} \\
& - (3\sqrt{2}/2)\{\langle \mathrm{x^2-y^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle \\
& + \sqrt{3}\langle \mathrm{z^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle\}\Delta E_3^{-1} \\
& + 3\sqrt{2}\langle \mathrm{xy}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle \Delta E_4^{-1}] \\
& - (\sqrt{3}/4)[\langle \mathrm{y}|\boldsymbol{V}_\mathrm{u}|\mathrm{x^2-y^2}\rangle \Delta E_\mathrm{u2}^{-1} \\
& + \langle \mathrm{x}|\boldsymbol{V}_\mathrm{u}|\mathrm{xy}\rangle \Delta E_\mathrm{u1}^{-1}] \\
& \times [\{\langle \mathrm{x^2-y^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle \\
& + \sqrt{3}\langle \mathrm{z^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle\}\Delta E_1^{-1} \\
& + 2\langle \mathrm{xy}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle \Delta E_2^{-1} \\
& - (3\sqrt{2}/2)\{\langle \mathrm{x^2-y^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle \\
& - \sqrt{3}\langle \mathrm{z^2}|\boldsymbol{V}_\mathrm{g}|\mathrm{yz}\rangle \Delta E_3^{-1} \\
& - 3\sqrt{2}\langle \mathrm{xy}|\boldsymbol{V}_\mathrm{g}|\mathrm{zx}\rangle \Delta E_4^{-1}].
\end{aligned} \tag{5}$$

$$\begin{aligned}
\text{Here, } & \Delta E_\mathrm{u1} = E(\mathrm{M_u}) - E(\mathrm{A_{1g}}),\ \Delta E_2 = E(\mathrm{E_g^a}) - E(\mathrm{A_{2g}}) \\
& \Delta E_\mathrm{u2} = E(\mathrm{M_u}) - E(\mathrm{A_{2g}}),\ \Delta E_3 = E(\mathrm{E_g^b}) - E(\mathrm{A_{1g}}) \\
& \Delta E_1 = E(\mathrm{E_g^a}) - E(\mathrm{A_{1g}}),\ \Delta E_4 = E(\mathrm{E_g^b}) - E(\mathrm{A_{2g}}).
\end{aligned} \tag{6}$$

We use an average energy $E(\mathrm{M_u})$ instead of the individual energy levels of odd parity states.

We are interested in the Cotton sign of $\mathrm{A_{1g}} \rightarrow \mathrm{A_{2g}}(\mathrm{D_{4h}})$ transition for the CD spectra of Λ-$[\mathrm{Co(NN)_2(OO)}]^{n+}$ and Λ-$[\mathrm{Co(NN)(OO)_2}]^{n-}$ complexes ($\mathrm{OO=CO_3^{2-}}$, $\mathrm{ox^{2-}}$, $\mathrm{mal^{2-}}$, or $\mathrm{2H_2O}$; NN=en or tn). To predict the Cotton sign, it is necessary to define the spherical coordinate ($\mathrm{R_i}$, θ_i, ϕ_i) of the ligating atom $\mathrm{L_i}$ (i=1,2,$\cdots$6). The adopted spherical and Cartesian coordinate systems are drawn in Fig. 1. In this model, we

TABLE 1. THE WAVEFUNCTIONS OF EXCITED STATES

$$|\mathrm{A_{2g}}\rangle = |(\mathrm{xy})(\mathrm{x^2-y^2})|$$
$$|\mathrm{E_g^a}1\rangle = |(\mathrm{yz})(\mathrm{y^2-z^2})|$$
$$|\mathrm{E_g^a}2\rangle = |(\mathrm{zx})(\mathrm{z^2-x^2})|$$
$$|\mathrm{E_g^b}1\rangle = |(\mathrm{yz})(\mathrm{x^2})|$$
$$|\mathrm{E_g^b}2\rangle = |(\mathrm{zx})(\mathrm{y^2})|$$
$$|\mathrm{B_{2g}}\rangle = |(\mathrm{xy})(\mathrm{z^2})|$$
$$|\mathrm{B_{1u}^a}\rangle = -\{|(\mathrm{yz})(\mathrm{x})| + |(\mathrm{zx})(\mathrm{y})| + |(\mathrm{xy})(\mathrm{z})|\}/\sqrt{3}$$
$$|\mathrm{B_{1u}^b}\rangle = -\{|(\mathrm{yz})(\mathrm{x})| + |(\mathrm{zx})(\mathrm{y})| - 2|(\mathrm{xy})(\mathrm{z})|\}/\sqrt{6}$$
$$|\mathrm{A_{1u}}\rangle = -\{|(\mathrm{yz})(\mathrm{x})| - |(\mathrm{zx})(\mathrm{y})|\}/\sqrt{2}$$
$$|\mathrm{A_{2u}}\rangle = \{|(\mathrm{zx})(\mathrm{x})| + |(\mathrm{yz})(\mathrm{y})|\}/\sqrt{2}$$
$$|\mathrm{B_{2u}}\rangle = -\{|(\mathrm{zx})(\mathrm{x})| - |(\mathrm{yz})(\mathrm{y})|\}/\sqrt{2}$$
$$|\mathrm{E_u^a}1\rangle = \{|(\mathrm{xy})(\mathrm{y})| + |(\mathrm{zx})(\mathrm{z})|\}/\sqrt{2}$$
$$|\mathrm{E_u^a}2\rangle = \{|(\mathrm{xy})(\mathrm{x})| + |(\mathrm{yz})(\mathrm{z})|\}/\sqrt{2}$$
$$|\mathrm{E_u^b}1\rangle = -\{|(\mathrm{xy})(\mathrm{y})| - |(\mathrm{zx})(\mathrm{z})|\}/\sqrt{2}$$
$$|\mathrm{E_u^b}2\rangle = -\{|(\mathrm{yz})(\mathrm{z})| - |(\mathrm{xy})(\mathrm{x})|\}/\sqrt{2}$$

TABLE 2. ZEROTH-ORDER d-p ELECTRIC DIPOLE TRANSITION MATRIX[a)]

$\boldsymbol{P}$	$\mathrm{z^2}$	$\mathrm{x^2-y^2}$	xy	zx	yz
z	$2\boldsymbol{k}$	0	0	$\sqrt{3}\boldsymbol{i}$	$\sqrt{3}\boldsymbol{j}$
x	$-\boldsymbol{i}$	$\sqrt{3}\boldsymbol{i}$	$\sqrt{3}\boldsymbol{j}$	$\sqrt{3}\boldsymbol{k}$	0
y	$-\boldsymbol{j}$	$-\sqrt{3}\boldsymbol{j}$	$\sqrt{3}\boldsymbol{i}$	0	$\sqrt{3}\boldsymbol{k}$

i,***j***, and ***k*** are unit vectors in the x, y, and z directions. a) In units of $e\langle \mathrm{R_p}|r|\mathrm{R_d}\rangle/\sqrt{15}$.

TABLE 3. ZEROTH-ORDER d-d MAGNETIC DIPOLE TRANSITION MATRIX[a)]

$\boldsymbol{M}$	$\mathrm{z^2}$	$\mathrm{x^2-y^2}$	xy	zx	yz
$\mathrm{z^2}$	0	0	0	$-\sqrt{3}\mathrm{i}\boldsymbol{j}$	$\sqrt{3}\mathrm{i}\boldsymbol{i}$
$\mathrm{x^2-y^2}$	0	0	$-\sqrt{2}\mathrm{i}\boldsymbol{k}$	$\mathrm{i}\boldsymbol{j}$	$\mathrm{i}\boldsymbol{i}$
xy	0	$\sqrt{2}\mathrm{i}\boldsymbol{k}$	0	$-\mathrm{i}\boldsymbol{i}$	$\mathrm{i}\boldsymbol{j}$
zx	0	$-\mathrm{i}\boldsymbol{j}$	$\mathrm{i}\boldsymbol{i}$	0	0
yz	0	$-\mathrm{i}\boldsymbol{i}$	$-\mathrm{i}\boldsymbol{j}$	0	0

i, ***j***, and ***k*** are unit vectors in x, y, and z directions. a) In units of $\sqrt{2}\ he/(4mc)$.

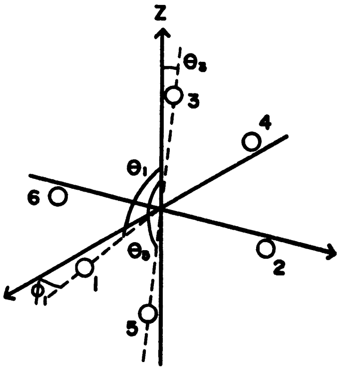

Fig. 1. The spherical and Cartesian coordinate systems.

consider a simplified arrangement of the ligating atoms, and ignore the existence of non-ligating atoms. The coordinate (R_i, θ_i, ϕ_i) of the ligating atom L_i (i=1,3,5) is converted into (R_{i+1}, θ_{i+1}, ϕ_{i+1}) by a C_2 axis intersecting the bidentate ligand L_iL_{i+1}. These three C_2 axes are supposed to deviate from the x, y, or z axis by 45°. The R_{i+1} coordinate is assumed to be equal to the R_i (i=1,3,5). On these assumptions, the $\boldsymbol{V}_u$ and $\boldsymbol{V}_g$ potentials at the non-vanishing matrix elements in Eq. 5 can be expressed as

$$\begin{aligned} V_u &= er^3\{A_{33}Y_3^3 + A_{3-3}Y_3^{-3}\} \\ V_g &= er^2(A_{21}Y_2^1 + A_{2-1}Y_2^{-1}) \\ &\quad + er^4(A_{41}Y_4^1 + A_{4-1}Y_4^{-1}) \\ &\quad + er^4(A_{43}Y_4^3 + A_{4-3}Y_4^{-3}), \end{aligned} \tag{7}$$

where r denotes the electron radical coordinate and e is the charge of an electron. The functions Y_l^m are spherical harmonics normalized to unity. The factors A_{lm} are defined as

$$\begin{aligned} A_{3\pm3} &= \mp (3\sqrt{5}/4) \sum_{k=1}^{6} q_k R_k^{-4} \sin^3\theta_k \exp(\mp 3\phi_k i) \\ A_{2\pm1} &= \pm\sqrt{6} \sum_{k=1}^{6} q_k R_k^{-3} \sin 2\theta_k \exp(\mp\phi_k i) \\ A_{4\pm1} &= \pm (\sqrt{5}/2) \sum_{k=1}^{6} q_k R_k^{-5} \sin 2\theta_k (7\cos^2\phi_k - 1) \exp(\mp\phi_k i) \\ A_{4\pm3} &= \pm (3\sqrt{5}/2) \sum_{k=1}^{6} q_k R_k^{-5} \sin 2\theta_k \sin^2\theta_k \exp(\mp 3\phi_k i), \end{aligned} \tag{8}$$

where q_k expresses the effective charge associated with the ligating atom L_k.

Table 4. Data of coordination angles and bond lengths

	Coordination angle of the ligand θ/°	Bond length between central metal ion and the ligand l/Å	Reference
CO_3^{2-}	70	1.93	a)
ox^{2-}	85	1.94	13
mal^{2-}	96	1.90	11
en	86	1.98	11,13
tn	96	1.99	b)

a) M. R. Snow, *Aust. J. Chem.*, **25**, 1307 (1972). b) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 1016 (1969); R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29** 2438 (1973); H.V.F. Schousboe-Jensen, *Acta Chem. Scand.*, **26**, 3413 (1972).

Idealized Model. We first consider the Cotton sign of $R(A_{2g})$ in Λ-[Co(NN)$_2$(OO)]$^{n+}$ and Λ-[Co(NN)(OO)$_2$]$^{n-}$ by an idealized model in which all ligating atoms are located on the xy, yz, and zx planes. The complexes can be classified into three groups.

Group 1) L_1CoL_2, L_3CoL_4, and L_5CoL_6<90°

Group 2) L_1CoL_2<90°, L_3CoL_4 and L_5CoL_6>90°

Group 3) L_1CoL_2>90°, L_3CoL_4 and L_5CoL_6<90°

The coordination angles of concerned complexes are cited in Table 4. The complexes Λ-[Co(CO$_3$)(en)$_2$]$^+$, Λ-[Co(ox)(en)$_2$]$^+$, Λ-[Co(CO$_3$)(ox)(en)]$^-$, and Λ-[Co(ox)$_2$(en)]$^-$ belong to Group 1), Λ-[Co(ox)(tn)$_2$]$^+$ and Λ-[Co(mal)$_2$(en)]$^-$ complexes to Group 2), and Λ-[Co(mal)(en)$_2$]$^+$, Λ-[Co(CO$_3$)(mal)(en)]$^-$, and Λ-[Co(ox)(mal)(en)]$^-$ complexes to Group 3).

The expressions for the rotatory strength of $R(A_{2g})$ in these groups are given in Table 5. Since the values of $\langle r^3\rangle$ and ΔE_{u2} are positive, the constant, K, becomes positive. In order to predict the sign of $R(A_{2g})$, the

Table 5. Rotatory strength of $R(A_{2g})$

Coordinates	Rotatory strength
Group 1) L_1 : (R_1, 90°, ϕ_1) L_2 : (R_1, 90°, 90°$-\phi_1$) L_3 : (R_3, θ_3, 180°) L_4 : (R_3, 90° $-\theta_3$, 180°) L_5 : (R_5, θ_5, 270°) L_6 : (R_5, 270° $-\theta_5$, 270°)	$R(A_{2g}) = -K\{(\cos 3\phi_1 - \sin 3\phi_1)q_1R_1^{-4} - \gamma(\sin^3\theta_3 + \cos^3\theta_3)q_3R_3^{-4}\} \times K_1 \sin 2\theta_5$ $- K\{(\cos 3\phi_1 - \sin 3\phi_1)\, q_1R_1^{-4} - \gamma(\sin^3\theta_5 - \cos^3\theta_5)q_5R_5^{-4}\} \times K_2 \sin 2\theta_3$
Group 2) L_1 : (R_1, 90°, ϕ_1) L_2 : (R_1, 90°, 90° $-$ ϕ_1) L_3 : (R_3, θ_3, 0) L_4 : (R_3, 90° + θ_3, 180°) L_5 : (R_5, θ_5, 90°) L_6 : (R_5, $-$90° + θ_5, 270°)	$R(A_{2g}) = K\{(\cos 3\phi_1 - \sin 3\phi_1)q_1R_1^{-4} + \gamma(\sin^3\theta_3 - \cos^3\theta_3)q_3R_3^{-4}\} \times K_1 \sin 2\theta_5$ $+ K\{(\cos 3\phi_1 - \sin 3\phi_1)q_1R_1^{-4} + \gamma(\sin^3\theta_5 + \cos^3{}_5)q_5R_5^{-4}\} \times K_2 \sin 2\theta_3$
Group 3) L_1 : (R_1, 90°, $-\phi_1$) L_2 : (R_1, 90°, 90° $+\phi_1$) L_3 : (R_3, θ_3, 180°) L_4 : (R_3, 90° $-\theta_3$, 180°) L_5 : (R_5, θ_5, 270°) L_6 : (R_5, 270° $-\theta_5$, 270°)	$R(A_{2g}) = -K\{(\cos 3\phi_1 + \sin 3\phi_1)q_1R_1^{-4} - \gamma(\sin^3\theta_3 + \cos^3\theta_3)q_3R_3^{-4}\} \times K_1 \sin 2\theta_5$ $- K\{(\cos 3\phi_1 + \sin 3\phi_1)q_1R_1^{-4} - \gamma(\sin^3\theta_5 - \cos^3\theta_5)q_5R_5^{-4}\} \times K_2 \sin 2\theta_3$

$K = (35/28)\langle r^3\rangle \Delta E_{u2}^{-1}$

$K_1 = (3/28)R_5^{-3}\langle r^2\rangle(2\Delta E_2^{-1} - 3\sqrt{2}\,\Delta E_4^{-1} + 2\Delta E_1^{-1})q_5 - (5/336)R_5^{-5}\langle r_4\rangle(16\Delta E_2^{-1} - 24\sqrt{2}\,\Delta E_4^{-1} - 12\Delta E_1^{-1})q_5$

$K_2 = (3/28)R_3^{-3}\langle r^2\rangle(2\Delta E_2^{-1} - 3\sqrt{2}\,\Delta E_4^{-1})q_3 - (5/336)R_3^{-5}\langle r^4\rangle(16\Delta E_2^{-1} - 24\sqrt{2}\,\Delta E_4^{-1} - 12\Delta E_1^{-1})q_3$

$\langle r^2\rangle = \langle d|r^2|d\rangle$

$\langle r^3\rangle = \langle d|r^3|d\rangle$

$\langle r^4\rangle = \langle d|r^4|d\rangle$

$\gamma = \Delta E_{u2}/\Delta E_{u1}$

Table 6. Energy differences ($\tilde{\nu}$ in 10^3 cm^{-1})

Complex	ΔE_1	ΔE_2	ΔE_4
$[Co(CO_3)_2(en)]^-$	17.0	−1.45	8.10
$[Co(CO_3)(ox)(en)]^-$	17.4	−1.31	7.50
$[Co(ox)_2(en)]^-$	17.8	−1.18	7.50
$[Co(CO_3)(mal)(en)]^-$	17.4	−1.31	7.53
$[Co(ox)(mal)(en)]^-$	17.7	−1.19	7.50
$[Co(mal)_2(en)]^-$	17.7	−1.21	7.40
$[Co(CO_3)(en)_2]^+$	19.9	1.01	8.26
$[Co(ox)(en)_2]^+$	20.1	1.18	8.10
$[Co(mal)(en)_2]^+$	20.1	1.21	7.85
$[Co(ox)(tn)_2]^+$	19.5	0.97	8.33
$[Co(ox)(H_2O)_2(en)]^+$	17.8	−1.18	7.50
$[Co(mal)(H_2O)_2(en)]^+$	17.7	−1.19	7.59
$[Co(H_2O)_2(en)_2]^{3+}$	20.1	1.18	7.50

following variables have to be estimated:

1) radial integrals $\langle r^2\rangle$ and $\langle r^4\rangle$,
2) coordinates of the ligating atom L_i, (R_i, θ_i, ϕ_i),
3) energy differences, ΔE_1, ΔE_2, and ΔE_4,
4) effective charges of ligating atoms, q_i.

The radial integrals can be evaluated by Watoson's Hartree-Fock wavefunction,[9] that is, $\langle r^2\rangle=0.293$ Å and $\langle r^4\rangle=0.184$ Å. The coordinates of the ligating atoms can be estimated from the X-ray analytical data listed in Table 4. As for the energy differences, the ΔE_1 and ΔE_2 values can be evaluated in terms of an angular overlap model,[10] and the ΔE_4 value is approximated by the energy difference between the absorption maximum of the first absorption band and that of the second absorption band, the values being listed in Table 6. It is difficult to estimate accurately the effective charges of the ligating atoms. Since this model ignores the existence of the non-ligating atoms, it is better to treat the effective charge of a ligating atom as an empirical parameter. The effect of the non-ligating atom upon the rotatory strength may be included into the parameter. We adopt a crude assumption that the effective charge on an anionic ligand of OO type is minus and that on a neutral ligand is plus.

The Cotton sign of $R(A_{2g})$ of the Λ-$[Co(en)(ox)(ox)]^-$ ($=\Lambda$-$[Co(L_1L_2)(L_3L_4)(L_5L_6)]^-$) complex is predicted as follows. From the data of the bond distances and the coordination angles, the coordinates of the ligating atoms in the complex are written as

$$\begin{aligned}(R_1, \theta_1, \phi_1) &= (1.98, 90°, 2°)\\ (R_3, \theta_3, \phi_3) &= (1.94, 2.5°, 180°)\\ (R_5, \theta_5, \phi_5) &= (1.94, 177.5°, 270°).\end{aligned} \tag{9}$$

Using these coordinates and the values of the radial integrals, $R(A_{2g})$ of Λ-$[Co(ox)_2(en)]^-$ is expressed as the product of an effective charge term and an energy difference term:

$$\begin{aligned}R(A_{2g}) &= -C\times q_{ox}(5.8q_{en}-7.0\gamma q_{ox})\\ &\times(8\ 5\,\Delta E_1^{-1}+6.1\,\Delta E_2^{-1}-13\,\Delta E_4^{-1}),\end{aligned} \tag{10}$$

where q_{en} and q_{ox} denote the effective charge of the ligating atoms of en and ox, respectively, and C is a positive constant. Since the ΔE_1, ΔE_2, and ΔE_4 values are evaluated as 17800, −1180, and 7500 cm^{-1} respectively (Table 6), the sign of the energy difference term in Eq. 10 becomes minus, on account of a small minus value of ΔE_2. It may be noted that the energy difference term becomes minus in all *cis*(*N*)-$[Co(N)_2(O)_4]$ complexes. The q_{en} value is evaluated to be plus and the q_{ox} value to be minus. Since the value of $\gamma=\Delta E_{u2}/\Delta E_{u1}$ becomes plus, $R(A_{2g})$ is considered to be negative in the Λ-$[Co(ox)_2(en)]^-$ complex. Similar procedures in calculation lead to the same result in the Λ-$[Co(CO_3)(ox)(en)]^-$ and Λ-$[Co(CO_3)_2(en)]^-$ complexes.

As to the Λ-$[Co(ox)(en)_2]^+$ complex, which also belongs to Group 1), the following equation of $R(A_{2g})$ is obtained by a similar calculation:

$$\begin{aligned}R(A_{2g}) &= -C\times q_{en}(6.1\,q_{ox}-6.5\,\gamma q_{en})\\ &\times(4.6\,\Delta E_2^{-1}-0.8\,\Delta E_4^{-1}+6.4\,\Delta E_1^{-1}).\end{aligned} \tag{11}$$

In this complex, the energy difference term in Eq. 11 becomes plus, on account of the small plus value of ΔE_2. It is worth noting that the energy difference term is always plus in *cis*(*O*)-$[Co(N)_4(O)_2]$ complexes. If $q_{en}>0$ and $q_{ox}<0$, the resultant sign of $R(A_{2g})$ in Λ-$[Co(ox)(en)_2]^+$ becomes positive. Similarly, $R(A_{2g})$ in Λ-$[Co(CO_3)(en)_2]^+$ is predicted to have a positive sign.

Since the coordination angle of mal^{2-} in Λ-$[Co(mal)_2(en)]^-$ is reported to be 96°,[11] this complex belongs to Group 2). Using the equation in Table 5, $R(A_{2g})$ of the complex can be written as

$$\begin{aligned}R(A_{2g}) &= Cq_{mal}(5.8\,q_{en}-7.6\,\gamma q_{mal})\\ &\times(7.7\,\Delta E_2^{-1}-16\,\Delta E_4^{-1}+11\,\Delta E_1^{-1}),\end{aligned} \tag{12}$$

where q_{mal} denotes the effective charge on the malonato ligand. Since the chromophore is *cis*(*N*)-$[Co(N)_2(O)_4]^-$, the energy difference term becomes minus on account of the minus value of ΔE_2. The malonato ligand is anionic, and q_{mal} is also regarded to be minus. Therefore, $R(A_{2g})$ in Λ-$[Co(mal)_2(en)]^-$ is predicted to have a positive sign.

The Λ-$[Co(ox)(tn)_2]^+$ complex is also of Group 2), and its $R(A_{2g})$ is written as

$$\begin{aligned}R(A_{2g}) &= Cq_{tn}(6.1\,q_{ox}-6.3\,\gamma q_{tn})\\ &\times(6.9\,\Delta E_2^{-1}-15\,\Delta E_4^{-1}+9.4\,\Delta E_1^{-1}).\end{aligned} \tag{13}$$

The energy difference term is estimated to be plus, and if $q_{tn}>o$, the effective charge term becomes minus. Consequently, the sign of $R(A_{2g})$ in the complex is regarded as negative.

For complexes of Group 3), when the angle ϕ_1 is measured to have a minus value, the equation for group 1) can be utilized. For example, the coordinates of Λ-$[Co(mal)(en)_2]^+$ are,

$$\begin{aligned}(R_1, \theta_1, \phi_1) &= (1.90, 90°, -3°)\\ (R_3, \theta_3, \phi_3) &= (1.98, 2°, 180°)\\ (R_5, \theta_5, \phi_5) &= (1.98, 178°, 270°).\end{aligned} \tag{14}$$

The sign of $R(A_{2g})$ is plus, which is the same as in the case of Λ-$[Co(ox)(en)_2]^+$.

If it is postulated that H_2O molecules are linked on the coordinate axes, the Λ-$[Co(en)_2(H_2O)_2]^{3+}$ and Λ-$[Co(ox)(en)(H_2O)_2]^+$ complexes may be classified into Group 1). The rotatory strength for the former complex is given by

$$\begin{aligned}R(A_{2g}) &= -C\times q_{en}(7.1\,q_{H_2O}-6.5\,\gamma q_{en})\\ &\times(6.4\,\Delta E_1^{-1}+4.6\,\Delta E_2^{-1}-9.8\,\Delta E_4^{-1})\end{aligned} \tag{15}$$

and, for the latter complex, by

$$R(A_{2g}) = -C \times q_{ox}(5.8\,q_{en} - 7.1\,\gamma q_{H_2O}) \times (8.5\,\Delta E_1^{-1} + 6.1\,\Delta E_2^{-1} - 13\,\Delta E_4^{-1}), \quad (16)$$

where q_{H_2O} denotes the effective charge of the ligating atom in H_2O. The energy difference term in the former complex is estimated to be plus, and that in the latter complex to be minus. According to the estimation of the q_{H_2O} value, the $R(A_{2g})$ in Eqs. 15 and 16 change their signs; if q_{H_2O} has a minus or slightly plus value, the $R(A_{2g})$ of the former complex exhibits positive sign and that of the latter complex a negative one. On the other hand, if q_{H_2O} has a considerable plus value compared with q_{en}, the $R(A_{2g})$ of the former shows a negative sign and that of the latter a positive one.

Deviated Ligand Model. In this model, the influence of the deviation of ligating atoms from xy, yz, and zx planes is studied. For example, the coordinates of a complex in Group 1) are given by

$$\begin{aligned}
(R_1, \theta_1, \phi_1) &= (R_1, 90^\circ + \Delta\theta, \phi_1) \\
(R_2, \theta_2, \phi_2) &= (R_1, 90^\circ - \Delta\theta, 90^\circ - \phi_1) \\
(R_3, \theta_3, \phi_3) &= (R_3, \theta_3, 180^\circ + \Delta\phi) \\
(R_4, \theta_4, \phi_4) &= (R_3, 90^\circ - \theta_3, 180^\circ - \Delta\phi) \quad (17) \\
(R_5, \theta_5, \phi_5) &= (R_5, \theta_5, 270^\circ - \Delta\phi) \\
(R_6, \theta_6, \phi_6) &= (R_5, 270^\circ - \theta_5, 270^\circ + \Delta\phi)
\end{aligned}$$

When the angles $\Delta\theta$ and $\Delta\phi$ were varied from 1° to 3° in the calculation, the predicted sign of $R(A_{2g})$ was essentially coincident with that obtained by the idealized model.

Results and Discussion

1) CD Sign. For the Λ-[Co(CO$_3$)$_2$(en)]$^-$, Λ-[Co(CO$_3$)(ox)(en)]$^-$, and Λ-[Co(ox)$_2$(en)]$^-$ complexes with *cis*(*N*)-[Co(N)$_2$(O)$_4$] chromophore, which are classified into Group 1),the signs of $R(A_{2g})$ are predicted to be negative. On the other hand, for the Λ-[Co(CO$_3$)(en)$_2$]$^+$ and Λ-[Co(ox)(en)$_2$]$^+$ complexes with *cis*(*O*)-[Co(N)$_4$(O)$_2$] chromophore, which are also classified into Group 1), the predicted sign of $R(A_{2g})$ is positive. For the Λ-[Co(mal)$_2$(en)]$^-$ and Λ-[Co(ox)(tn)$_2$]$^+$ complexes of Group 2), the sign of $R(A_{2g})$ in the former is predicted to be positive, and that in the latter to be negative. Therefore, we can say that the sign of $R(A_{2g})$ in a Λ-[Co(N)$_2$(O)$_4$]$^-$ complex is reverse to that in a Λ-[Co(N)$_4$(O)$_2$]$^+$ complex, provided that the two complexes belong to the same group. This is because the equation of $R(A_{2g})$ is expressed as a product of two terms, one of which is an effective charge term and the other is an energy difference term, which is a function of inverted ΔE_1, ΔE_2, and ΔE_4. In both the Λ-[Co(N)$_2$(O)$_4$]$^-$ and the Λ-[Co(N)$_4$(O)$_2$]$^+$ complexes, the effective charge terms become minus. Since $|E_2|$ is much smaller than ΔE_1 and ΔE_4, the sign of the energy difference term depends upon the sign of ΔE_2, which is a energy difference between E_g^a and A_{2g} states. The ΔE_2 value becomes minus and plus in the Λ-[Co(N)$_2$(O)$_4$]$^-$ complexes and in the Λ-[Co(N)$_4$(O)$_2$]$^+$ complexes, respectively. Accordingly, the energy difference term becomes minus in the former complexes, and plus in the latter complexes.

With complexes with the same chromophore, the $R(A_{2g})$ in a complex of Group 1) is predicted to have the reverse sign to that in a complex of Group 2). This is because, for both the complexes, the products of the effective charge term and the energy difference term have the same sign, provided that the complexes have the same chromophore. However, the product has a minus coefficient in a complex of Group 1) and a plus one in a complex of Group 2), so these coefficients depend upon the coordinates of the ligating atoms. When the coordination angle of a bidentate ligand is smaller than 90°, the coefficient has a minus sign, whereas when the angle is larger than 90°, the coefficient has a plus sign.

Piper and Karipides[6] have predicted that the Cotton sign for $E^a(D_3)$ component in Λ-[Co(tn)$_3$]$^{3+}$ would be opposite to that in Λ-[Co(en)$_3$]$^{3+}$. The coordination angle in the trimethylenediamine complex is larger than 90° and that in the ethylenediamine complex is smaller than 90°. By the measurement of a single crystal CD spectrum in Λ-(+)$_{589}$[Co(tn)$_3$]$^{3+}$, Judkins and Royer[12] have concluded that a Cotton sign of a given transition should change when the coordination angle of the bidentate chelate ring changes from less than 90° to more than 90°. Our predictions in the mixed-complexes with lower symmetry corresponds well to these conclusions.

2) Absolute Configuration. It has been reported[1] that the (−)$_{589}$[Co(CO$_3$)$_2$(en)]$^-$, (−)$_{589}$[Co(CO$_3$)(ox)(en)]$^-$ and (−)$_{589}$[Co(ox)$_2$(en)]$^-$ complexes have Λ configurations, and the CD spectra of these complexes exhibit a single positive Cotton peak in the first absorption band region. In our previous paper,[2] these positive Cotton peaks were assigned to a component of $A_{1g} \rightarrow E_g(D_{4h})$. On the other hand, a component of $A_{1g} \rightarrow A_{2g}(D_{4h})$ was regarded as having a negative Cotton sign. Since these complexes have a *cis*(*N*)-[Co(N)$_2$(O)$_4$] chromophore and belong to Group 1), the assignments agree well with our calculation results.

The CD spectra of (+)$_{589}$[Co(CO$_3$)(en)$_2$]$^+$, (+)$_{589}$-[Co(ox)(en)$_2$]$^+$, and (+)$_{589}$[Co(mal)(en)$_2$]$^+$ show a single positive Cotton peak in the first absorption band region. The first two complexes belong to Group 1), and the third to Group 3). Previously, the positive Cotton peaks in these complexes were assigned to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ transition component.[2] The absolute configuration of (+)$_{589}$[Co(ox)(en)$_2$]$^+$ was determined to be Λ by an X-ray analysis.[13] Since the (+)$_{589}$-isomers of [Co(ox)(en)$_2$]$^+$ and [Co(mal)(en)$_2$]$^+$ can be derived from the (+)$_{589}$-isomer of [Co(CO$_3$)(en)$_2$]$^+$ by the reaction with oxalic and malonic acids, respectively, the absolute configurations of the carbonato and malonato complexes are also regarded to be Λ. Our calculation for $R(A_{2g})$of these three complexes predicts positive signs, which agrees with the previous experimental results.

The (−)$_{589}$[Co(mal)$_2$(en)]$^-$ complex that belongs to Group 2) exhibits three Cotton peaks with (+), (−), and (+) signs from the lower-frequency side in the first absorption band region.[14] The absolute configuration of the complex has been determined to Λ,[11] and the component with the (−) sign has been assigned to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component.[1] However, our calculation for $R(A_{2g})$ of this complex predicts a positive sign. This discrepancy seems to arise from the neglect of non-ligating atoms in our model. It is known that non-ligating atoms have an important role in the optical activities of tris(diamine) cobalt(III) complexes.[7] The degenerate $E_g^a(D_{4h})$ state may split into two non-degenerate states by an action of the non-ligating atoms.

The $(+)_{589}[Co(ox)(tn)_2]^+$ complex that also belongs to Group 2) exhibits a single (+) Cotton peak in the first absorption band region. Although the absolute configuration of the complex has not yet been determined, if the positive peak is assignable to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component, as in the case of the $(+)_{589}[Co(ox)(en)_2]^+$ complex, our calculation predicts a Δ configuration.

3) The CD Spectra of Diaqua Complexes. As mentioned in the Introduction, when an optically active diaqua complex is derived from an optically active carbonato complex by an acid-hydrolysis, the CD spectrum of the diaqua complex is quite different from that of the parent carbonato complex. For example, Λ-$(-)_{589}[Co(CO_3)(ox)(en)]^-$ exhibits a Cotton peak with a positive sign in the first absorption band region. The Λ-$[Co(ox)(en)(H_2O)_2]^+$ complex which is derived from the Λ-$(-)_{589}[Co(CO_3)(ox)(en)]^-$ complex exhibits (−) and (+) Cotton peaks from the lower-frequency side in the region.

This phenomenon can be understood in terms of the effective charge of the ligating O atom of the water molecule; the rotatory strength $R(A_{2g})$ is expressed as a product of the effective charge term and the energy difference term, and the energy difference terms have a negative sign in the above two complexes. If q_{CO_3} is evaluated to be minus, the effective charge term in the $[Co(CO_3)(ox)(en)]^-$ complex becomes minus, the resultant sign of $R(A_{2g})$ being negative. In the previous section, it is pointed out that, if q_{H_2O} has a large, plus value, the effective charge term attains a plus value, resulting in a positive sign of $R(A_{2g})$. In order to understand the CD spectrum of the diaqua complex, it is better to regard the empirical q_{H_2O} parameter as plus. Since the aqua ligand is a neutral molecule and the diaqua complex is a cation, it is probable that the donor atom of the aqua ligand has a plus effective charge.

The CD spectrum of Λ-$[Co(CO_3)(en)_2]^+$ exhibits a positive Cotton peak which is assignable to $A_{1g} \rightarrow A_{2g}$ component.[2] Two Cotton peaks with opposite signs are observed in the CD spectrum of Λ-$[Co(en)_2(H_2O)_2]^{3+}$, and the negative peak is assigned to the $A_{1g} \rightarrow A_{2g}$ component. The significant difference of CD spectral shapes between the carbonato and the diaqua complex can also be understood by the difference between the effective charge of the donor atoms in the aqua molecules and that in the carbonato ligand. Our model is useful to explain the CD spectral behavior of the diaqua complexes.

4) CT States in the Crystal Field Model. Since a d-d transition is electronically forbidden, d-orbitals need to admix with an odd parity state. Piper and Karipides[6] have considered the admixture of p-orbitals of a central metal ion in their crystal field model of the optical activities. Our model is also constructed by considering the admixture of p-orbitals of a central metal ion. However, it is possible to consider the admixture of p-orbitals of a ligand, (*i.e.* CT states). Since the wavefunctions of the metal to ligand CT states have the same forms as those listed in Table 1,[15] the formula of rotatory strength expressed in Table 5 is obtained for the d-CT mixing model. The differen point between the d-p mixing model and the d-CT mixing model appears at the evaluation of the $\gamma = E_{u2}/E_{u1}$ value. However, the evaluation of the γ value has no influence upon predicting the sign of $R(A_{2g})$, since the γ value is always plus. Therefore, it is concluded that the d-CT mixing model gives the same results as the d-p mixing model, for the prediction of Cotton signs of a given transition.

Experimental

Derivation of the Malonato Complex. To an aqueous solution of $(+)_{546}[Co(CO_3)(en)_2]Cl$[16] (10 mg, 0.04 mmol in 10 cm^3 H_2O), potassium malonate (1 g, 5 mmol) and malonic acid (0.5 g, 5 mmol) were added, and the mixed solution was stirred at 40 °C for 3 h. The resulting solution was kept in a refrigerator for 2 d, and then filtered. The filtrate was diluted by water (250 cm^3), and charged onto a column of Dowex 50W-X8 resin in Na^+ form (100—200 mesh, 1 cm × 5 cm). By elution with a 0.1 mol/dm^3 NaCl solution, one red band was discharged. The absorption and CD spectral data of the effluent were identical with those of $(+)_{546}[Co(mal)(en)_2]^+$.[17]

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