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Circular Dichroism Spectra and Absolute Configurations of *cis,cis,cis*-(*C,N,O*)-Dicyanobis(glycinato)cobaltate(III) and Dicyanobis-(β-alaninato)cobaltate(III) Complexes

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The $[Co(CN)_2(NO)_2]^-$-type complexes (NO: gly$^-$ and β-ala$^-$), which have *cis,cis,cis* geometry with respect to the donor atoms C, N, and O, have been prepared by a new method, and resolved into their optical antipodes. The CD spectra of the resolved complexes have been measured, and compared with that of $(-)_{589}[Co(CN)_2(ox)(en)]^-$ complex which has the same chromophore with the bis(glycinato) complex. It is found that the optical activity of the *cis,cis,cis*-$[Co(C)_2(N)_2(O)_2]^-$-type complex mainly arises from the arrangement of the donor atoms; the non-ligating atoms of NO ligand make minor contribution to the optical activity.

Recent years have seen dramatic development in CD spectral studies of transition metal complexes, on account of development of theoretical treatment. In particular, many investigations have been carried out on tris(diamine)-type complexes, and the optical rotatory strength of a d-d transition has been connected in detail with the structure of a given complex.$^{1)}$ Evans *et al.*$^{2)}$ have calculated the optical activity of $[Co(en)_3]^{3+}$ complex by a molecular orbital method, and obtained good coincidence with the experimental values. Mason and Seal$^{3)}$ have applied the dynamic coupling model to the complexes of this type, and given numerical evaluations of the optical activities, differentiating between the contribution from donor atoms and that from non-ligating atoms.

In contrast to the above complexes whose absolute configurations are designated with Λ and Δ notation, a few studies of optically active complexes such as *cis,cis*-$[Co(CN)_2(CO_3)(NH_3)_2]^-$,$^{4)}$ $[Co(Br)(CN)(NH_3)(tacn)]^{+}$$^{5)}$ and $[Co(NO_2)(gly)(tacn)]^{+}$$^{6)}$(tacn represents 1,4,7-triazacyclononane), whose absolute configurations cannot be defined in Λ and Δ notation, have been reported in our laboratory. We have expressed the absolute configurations of those complexes in the *R* and *S* notation proposed by Cahn *et al.*$^{7)}$ and it has been found that the arrangement of donor atoms plays an important role in the optical activity of these complexes. However, an apparent role of the non-ligating atoms in the chelate rings has not been examined.

On the other hand, the CD spectrum of a $(-)_{589}$-$[Co(CN)_2(ox)(en)]^-$ complex$^{4)}$ is interesting, because the optical activity of the complex is considered to be derived from two origins; one is due to the arrangement of the donor atoms of the ligands as in the *cis,cis,cis*-$[Co(CN)_2(NH_3)_2(H_2O)_2]^+$,$^{4)}$ and another due to the helical distribution of the two bidentate ligands. If the deviation of the donor atoms from the octahedral sites due to the chelations does not have a large influence on the optical activity, the contribution to the optical activity from the non-ligating atoms is intimately associated with the "Λ or Δ" configuration, and that from the donor atoms, with "*R* or *S*" configuration. It is significant to elucidate with contribution is dominant in the complex. In order to clarify this problem, we attempted to prepare a *cis,cis,cis*(*C,N,O*)-$[Co(CN)_2(gly)_2]^-$ complex, whose chromophore was the same as the $[Co(CN)_2(ox)(en)]^-$ complex, and then to resolve it into a pair of enantiomers. The absolute configuration of an enantiomer in the bis(glycinato) complex is represented with either $\Delta(R)$ or $\Lambda(S)$. Since the absolute configuration of the $(-)_{589}[Co(CN)_2(ox)(en)]^-$ isomer is known to be $\Lambda(R)$,$^{4)}$ the comparison between the CD spectra of the two dicyano complexes will be helpful to determine the origin of the optical activities of the complexes. We also attempted to determine the absolute configuration of a diastereoisomeric salt $(-)_{589}[Co(ox)(en)_2]\cdot$*cis, cis, cis*(*C, N, O*)-$(+)^{CD}_{500}[Co(CN)_2(gly)_2]\cdot 3H_2O$ by X-ray analysis, in order to facilitate the analyses of the CD spectra.

There are five possible geometrical isomers for the $[Co(CN)_2(gly)_2]^-$ complex. Poznjak and Pawlowski$^{8)}$ have isolated three isomers with *cis*(*CN*) geometry, modifying the method devised in our laboratory.$^{9)}$ In this paper, a new method to prepare the dicyano complex will be reported.

Experimental

Preparation of $[Co(CN)_2(gly)_2]^-$ *Complex.* The complex has been prepared from $[Co(gly)_3]$ by reaction with KCN in the presence of activated charcoal,$^{8)}$ but this method yields a poor product. We devised a new method: To a cold green solution of the so-called tricarbonato solution ($Co(NO_3)_2\cdot 6H_2O$, 29 g, 0.1 mol scale),$^{10)}$ potassium cyanide (16.3 g, 0.25 mol) was added, and the mixed solution was stirred for 1 h at room temperature in order to prepare *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$.$^{11)}$ The solution was slowly neutralized by 30% $HClO_4$ in an ice bath. After the precipitated $KClO_4$ was filtered off, glycine (18.8 g, 0.25 mol) was added to the filtrate. With occasional neutralization by 30% $HClO_4$, the reaction mixture was stirred for 10 h. The dominant species in the solution was considered to be $[Co(CN)_2(gly)(CO_3)]^{2-}$. The solution was adjusted to pH 1 with 30% $HClO_4$, and stirred again for 1 h to complete the acid hydrolysis. The solution was adjusted to pH 9 with 6 mol/dm^3 KOH and then the precipitated material was filtered off. The filtrate was stirred for 2 h at 40 °C. The reaction mixture was sufficiently diluted with water (3—4 dm^3) and poured onto a column of Dowex 1-X8 resin (Cl^- form, 4×25 cm). By elution with 0.2 mol/dm^3 KCl solution, complex species of univalent anion were collected in a fraction . After concentration and removal of the eluent, the filtrate was diluted with 2 dm^3 of water and rechromatographed on a column of Dowex 1-X8 (Cl^- form, 4×30 cm). When the adsorbed band was eluted with 0.1

mol/dm^3 $CaCl_2$ solution, nine bands were distinguished (labeled A1-A9 in the order of elution). The yellow A4, orange A8 and rose A9 bands were the main products. Hereafter, the notations A1—A9 will be used to designate the isomer contained in each band. A4, A8 and A9 were identified with the *trans*(*N*)-*cis*(*C*), *cis,cis,cis*(*C, N, O*), and *trans*(*O*)-*cis*(*C*) isomers, respectively, on the basis of the absorption spectral data.[8] The other bands contained no dicyano complex species.

Preparation of the [*Co*(*CN*)$_2$(*β-ala*)$_2$]$^-$ *Complex.* This complex was prepared in the same way as the bis(glycinato) complex except for the use of *β*-alanine in the place of glycine. Upon rechromatography, three bands were obtained as univalent species (B1—B3 in the order of elution), by elution with 0.1 mol/dm^3 $CaCl_2$ solution, After removal of the eluting agent from each fraction, the counter ions were converted to sodium ions by means of column chromatography. The effluents were concentrated and then kept in a refrigerator. Found for B2: C, 28.54; H, 4.50; N, 16.62%. Found for B3: C, 28.67; H, 4.30; N, 16.89%. Calcd for Na[Co(CN)$_2$(*β*-ala)$_2$]·1.5H_2O: C, 28.50; H, 4.48; N, 16.62%. B1 was not a sought complex species.

Resolution. The crystals of *cis,cis,cis*(*C,N,O*)-Na[Co(CN)$_2$(gly)$_2$]·2H_2O (3.2 g, 0.01 mol) were dissolved in a minimum amount of warm water (60 °C). The solution was mixed with a warm solution of $(-)_{589}$[Co(ox)(en)$_2$](CH_3COO), which had been prepared using $(-)_{589}$ [Co(ox)(en)$_2$]I (1.7 g, 0.005 mol) and CH_3COOAg (0.84 g, 0.005 mol). The mixed solution was mechanically stirred and cooled in an ice bath. The diastereoisomeric salt obtained was recrystallized several times, until the Δε values became constant. Found: C, 24.79; H, 5.41; N, 19.47%. Calcd for $(-)_{589}$[Cn(ox)(en)$_2$]·$(+)^{CD}_{500}$[Co(CN)$_2$(gly)$_2$]·3H_2O: C, 24.84; H, 5.21; N, 19.31%.

The *trans*(*N*)-*cis*(*C*)- and *trans*(*O*)-*cis*(*C*)-[Co(CN)$_2$(gly)$_2$]$^-$ complexes were resolved into each optical antipodes in a similar way as the *cis,cis,cis*(*C,N,O*)-[Co(CN)$_2$(gly)$_2$]$^-$ complex, by using $(-)_{589}$[Co(ox)(en)$_2$](CH_3COO) as resolving agent. The *trans*(*N*)-*cis*(*C*)- (B2) and *cis,cis,cis*(*C,N,O*)-[Co(CN)$_2$(*β*-ala)$_2$]$^-$ (B3) complexes were also resolved by use of $(-)_{589}$[Co(NO_2)$_2$(en)$_2$](CH_3COO).

Measurements. The absorption spectra in aqueous solution were measured with a Hitachi 323 recording spectrophotometer. The CD spectra were recorded on a JASCO J-40C automatic recording spectropolarimeter equipped with a JASCO Model J-DPZ data processor for CD. The less-soluble diastereoisomeric salts obtained were passed through columns of cation exchanger in sodium form, and the effluents were submitted to the measurements of CD spectra. The Δε values were evaluated from the absorption spectral data.

Results and Discussion

Absorption and CD Spectra. Absorption spectral data of the complexes obtained are listed in Table 1. Absorption spectra of the isomers of the bis(glycinato) complex coincided with those of the literature.[8] Therefore, A4 is identified as *trans*(*N*)-*cis*(*C*) isomer, A8 as *cis,cis,cis*(*C,N,O*) one, and A9 as *trans*(*O*)-*cis*(*C*) one. As for the bis(*β*-alaninato) complex, B2 exhibited a narrow absorption band in the first absorption band region, and B3 two maxima in the region. By comparison with the spectra of the bis(glycinato) complex, B2 is assignable to *trans*(*N*)-*cis*(*C*) isomer and B3 to *cis,cis,cis*(*C,N,O*) isomer. As shown in Fig. 1, the absorption spectrum of the *cis, cis,cis*(*C,N,O*)-bis(glycinato) complex resembles that of the [Co(CN)$_2$(ox)(en)]$^-$ complex in shape and intensity, that is, two maxima in the first absorption band region have comparable intensity to each other. However, an intense band is observed at a lower frequency in the *cis,cis,cis*(*C,N,O*)-bis(*β*-alaninato) complex, and at a higher frequency in the *cis,cis*-[Co(CN)$_2$(ox)(NH_3)$_2$]$^-$ complex. These phenomena are considered to be associated with the rigidity of the chelate rings in terms of the vibronic mechanism of an intensity borrowing.[12] The absorption maxima of the bis(*β*-alaninato) isomers appear at a lower frequency than those of the corresponding bis(glycinato) isomers.

The CD spectral data are also collected in Table 1. The CD spectrum of the *trans*(*N*)-*cis*(*C*)-[Co(CN)$_2$(gly)$_2$]$^-$ exhibits a single Cotton peak at the maximum position of the first absorption band. An attempt to isolate an enantiomer of the *trans*(*N*)-*cis*(*C*)-bis(*β*-

Table 1. Absorption and CD spectral data of the dicyano complexes

Complex	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1}(Δε)
A4: *trans*(*N*)-*cis*(*C*)-$(+)^{CD}_{400}$[Co(CN)$_2$(gly)$_2$]$^-$	23.3(2.34)	23.5(+4.09)
	30.9(2.13)	31.0(−0.59)
A8: *cis,cis,cis*(*C,N,O*)-$(+)^{CD}_{500}$[Co(CN)$_2$(gly)$_2$]$^-$	21.1(2.04)	20.3(+1.28)
	24.4(2.05)	24.7(−1.63)
	30.5(2.16)	*ca.* 28(−0.7)sh
		31.0(+0.08)
		33.0(−0.02)
A9: *trans*(*O*)-*cis*(*C*)-$(+)^{CD}_{500}$[Co(CN)$_2$(gly)$_2$]$^-$	19.2(1.84)	16.8(−0.004)
		18.7(+0.015)
	ca. 26(1.9)sh	*ca.* 25(−0.002)sh
	30.7(2.14)	27.0(−0.003)
B2: *trans*(*N*)-*cis*(*C*)-$(+)^{CD}_{450}$[Co(CN)$_2$(*β*-ala)$_2$]$^-$	23.0(2.42)	22.7(+0.045)
	30.3(2.06)	*ca.* 31(−0.004)sh
B3: *cis,cis,cis*(*C,N,O*)-$(+)^{CD}_{500}$[Co(CN)$_2$(*β*-ala)$_2$]$^-$	20.7(2.29)	20.4(+1.56)
	23.9(2.12)	24.8(−0.82)
	30.2(2.00)	*ca.* 27(−0.6)sh
		ca. 30(−0.2)sh

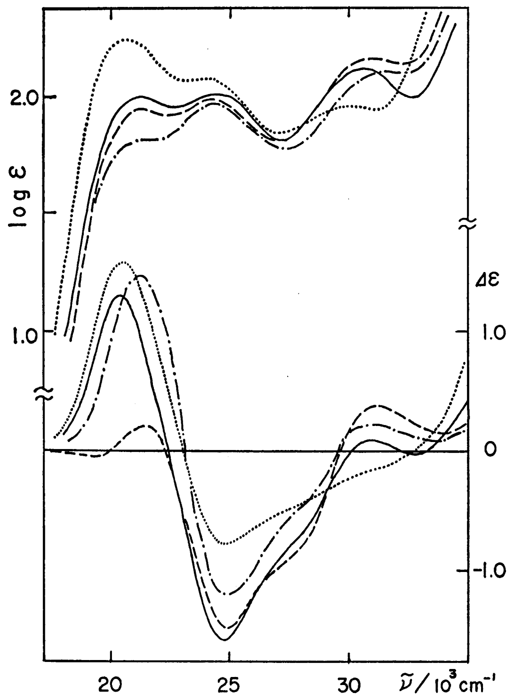

Fig. 1. Visible absorption and CD spectra of;
——: *cis, cis, cis*(*C, N, O*)-$(+)^{CD}_{500}[Co(CN)_2(gly)_2]^-$,
······: *cis, cis, cis*(*C, N, O*)-$(+)^{CD}_{500}[Co(CN)_2(\beta\text{-ala})_2]^-$,
- - -: *cis*-$(-)_{589}[Co(CN)_2(ox)(en)]^-$, —·—·—: *cis, cis*-$(+)_{589}[Co(CN)_2(ox)(NH_3)_2]^-$.

alaninato) isomer using $(-)_{589}[Co(ox)(en)_2]^+$ and $(-)_{589}[Co(CO_3)(en)_2]^+$, *etc.* as resolving agents failed. However, when $(-)_{589}[Co(NO_2)_2(en)_2]^+$ was used, an extremely weak Cotton peak with a negative sign was observed at 22700 cm^{-1} for an enantiomer obtained in the form of the less-soluble diastereomer. The *trans*(*O*)-*cis*(C)-$[Co(CN)_2(gly)_2]^-$ complex could be resolved by using $(-)_{589}[Co(ox)(en)_2]^+$, however, the optical purity of the diastereoisomeric salt obtained was very low. The CD spectrum of *trans*(*O*)-*cis*(*C*)-$[Co(CN)_2(gly)_2]$ exhibits two extrema with opposite signs in the region of the absorption band at 19200 cm^{-1} which is assigned to $^1A_{1g} \rightarrow {}^1E_g$ in a holohedrized symmetry[13] D_{4h}. A Cotton peak corresponding to $^1A_{1g} \rightarrow {}^1A_{2g}$ is observed as a shoulder at *ca.* 25000 cm^{-1}. As shown in Fig. 1, the CD spectrum of *cis,cis,cis*(*C,N,O*)-$[Co(CN)_2(gly)_2]^-$ exhibits two extrema with opposite signs in the first absorption band region, and a shoulder, observed at *ca.* 27000 cm^{-1}, is considered to be a splitting component of the second absorption band. The spectra of *cis,cis,cis*(*C,N,O*)-bis-(*β*-alaninato) isomer also exhibits two extrema in the first absorption band region; the Cotton peak at the lower frequency is dominant.

Optical Activity of cis,cis,cis-$[Co(C)_2(N)_2(O)_2]^-$ *Complexes.* The CD spectra of *cis,cis*-$[Co(CN)_2(OO)(NH_3)_2]^-$ and *cis*-$[Co(CN)_2(OO)(en)]^-$ complexes (OO: CO_3^{2-} and ox^{2-}) have been reported.[4] The optical activities of the former complexes are mainly derived from the chiral arrangement of three kinds of donor atoms. However, the chirality of the latter complexes are considered to have two origins; one is the arrangement of the donor atoms, and another is a chiral distribution of the chelate rings. The absolute configurations of these dicyano complexes have been predicted in terms of the sign of the Cotton peak observed at the higher frequency in the first absorption band region. For example, the absolute configuration of $(-)_{589}[Co(CN)_2(ox)(en)]^-$ complex, which exhibits three Cotton peaks with alternating signs, has been assigned as shown in Fig. 2, being denoted as $\Lambda(R)$ according to the two origins of the chirality. The *cis,cis,cis*(*C,N,O*)-$[Co(CN)_2(gly)_2]^-$ complex has also two chiral origins as for *cis*-$[Co(CN)_2(ox)(en)]^-$, however, the absolute configuration is denoted with either $\Delta(R)$ or $\Lambda(S)$.

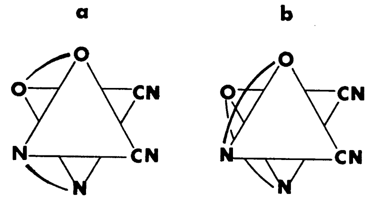

Fig. 2. Absolute configurations of;
a. *cis*-$\Lambda(R)$-$(-)_{589}[Co(CN)_2(ox)(en)]^-$, b. *cis, cis, cis*(*C, N, O*)-$\Delta(R)$-$(+)^{500}_{CD}[Co(CN)_2(gly)_2]^-$.

Mason and Seal[3] have applied a dynamic coupling model to the $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$ complexes. In their treatment, the contribution to the optical activity from the donor atoms was separated from that of the non-ligating atoms. It is possible to apply such a treatment in the present complexes. If the deviation of the donor atoms from the octahedral sites due to chelations can be disregarded, the contribution from the donor atoms intimately associates with the *R* (or *S*) configuration, while the contribution from the non-ligating atoms associates with the Δ (or Λ) configuration. The CD spectrum of the *cis,cis,cis*(*C,N,O*)-$(+)^{CD}_{500}[Co(CN)_2(gly)_2]^-$ isomer roughly resembles that of the $(-)_{589}[Co(CN)_2(ox)(en)]^-$ isomer. This suggests that either the donor atoms or the non-ligating atoms mainly contribute to the optical activity of the complexes. The resemblance between the CD spectrum of *cis,cis,cis*-(*C,N,O*)-$(+)^{CD}_{500}[Co(CN)_2(gly)_2]^-$ and that of *cis,cis*-*R*$(+)_{589}[Co(CN)_2(ox)(NH_3)_2]^-$ (shown in Fig. 1) suggests the larger contribution from the donor atoms, and predicts the absolute configuration of the bis(glycinato) isomer as $\Delta(R)$, since the chirality of the *cis,cis*-$[Co(CN)_2(ox)(NH_3)_2]^-$ complex is considered to be derived from the arrangement of the donor atoms.

In order to confirm the above suggestion, an X-ray crystal analysis of $(-)_{589}[Co(ox)(en)_2]$·*cis,cis,cis*(*C,N,O*)-$(+)^{CD}_{500}[Co(CN)_2(gly)_2]\cdot 3H_2O$ was attempted, and the detailed data will be presented elsewhere. The absolute configuration of the bis(glycinato) isomer was determined as $\Delta(R)$, as illustrated in Fig. 2. This result shows that the optical activity of the *cis,cis,cis*-$[Co(C)_2(N)_2(O)_2]^-$-type complexes mainly arises from the chiral arrangement of the donor atoms and the non-ligating atoms cause auxiliary optical activity. It is found that the deviation of the donor atoms from the octahedral sites due to the chelations also makes a minor contribution to the optical activity. The results supports the

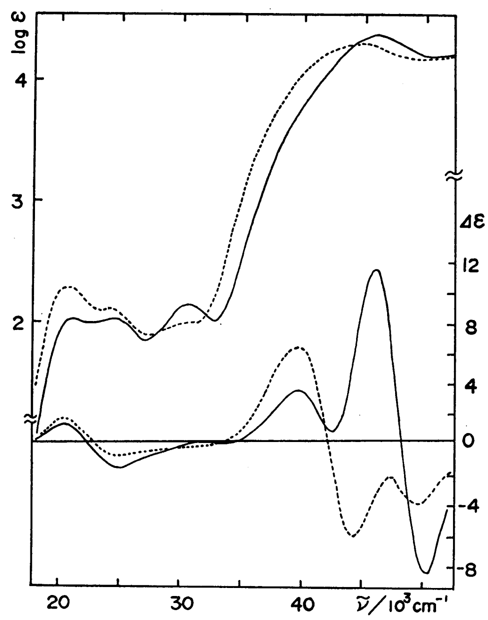

Fig. 3. Visible and ultra-violet absorption and CD spectra of;
——: *cis, cis, cis(C, N, O)*-(+)$^{CD}_{500}$ [$Co(CN)_2(gly)_2$]$^-$,
……: *cis, cis, cis(C, N, O)*-(+)$^{CD}_{500}$ [$Co(CN)_2(\beta\text{-ala})_2$]$^-$.

evaluation of the absolute configurations of the *cis,cis*-[$Co(CN)_2(OO)(NH_3)_2$]$^-$ and *cis*-[$Co(CN)_2(OO)(en)$]$^-$ complexes reported in the previous paper,[4] by the CD spectral comparison.

At a glance, the results obtained are incompatible with those for the tris(diamine) complexes, where the non-ligating atoms play an important role in the optical activities of the complexes. As to the tris(diamine) complexes, if the existence of the non-ligating atoms and the deviation of the donor atoms from the octahedral sites be disregarded, the distribution of the donor atoms around a metal ion creates no optical activity. On the contrary, as to the *cis,cis,cis*-[$Co(C)_2(N)_2(O)_2$]$^-$ complexes, such a distribution is considered to generate large optical activity, because the ligand field strengths of the C, N, and O donors are very different from each other.

The isomer (+)$^{CD}_{500}$[$Co(CN)_2(\beta\text{-ala})_2$]$^-$ is also assignable to $\Delta(R)$ configuration by comparison with the CD spectrum of the bis(glycinato) complex in the first absorption band region, since the change from gly to *β*-ala chelate rings results in a slight change of the intensities of the Cotton peaks. This is supported by the comparison with the spectra in the ultra-violet region, illustrated in Fig. 3. Since several transitions lie closely in the same region, the CD spectra of the isomers are complicated. However, both isomers exhibit the positive Cotton peaks at *ca.* 40000 cm^{-1} which correspond to the lowest lying allowed-transition.

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