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Studies of the Mixed Amino Acid Complexes of Cobalt(III). III.[1] Absorption and Circular Dichroism Spectra of Bis(amino acidato)ethylenediamine-cobalt(III) and Bis(amino acidato)oxalatocobaltate(III) Complexes

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Three isomers of *cis(O)*-bis(L-alaninato)ethylenediaminecobalt(III) perchlorate, four isomers of potassium *cis(N)*-bis(L-alaninato)oxalatocobaltate(III) and two isomers of potassium *trans(N)*-bis(L-prolinato)oxalatocobaltate(III) have been prepared, and their configurations have been assigned by absorption and circular dichroism spectra. From analysis of the circular dichroism spectra of about 25 complexes of these types (the aminoacidato ligands are glycinato, L-alaninato, L-serinato and L-prolinato), the configurational and the vicinal circular dichroism curves have been separated and discussed. The vicinal circular dichroism curve shows a pattern characteristic of the absolute configuration of α-aminoacidato ligand and of the geometrical structure of the complex.

Three geometrical isomers, *trans*, C_2-*cis* and C_1-*cis*, exist for $[Co(amac)_2en]^+$ or $[Co(amac)_2ox]^-$ type complexes[1] (amac=aminoacidato, en=ethylenediamine, and ox=oxalato ligand). In earlier works, we reported the circular dichroism (CD) spectra of all the geometrical isomers of the glycinato and L-serinato complexes and of the *trans* isomers of the L-alaninato complexes.[2,3] Because more data are required to investigate the so-called vicinal effect displayed by the coordinated optically active α-aminoacidato ligand, we have prepared three *cis(O)* isomers of $[Co(\text{L-ala})_2en]^+$ and four *cis(N)* isomers of $[Co(\text{L-ala})_2ox]^-$ and two *trans(N)* isomers of $[Co(\text{L-prol})_2ox]^-$. In the present paper, details are given for the preparation and separation of the isomers, the assignments of their geometrical structures and absolute configurations. The CD spectra of several complexes of the general types, $[Co(amac)_2en]^+$ and $[Co(amac)_2ox]^-$, are discussed and summarized.

Experimental

Preparation and Separation of Complexes. 1) Isomers of Bis(L-alaninato)ethylenediaminecobalt(III) Perchlorate. A solution of $[Co(\text{L-ala})_2en]^+$ was prepared from cobalt(II) chloride hexahydrate, L-alanine and ethylenediamine by the method described in the previous paper,[3] and it was poured into a column (3 cm×90 cm) of cation-exchange resin (Dowex 50W-X8, 200—400 mesh, H^+ form). The neutral species, *mer*- and *fac*-$[Co(\text{L-ala})_3]$, were swept out with water, and the two dark red species, Δ- and Λ-*trans(O)*-$[Co(\text{L-ala})_2en]^+$, were eluted out with 0.02 M $NaClO_4$ solution. The separation and optical properties of these two *trans(O)* isomers have already been reported.[3] With further elution, three red bands appeared in the middle region of the column. The first red band was composed of $(-)_{546}$-isomers, which showed absorption maxima at 502 and 360 nm in the earlier eluted part and at 500 and 356 nm in the later eluted part. The second and the third red bands contained $(+)_{546}$-isomers. The species in the second band had absorption maxima at 503 and 360 nm, and that in the third band at 500 and 356 nm. By comparing the above experimental data with those of the corresponding glycinato and L-serinato complexes,[3] it was confirmed that the first band consisted of the two isomers, $(-)_{546}$-(Δ)-C_1-*cis(O)* and $(-)_{546}$-(Δ)-C_2-*cis(O)*, and that the second band contained $(+)_{546}$-(Λ)-C_1-*cis(O)* and the third band $(+)_{546}$-(Λ)-C_2-*cis(O)*.

$(-)_{546}$-*C_1*-cis(O)-*$[Co(\text{L-ala})_2en]ClO_4$*: The earlier eluate of first red band was concentrated with a vacuum evaporator, and ethanol and ether were added to it. A large amount of white precipitate of sodium perchlorate deposited and it was filtered off. If an oily substance was formed, the supernatant was removed by decantation. The oil was treated with a little amount of water, and ethanol and ether were again added to it. After repeated precipitation and removal of sodium perchlorate by the same procedure, red crystals were deposited. They were isolated by using a centrifuge and recrystallized from water by adding ethanol and ether. Pure crystals (E–C–1) were filtered, washed with water-ethanol mixture and ethanol, and dried in air.

From the later eluate of the first red band, no pure complex could be obtained.

$(+)_{546}$-*C_1*-cis(O)-*$[Co(\text{L-ala})_2en]ClO_4$*: This isomer (E–C–2) was obtained from the eluate of second red band by the same method used for the $(-)_{546}$-C_1-*cis(O)* isomer.

$(+)_{546}$-*C_2*-cis(O)-*$[Co(\text{L-ala})_2en]ClO_4$*: The eluate of third red band was evaporated to dryness with a vacuum evaporator, and the red substance was extracted with methanol. When ether was added to the methanol solution a large amount of white sodium perchlorate precipitate was formed, which was filtered off. After repeated precipitation and removal of sodium perchlorate, red crystals began to deposit. They were isolated by using a centrifuge. The crude complex was dissolved in water, and a small amount of insoluble material was filtered off. The pure complex (E–C–3) was obtained by evaporating the mother liquor in a vacuum desiccator.

2) Isomers of Potassium Bis(L-alaninato)oxalatocobaltate(III). A solution of $[Co(\text{L-ala})_2ox]^-$ was prepared from cobalt(II) chloride hexahydrate, L-alanine and potassium oxalate by the method described in the previous paper.[4] From a column (3 cm×90 cm) of anion-exchange resin (Dowex 1-X8, 200—400 mesh, Cl^- form) the upper layer (about 4 cm) of resin was sucked out by a syringe, and stirred in a separate beaker with a saturated potassium acetate solution. It was again stirred with the solution of $[Co(\text{L-ala})_2ox]^-$ and the resulting resin which adsorbed several isomers of the complex ion returned to the top of the column. By elution with 0.02—0.01 M KCl solution, a colored band was progressively separated into the three bands which were, in order of elution, blue-violet, red-violet and blue-violet. From their visible and ultraviolet absorption spectra, CD and ORD curves, these bands were assigned as follows. The first blue-violet band consisted of two species, $(-)_{546}$-(Λ)-*trans(N)*- and $(+)_{546}$-(Δ)-*trans(N)*-$[Co(\text{L-ala})_2ox]^-$, which were eluted in this order. In the second red-violet band there were also two species, $(-)_{546}$-(Λ)-C_1-*cis(N)*- (eluted earlier) and $(+)_{546}$-(Δ)-C_1-*cis(N)*-$[Co(\text{L-ala})_2ox]^-$ (eluted later), both of which showed absorption maxima at 542 and 386 nm. The last blue-violet band was further separated into two bands. The species in the earlier eluted band was $(+)_{546}$-(Δ)-C$_2$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$ which had absorption maxima at 548 and 381 nm, and the species in the later eluted band was $(-)_{546}$-(Λ)-C$_2$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$ which had absorption maxima at 551 and 381 nm.

$(-)_{546}$-(Λ)- and $(+)_{546}$-(Δ)-trans(N)-*K[Co(*L*-ala)$_2$ox]*: The $(-)_{546}$- and $(+)_{546}$-isomers in the first blue-violet band were identical to the less soluble and the more soluble isomers, respectively, in the earlier paper.[4] Therefore the isolation and purification were carried out as before.

$(-)_{546}$-(Λ)- and $(+)_{546}$-(Δ)-*C$_1$*-cis(N)-*K[Co(*L*-ala)$_2$ox]*: The eluate of the second red-violet band was concentrated with a vacuum evaporator. By adding a limited amount of ethanol in portions to the concentrated solution, several fractions of the complex were obtained, after the white precipitates of potassium chloride formed at first had been removed. By measurement of their ORD, these fractions were divided into two groups, $(-)_{546}$- and $(+)_{546}$-fractions. It was found that the isomer in the $(-)_{546}$-fraction (O–C–1) was less soluble and the one in $(+)_{546}$-fraction (O–C–2) more soluble. Both isomers were independently recrystallized from water by adding ethanol (and ether too for the $(+)_{546}$-isomer), and they were filtered, washed with ethanol and dried in a desiccator. The $(-)_{546}$-isomer was also isolated by adding ethanol to the earlier eluted part of the second band.

$(+)_{546}$-(Δ)-*C$_2$*-cis(N)-*K[Co(*L*-ala)$_2$ox]*: The earlier eluted part of the third blue-violet band was evaporated to dryness with a vacuum evaporator. The complex was extracted with methanol, and then ether was added to this methanol solution. The crude complex deposited was recrystallized from water by adding ether. Pure violet crystals (O–C–3) were filtered, washed with ether and dried in a vacuum desiccator.

$(-)_{546}$-(Λ)-*C$_2$*-cis(N)-*K[Co(*L*-ala)$_2$ox]*: This isomer (O–C–4) was obtained from the later eluted part of the third band by the same method used for the $(+)_{546}$-isomer.

3) Trans(N) *Isomers of Potassium Bis(*L*-prolinato)oxalatocobaltate(III).* A solution of 4.7 g (0.02 mol) of cobalt (II) chloride hexahydrate in 20 ml of water was mixed with a solution of 4 g (0.02 mol) of potassium oxalate and 5 g (0.04 mol) of L-proline in 40 ml of water. The resulting solution was mechanically stirred with 5 g of lead dioxide and a small amount of active charcoal at 60 °C for about 40 min, and cooled to room temperature. After standing overnight, insoluble material was removed. The resin which adsorbed the resulting complex ion was prepared by the method described for [Co(L-ala)$_2$ox]$^-$, and it was transferred into the top of a 3 cm × 90 cm column packed with anion-exchange resin (Dowex 1-X8, 200—400 mesh, Cl$^-$ form). The adsorbed complexes were progressively separated into two bands colored blue-violet and violet, by elution with about 0.05 M KCl solution. From the absorption and CD spectra, it was shown that the blue-violet band contained two isomers of *trans(N)*-[Co(L-prol)$_2$ox]$^-$, which was the Δ-isomer in the earlier eluted fraction and the Λ-isomer in the later eluted fraction. Similarly, the violet band was shown to contain *cis(N)*-[Co(L-prol)$_2$ox]$^-$ isomer.

Only two *trans* isomers have been successfully isolated as follows.

$(+)_{546}$-(Δ)-trans(N)-*K[Co(*L*-prol)$_2$ox]*: The earlier eluted fraction of the blue-violet band was evaporated to dryness with a vacuum evaporator, and then the violet substance was extracted with methanol. An insoluble mixture of white precipitate (potassium chloride) and reddish violet solid (Λ-*trans* isomer) was filtered off, and then ether was added to the mother liquor. Violet crystals were deposited. They were recrystallized from methanol by adding ether. After repeated recrystallizations, pure crystals (P–T–1) were filtered, washed with ether and dried in a desiccator.

$(+)_{546}$-(Λ)trans(N)-*K[Co(*L*-prol)$_2$ox]*: The later eluted fraction of the blue-violet band was concentrated with a vacuum evaporator. By adding ethanol to the concentrate, a large amount of pinkish violet crystals was deposited. If a precipitate of potassium chloride was formed prior to precipitating the complex, it was removed, and ethanol was again added to the mother liquor. The crude complex was recrystallized from water by adding ethanol. The pure crystals (P–T–2) were filtered, washed with ethanol–water mixture and then with ethanol and dried in air.

Measurements. The electronic absorption spectra were measured with a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded with a JASCO Model MOE-1 spectropolarimeter or with a Roussel-Jouan Dichrograph. The ORD curves were recorded with a Yanagimoto Model-185 spectropolarimeter. All measurements were made in aqueous solutions at room temperature.

Results and Discussion

The three newly obtained isomers of *cis*(*O*)-[Co(L-ala)$_2$en]$^+$ were labeled as E–C–1, E–C–2 and E–C–3, the four isomers of *cis*(*N*)-[Co(L-ala)$_2$ox]$^-$ as O–C–1, O–C–2, O–C–3 and O–C–4, and the two isomers of *trans*(*N*)-[Co(L-prol)$_2$ox]$^-$ as P–T–1 and P–T–2, in the order of elution. The analytical data for these complexes are presented in Table 1, together with

TABLE 1. ANALYTICAL DATA OF [Co(L-ala)$_2$en]ClO$_4$, K[Co(L-ala)$_2$ox] AND K[Co(L-prol)$_2$ox]

Label	Complex	Found			Calcd		
		C	H	N	C	H	N
E-C-1	$(-)_{546}$-Δ-C$_1$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$·2H$_2$O	22.61	5.72	13.10	23.31	5.62	13.01
E-C-2	$(+)_{546}$-Λ-C$_1$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$	24.11	5.11	14.21	24.35	5.11	14.20
E-C-3	$(+)_{546}$-Λ-C$_2$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$·2H$_2$O·0.5NaClO$_4$	20.17	4.77	10.84	19.53	4.92	11.39
O-T-1	$(-)_{546}$-Λ-*trans*(*N*)-K[Co(L-ala)$_2$ox]	26.26	3.53	7.76	26.53	3.33	7.74
O-T-2	$(+)_{546}$-Δ-*trans*(*N*)-K[Co(L-ala)$_2$ox]·2.5H$_2$O	23.47	4.19	6.87	23.59	4.21	6.88
O-C-1	$(-)_{546}$-Λ-C$_1$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O	22.94	4·30	6.69	23.08	4.36	6.73
O-C-2	$(+)_{546}$-Δ-C$_1$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3.5H$_2$O	22.35	4.34	6.44	22.59	4.50	6.59
O-C-3	$(+)_{546}$-Δ-C$_2$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O·2.4KCl	16.48	2.96	4.59	16.14	3.05	4.71
O-C-4	$(-)_{546}$-Λ-C$_2$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O·2.3KCl	16.56	2.95	4.85	16.35	3.09	4.77
P-T-1	$(+)_{546}$-Δ-*trans*(*N*)-K[Co(L-prol)$_2$ox]·2.5H$_2$O	30.68	4.66	6.12	31.38	4.61	6.10
P-T-2	$(+)_{546}$-Λ-*trans*(*N*)-K[Co(L-prol)$_2$ox]·2.5H$_2$O	31.36	4.55	6.15	31.38	4.61	6.10

those of the two isomers of *trans*(*N*)-[Co(L-ala)$_2$ox]$^-$ (O-T-1 and O-T-2).

The sample of Δ-*trans*(*N*)-K[Co(L-ala)$_2$ox] prepared in the present work (O-T-2) had 2.5 mol of water of crystallization (*cf.* Table 1), although the sample prepared in the earlier paper[4] was anhydrous. The optical purity of the present sample is greater than that of the previous one. It seems that the sample in the earlier work was partly racemic, *i.e.* it was mixed with a little of the Λ-*trans*(*N*) isomer. The E-C-3 isomer of [Co(L-ala)$_2$en]$^+$ and O-C-3 and O-C-4 isomers of [Co(L-ala)$_2$ox]$^-$ are contaminated with small amounts of sodium perchlorate or potassium chloride. However, further purifications have not been carried out, because of the low yields of the complexes.

Structural Assignments of Isomers. The geometrical structures of [Co(amac)$_2$en]$^+$ or [Co(amac)$_2$ox]$^-$ complexes can be determined from their absorption spectra in the d-d transition region. Thus the O-T-1, O-T-2, P-T-1 and P-T-2 isomers are easily identified as *trans*-(*N*) structures from the large splitting of their first absorption bands[1] (*cf.* Fig. 1).

The absorption spectra of the C$_2$-*cis* and C$_1$-*cis* isomers of the present complexes are similar in appearance in the d-d transition region, as seen in Figs. 2 and 3. However, we have found previously some regular differences in the absorption maxima between the C$_2$-*cis* and the C$_1$-*cis* isomers in both series of [Co(gly)$_2$en]$^+$ and [Co(gly)$_2$ox]$^-$. The geometrical structures of these bis(glycinato) isomers were determined unambiguously from their NMR spectra.[1] For instance, the C$_2$-*cis*(*O*) isomer of [Co(gly)$_2$en]$^+$ shows a second absorption maxima at a higher energy than that of the corresponding C$_1$-*cis*(*O*) isomer. The same behavior has also been observed for the [Co(L-ser)$_2$en]$^+$ isomers. The data are presented in Table 2 together with those of the [Co(L-ala)$_2$en]$^+$ isomers,

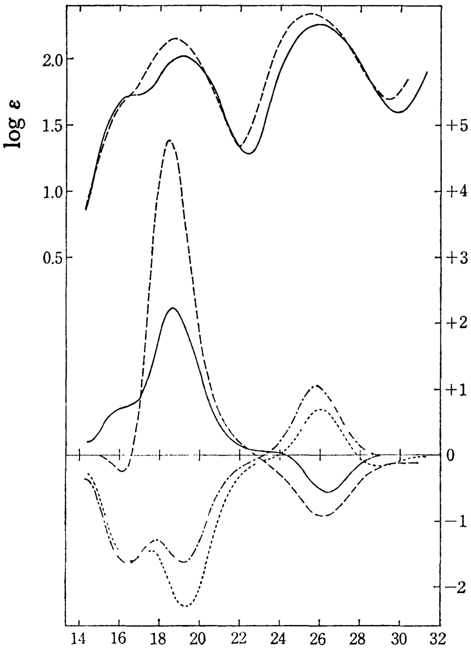

Fig. 1. Absorption and CD spectra of *trans*(*N*)-[Co(L-amac)$_2$ox]$^-$.
——: Λ-L-alaninato complex (O-T-1), ----: Δ-L-alaninato complex (O-T-2), ———: Δ-L-prolinato complex(P-T-1), ——: Λ-L-prolinato complex (P-T-2).

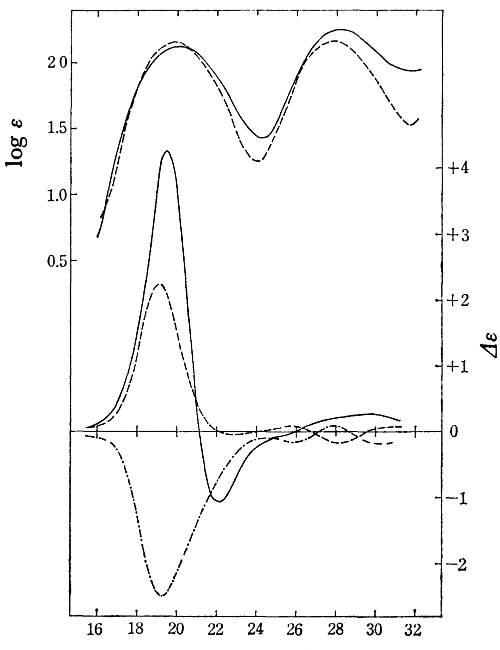

Fig. 2. Absorption and CD spectra of *cis*(*O*)-[Co(L-ala)$_2$en]$^+$.
------: Δ-C$_1$-*cis*(*O*) isomer (E-C-1), ———: Λ-C$_1$-*cis*(*O*) isomer (E-C-2), ——: Λ-C$_2$-*cis*(*O*) isomer (E-C-3).

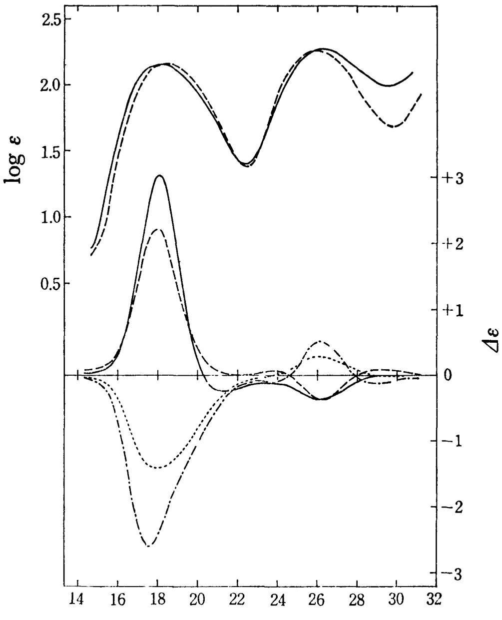

Fig. 3. Absorption and CD spectra of *cis*(*N*)-[Co(L-ala)$_2$ox]$^-$.
———: Λ-C$_1$-*cis*(*N*) isomer (O-C-1); ———: Δ-C$_1$-*cis*(*N*) isomer (O-C-2); ----: Δ-C$_2$-*cis*(*N*) isomer (O-C-3); ——: Λ-C$_2$-*cis*(*N*) isomer (O-C-4).

E-C-1, E-C-2, and E-C-3. By comparing these values, the geometrical structures of E-C-1 and E-C-2, both of which have their second absorption maxima at 27800 cm^{-1}, are assigned to C$_1$-*cis*(*O*), and E-C-3, which has a second absorption maximum at 28200 cm^{-1}, to C$_2$-*cis*(*O*). In the oxalato complexes such as [Co(gly)$_2$ox]$^-$ and [Co(L-ser)$_2$ox]$^-$, the C$_2$-*cis*(*N*) isomer has its first absorption maximum at a lower energy and the second absorption maximum at a higher energy than the C$_1$-*cis*(*N*) isomer, as seen in Table 2. Therefore, the geometrical structures of O-C-1 isomer (absorption maxima at 18500 and 25900 cm^{-1}) and the O-C-2 isomer (maxima at 18400 and 25900 cm^{-1}) are assigned as C$_1$-*cis*(*N*), while the structures of O-C-3 (maxima at 18200 and 26200 cm^{-1}) and O-C-4 isomers (maxima at 18200 and 26300 cm^{-1}) are assigned as C$_2$-*cis*(*N*).

The absolute configurations of all the isomers were assigned from the sign of major CD band in the region of the first absorption band.[5] It has been confirmed that the absolute configurations derived from this CD method agree with conclusions from PMR studies, which were reported for several mixed aminoacidato-cobalt(III) complexes including *trans*(*O*)-[Co(L-ala)$_2$en]$^+$ and *trans*(*N*)-[Co(L-ala)$_2$ox]$^-$.[6,7] Since the E-C-2, E-C-3, O-C-1, O-C-4, and P-T-2 isomers have a positive major CD band in the region of the first absorption band (Figs. 2 and 3), these isomers are assigned to the Λ-configuration. The other four complexes have a negative major CD band, and they are assigned to the Δ-configuration. Consequently, the nine newly obtained complexes are characterized as follows: in the [Co(L-ala)$_2$en]$^+$ series, E-C-1 is Δ-C$_1$-*cis*(*O*), E-C-2 Λ-C$_1$-*cis*(*O*), and E-C-3 Λ-C$_2$-*cis*(*O*); in the [Co(L-ala)$_2$ox]$^-$ series, O-C-1 is Λ-C$_1$-*cis*(*N*), O-C-2 Δ-C$_1$-*cis*(*N*), O-C-3 Δ-C$_2$-*cis*(*N*), and O-C-4 Λ-C$_2$-*cis*(*N*); in the [Co(L-prol)$_2$ox]$^-$ series, P-T-1 is Δ-*trans*(*N*), and P-T-2 Λ-*trans*(*N*). We have failed in isolation of the Δ-C$_2$-*cis*(*O*) isomer in the [Co(L-ala)$_2$en]$^+$ series, though it has been confirmed that this isomer certainly exists in a fraction eluted from the column after the E-C-1 fraction.

Absorption Spectra. The absorption spectra of the complexes in the [Co(amac)$_2$en]$^+$ and [Co(amac)$_2$ox]$^-$ series are summarized in Table 2. As mentioned above, the second absorption band maximum of

Table 2. d-d Absorption data of [Co(amac)$_2$en]$^+$ and [Co(amac)$_2$ox]$^-$ complexes

Complex	I-Band		II-Band		Ref.
	σ_{max}[a]	(log ε_{max})	σ_{max}[a]	(log ε_{max})	
trans(*O*)-[Co(gly)$_2$en]I·H$_2$O	18.9	(1.94)	27.8	(2.12)	1
Δ-*trans*(*O*)-[Co(L-ala)$_2$en]ClO$_4$	18.9	(1.98)	27.6	(2.13)	3
Λ-*trans*(*O*)-[Co(L-ala)$_2$en)ClO$_4$	18.8	(1.97)	27.7	(2.17)	3
Δ-*trans*(*O*)-[Co[L-ser)$_2$en]I	18.9	(1.95)	27.8	(2.13)	3
Λ-*trans*(*O*)-[Co(L-ser)$_2$en]ClO$_4$	18.9	(1.95)	27.7	(2.13)	3
C$_2$-*cis*(*O*)-[Co(gly)$_2$en]Br·H$_2$O	19.9	(2.04)	28.0	(2.11)	1
Λ-C$_2$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$·2H$_2$O·0.5NaClO$_4$	20.1	(2.12)	28.2	(2.25)	
Δ-C$_2$-*cis*(*O*)-[Co(L-ser)$_2$en]I·2H$_2$O·0.5serH	20.0	(2.10)	28.3	(2.29)	3
Λ-C$_2$-*cis*(*O*)-[Co(L-ser)$_2$en]I	20.0	(2.05)	28.1	(2.14)	3
C$_1$-*cis*(*O*)-[Co(gly)$_2$en]Br·3H$_2$O	20.0	(2.09)	27.7	(2.13)	1
Δ-C$_1$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$·2H$_2$O	19.9	(2.16)	27.8	(2.17)	
Λ-C$_1$-*cis*(*O*)-[Co(L-ala)$_2$en]ClO$_4$	19.8	(2.15)	27.8	(2.15)	
Δ-C$_1$-*cis*(*O*)-[Co(L-ser)$_2$en]I	20.0	(2.12)	27.8	(2.14)	3
Λ-C$_1$-*cis*(*O*)-[Co(L-ser)$_2$en]ClO$_4$	20.0	(2.12)	27.9	(2.15)	3
trans(*N*)-K[Co(gly)$_2$ox]	18.9	(2.00)	25.8	(2.23)	1
Δ-*trans*(*N*)-K[Co(L-ala)$_2$ox]·2.5H$_2$O	19.0	(2.02)	25.9	(2.25)	
Λ-*trans*(*N*)-K[Co(L-ala)$_2$ox]	19.1	(2.02)	25.9	(2.26)	
Δ-*trans*(*N*)-K[Co(L-ser)$_2$ox]·3.5H$_2$O	19.0	(1.96)	26.0	(2.21)	2
Λ-*trans*(*N*)-K[Co(L-ser)$_2$ox]·3H$_2$O	19.0	(1.97)	26.0	(2.20)	2
Δ-*trans*(*N*)-K[Co(L-prol)$_2$ox]·2.5H$_2$O	18.9	(2.08)	25.5	(2.29)	
Λ-*trans*(*N*)-K[Co(L-prol)$_2$ox]·2.5H$_2$O	18.7	(2.15)	25.5	(2.34)	
C$_2$-*cis*(*N*)-Na[Co(gly)$_2$ox]	17.8	(2.08)	25.9	(2.20)	1
Δ-C$_2$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O·2.4KCl	18.2	(2.17)	26.2	(2.26)	
Λ-C$_2$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O·2.3KCl	18.2	(2.15)	26.3	(2.27)	
Δ-C$_2$-*cis*(*N*)-K[Co(L-ser)$_2$ox]·2.5H$_2$O	18.0	(2.07)	26.0	(2.17)	2
Λ-C$_2$-*cis*(*N*)-K[Co(L-ser)$_2$ox]·2.5H$_2$O	18.0	(2.14)	26.1	(2.25)	2
C$_1$-*cis*(*N*)-Na[Co(gly)$_2$ox]	18.3	(2.15)	25.8	(2.24)	1
Δ-C$_1$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3.5H$_2$O	18.4	(2.16)	25.9	(2.26)	
Λ-C$_1$-*cis*(*N*)-K[Co(L-ala)$_2$ox]·3H$_2$O	18.5	(2.16)	25.9	(2.26)	
Δ-C$_1$-*cis*-(*N*)-K[Co(L-ser)$_2$ox]·2H$_2$O	18.5	(2.16)	25.9	(2.29)	2
Λ-C$_1$-*cis*(*N*)-K[Co(L-ser)$_2$ox]·1.5H$_2$O	18.5	(2.09)	25.9	(2.20)	2

a) In the unit of 10^3 cm^{-1}.

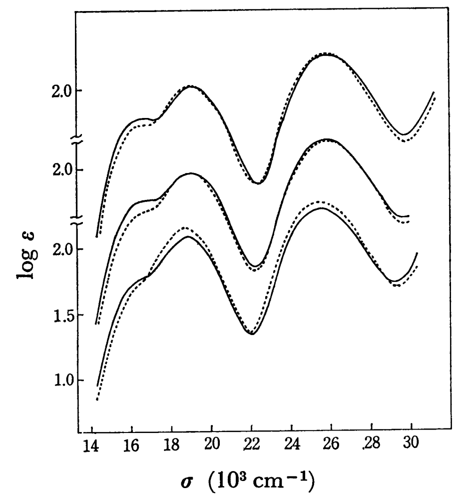

Fig. 4. Absorption spectra of *trans*(*N*)-[Co(L-amac)$_2$ox]$^-$. {L-amac = L-ala (upper); L-ser (middle); L-prol (lower)}: ——: Δ-isomer, ----: Λ-isomer

C$_2$-*cis* isomer is generally at a higher energy than that of the corresponding C$_1$-*cis* isomer.

For the *trans*(*N*)-[Co(amac)$_2$ox]$^-$ complexes, the position of the first absorption band maximum shifts to higher energies in the order of aminoacidato ligands: L-prolinato, glycinato, L-serinato and L-alaninato. The same order is also observed for the C$_2$-*cis*(*O*)-[Co(amac)$_2$en]$^+$ and C$_2$-*cis*(*N*)-[Co(amac)$_2$ox]$^-$ complexes. This spectrochemical series for aminoacids agrees with that observed for the [Co(amac) (NH$_3$)$_4$]$^{2+}$ complexes.[8] In Fig. 4, it is interesting to note that the intensity of the longer wavelength component of the first absorption band is always stronger in the Δ diastereomer of the *trans*(*N*)-[Co(L-amac)$_2$ox]$^-$ complex than in the corresponding Λ one.

Configurational Circular Dichroism. The observed CD data for the [Co(L-amac)$_2$en]$^+$ and [Co(L-amac)$_2$ox]$^-$ complexes are summarized in Table 3. By applying the following relations,[2,3] the configurational (Figs. 5 and 6) and the vicinal (Fig. 7) curves have been derived from the observed curves.

$$\Delta\varepsilon(2\mathrm{L}) = 1/2\{\Delta\varepsilon(\Lambda_{2\mathrm{L}})+\Delta\varepsilon(\Delta_{2\mathrm{L}})\}$$

$$\Delta\varepsilon(\Delta) = 1/2\{\Delta\varepsilon(\Delta_{2\mathrm{L}})-\Delta\varepsilon(\Lambda_{2\mathrm{L}})\}$$

$$\Delta\varepsilon(\Lambda) = 1/2\{\Delta\varepsilon(\Lambda_{2\mathrm{L}})-\Delta\varepsilon(\Delta_{2\mathrm{L}})\}$$

where $\Delta\varepsilon(\Delta_{2\mathrm{L}})$ and $\Delta\varepsilon(\Lambda_{2\mathrm{L}})$ are the observed CD for the Δ and Λ diastereomers, respectively, of the [Co(L-amac)$_2$en]$^+$ or [Co(L-amac)$_2$ox]$^-$ complex, and $\Delta\varepsilon(\Delta)$ and $\Delta\varepsilon(\Lambda)$ the configurational CD, and $\Delta\varepsilon(2\mathrm{L})$ the vicinal CD of the two mol of L-aminoacidato ligands.

The configurational CD curves agree well with the observed ones of the corresponding glycinato isomers, as seen in Figs. 5 and 6. Each configurational curve is quite characteristic of its geometrical structure irrespective of the kind of aminoacidato ligand. This means that the configurational chiralities of these complexes are almost identical regardless of the sub-

TABLE 3. OBSERVED CD DATA OF [Co(L-amac)$_2$en]$^+$ AND [Co(L-amac)$_2$ox]$^-$ COMPLEXES

Complex	First band region		Second band region			Ref.
	σ_{ext}[a] ($\Delta\varepsilon_{\mathrm{ext}}$)	σ_{ext}[a] ($\Delta\varepsilon_{\mathrm{ext}}$)	σ_{ext}[a] ($\Delta\varepsilon_{\mathrm{ext}}$)	σ_{ext}[a] ($\Delta\varepsilon_{\mathrm{ext}}$)	σ_{ext}[a] ($\Delta\varepsilon_{\mathrm{ext}}$)	
Δ-*trans*(*O*)-[Co(L-ala)$_2$en]$^+$	18.3(−2.63)	21.9(−1.40)		27.8(+0.36)		3
Λ-*trans*(*O*)-[Co(L-ala)$_2$en]$^+$	19.2(+2.88)			28.2(−0.74)		3
Δ-*trans*(*O*)-[Co(L-ser)$_2$en]$^+$	18.6(−2.81)	21.3(−1.26)		28.1(+0.51)		3
Λ-*trans*(*O*)-[Co(L-ser)$_2$en]$^+$	18.4(+2.13)	21.9(+0.75)		28.1(−0.30)		3
Λ-C$_2$-*cis*(*O*)-[Co(L-ala)$_2$en]$^+$	19.5(+4.26)	22.1(−1.07)		29.5(+0.25)		
Δ-C$_2$-*cis*(*O*)-[Co(L-ser)$_2$en]$^+$	19.7(−3.67)			27.8(+0.33)		3
Λ-C$_2$-*cis*(*O*)-[Co(L-ser)$_2$en]$^+$	19.5(+3.38)	22.1(−0.83)		29.9(+0.18)		3
Δ-C$_1$-*cis*-(*O*)-[Co(L-ala)$_2$en]$^+$	19.3(−2.48)		25.9(−0.15)	27.9(+0.09)	30.3(−0.18)	
Λ-C$_1$-*cis*(*O*)-[Co(L-ala)$_2$en]$^+$	19.1(+2.24)	22.8(−0.04)	25.8(+0.07)	28.2(−0.18)	30.8(+0.06)	
Δ-C$_1$-*cis*(*O*)-[Co(L-ser)$_2$en]$^+$	19.3(−2.84)		25.8(−0.08)	28.0(+0.24)	30.5(−0.11)	3
Λ-C$_1$-*cis*(*O*)-[Co(L-ser)$_2$en]$^+$	19.3(+1.64)		26.0(+0.09)	28.1(−0.18)	30.8(+0.08)	3
Δ-*trans*(*N*)-[Co(L-ala)$_2$ox]$^-$	16.6(−1.60)	19.3(−2.30)		26.0(+0.69)	28.9(−0.16)	
Λ-*trans*(*N*)-[Co(L-ala)$_2$ox]$^-$	15.9(+0.68)	18.6(+2.23)		26.4(−0.55)		
Δ-*trans*(*N*)-[Co(L-ser)$_2$ox]$^-$	16.7(−1.79)	19.4(−2.06)		26.0(+0.39)	28.8(−0.19)	2
Λ-*trans*(*N*)-[Co(L-ser)$_2$ox]$^-$	16.7(+0.45)	18.7(+2.08)		26.5(−0.41)		2
Δ-*trans*(*N*)-[Co(L-prol)$_2$ox]$^-$	16.5(−1.64)	19.2(−1.64)		25.8(+1.05)		
Λ-*trans*(*N*)-[Co(L-prol)$_2$ox]$^-$	16.1(−0.23)	18.5(+4.77)		26.2(−0.91)		
Δ-C$_2$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$	18.0(−1.41)			26.1(+0.27)		
Λ-C$_2$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$	18.0(+3.02)	21.3(−0.23)		26.2(−0.35)		
Δ-C$_2$-*cis*(*N*)-[Co(L-ser)$_2$ox]$^-$	18.2(−2.76)			26.2(+0.42)		2
Λ-C$_2$-*cis*(*N*)-[Co(L-ser)$_2$ox]$^-$	18.0(+3.24)	22.4(−0.05)		26.1(−0.41)		2
Δ-C$_1$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$	17.6(−2.60)		23.8(−0.11)	26.2(+0.51)	29.2(−0.12)	
Λ-C$_1$-*cis*(*N*)-[Co(L-ala)$_2$ox]$^-$	18.0(+2.24)		23.9(+0.05)	26.3(−0.36)	29.2(+0.07)	
Δ-C$_1$-*cis*(*N*)-[Co(L-ser)$_2$ox]$^-$	18.0(−2.91)		24.1(−0.09)	26.3(+0.38)	29.2(−0.08)	2
Λ-C$_1$-*cis*(*N*)-[Co(L-ser)$_2$ox]$^-$	18.0(+2.46)	21.6(−0.06)	24.2(+0.05)	26.2(−0.33)	29.1(+0.09)	2

a) In the unit of 10^3 cm^{-1}.

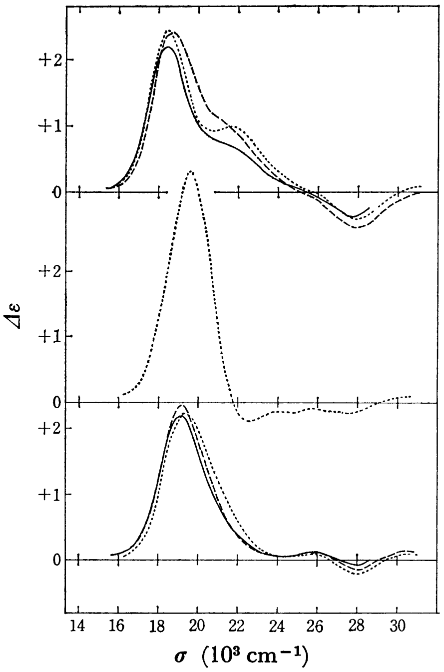

Fig. 5. Configurational CD curves of Λ-$[Co(amac)_2en]^+$ for *trans(O)* (upper), C_2-*cis(O)* (middle) and C_1-*cis(O)* (lower) isomers.
——: glycinato complexes (observed curves); — — —: L-alaninato complexes (calculated curves); ----: L-serinato complexes (calculated curves).

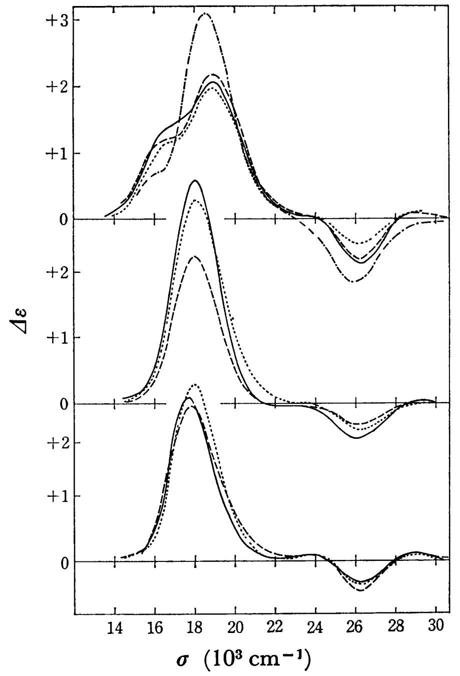

Fig. 6. Configurational CD curves of Λ-$[Co(amac)_2ox]^-$ for *trans(N)* (upper), C_2-*cis(N)* (middle) and C_1-*cis(N)* (lower) isomers.
——: glycinato complexes (observed curves); — — —: L-alaninato complexes (calculated curves); ----: L-serinato complexes (calculated curves); — - — -: L-prolinato complex (calculated curves).

stituent on the α carbon atom of the aminoacidato chelate ring. The configurational CD of the *trans* isomers show two bands of the same sign in the first absorption band region. On the other hand, those of the C_2-*cis* and C_1-*cis* isomers show a single main band in this region. A clear difference between the C_2-*cis* and C_1-*cis* isomers appears in the second absorption band region. The C_1-*cis* isomer shows three bands whose signs are positive, negative and positive (for the Λ isomer) from lower energy side, while the C_2-*cis* isomer shows one (or two) negative band (for the Λ isomer), in the second absorption band region. This behavior of the C_1-*cis* and C_2-*cis* isomers is common to both the $[Co(amac)_2en]^+$ and $[Co(amac)_2ox]^-$ complexes.

Table 4. CD extrema in configurational CD curves of Λ-$[Co(amac)_2en]^+$ and Λ-$[Co(amac)_2ox]^-$

Complex	First band region		Second band region		
	σ_{ext}[a] ($\Delta\varepsilon_{ext}$)	σ_{ext}[a] ($\Delta\varepsilon_{ext}$)	σ_{ext}[a] ($\Delta\varepsilon_{ext}$)	σ_{ext}[a] ($\Delta\varepsilon_{ext}$)	σ_{ext}[a] ($\Delta\varepsilon_{ext}$)
trans(O)-$[Co(gly)_2en]^+$	18.4(+2.19)	21.6(+0.64)		27.7(−0.32)	
trans(O)-$[Co(L\text{-}ala)_2en]^+$	18.8(+2.40)	21.2(+1.12)		28.0(−0.54)	
trans(O)-$[Co(L\text{-}ser)_2en]^+$	18.5(+2.44)	21.6(+0.98)		27·9(−0.22)	
C_2-*cis(O)*-$[Co(L\text{-}ser)_2en]^+$	19.6(+3.51)	22.5(−0.30)		27.5(−0.17)	
C_1-*cis(O)*-$[Co(gly)_2en]^+$	19.0(+2.21)		25.8(+0.11)	27.9(−0.08)	
C_1-*cis(O)*-$[Co(L\text{-}ala)_2en]^+$	19.2(+2.36)		25.6(+0.11)	27.9(−0.13)	30.8(+0.12)
C_1-*cis(O)*-$[Co(L\text{-}ser)_2en]^+$	19.4(+2.24)		25.8(+0.09)	27.9(−0.10)	30.7(+0.09)
trans(N)-$[Co(gly)_2ox]^-$	16.7(+1.37)	18.8(+2.07)		26.2(−0.69)	
trans(N)-$[Co(L\text{-}ala)_2ox]^-$	16.7(+1.19)	18.9(+2.20)		26.2(−0.61)	29.0(+2.07)
trans(N)-$[Co(L\text{-}ser)_2ox]^-$	16.7(+1.16)	18.9(+1.94)		26.2(−0.40)	
trans(N)-$[Co(L\text{-}prol)_2ox]^-$	16.0(+0.66)	18.5(+3.13)		25.8(−1.98)	
C_2-*cis(N)*-$[Co(gly)_2ox]^-$	18.0(+3.39)	22.5(−0.04)		26.0(−0.52)	
C_2-*cis(N)*-$[Co(L\text{-}ala)_2ox]^-$	18.0(+2.22)	22.2(−0.03)		26.0(−0.31)	
C_2-*cis(N)*-$[Co(L\text{-}ser)_2ox]^-$	18.0(+3.08)			26.3(−0.42)	
C_1-*cis(N)*-$[Co(gly)_2ox]^-$	17.7(+2.48)	22.3(+0.04)	23.9(+0.09)	26.3(−0.32)	29.0(+0.10)
C_1-*cis(N)*-$[Co(L\text{-}ala)_2ox]^-$	17.8(+2.36)		23.8(+0.08)	26.3(−0.44)	29.2(+0.09)
C_1-*cis(N)*-$[Co(L\text{-}ser)_2ox]^-$	18.0(+2.68)		23.9(+0.08)	26.3(−0.35)	29.0(+0.09)

a) In the unit of 10^3 cm^{-1}.

The extrema in the calculated configurational CD curves are listed in Table 4. In general, the positions of the CD extrema in the calculated configurational CD curves coincide closely with those of the absorption maxima in the first absorption band region. However, in $\mathrm{C_1}$-*cis* isomers of both types, $[\mathrm{Co(amac)_2en}]^+$ and $[\mathrm{Co(amac)_2ox}]^-$, the configurational CD extrema are 500—1000 $\mathrm{cm^{-1}}$ lower in energy than the absorption maxima.

Vicinal Circular Dichroism. The calculated vicinal CD curves also show systematic patterns characteristic of the geometrical structures, as seen in Fig. 7. The vicinal CD curve of $\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(L\text{-}ala)_2en}]^+$ has been drawn by subtracting the configurational curve of Λ-$\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(L\text{-}ser)_2en}]^+$ from the observed curve of Λ-$\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(L\text{-}ala)_2en}]^+$, because neither Δ-$\mathrm{C_2}$-*cis*-(*O*)-$[\mathrm{Co(L\text{-}ala)_2en}]^+$ nor optically active $\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(gly)_2en}]^+$ has been isolated. The three bands whose signs are negative, positive and negative from lower energy side are observed for the *trans* isomers of $[\mathrm{Co(L\text{-}ala)_2en}]^+$, $[\mathrm{Co(L\text{-}ala)_2ox}]^-$ and $[\mathrm{Co(L\text{-}ser)_2ox}]^-$ complexes. In these three bands, the highest energy band of $[\mathrm{Co(L\text{-}amac)_2en}]^+$ and the lowest energy band of $[\mathrm{Co(L\text{-}amac)_2ox}]^-$ appeared in the region of the shoulder of the first absorption band. Thus the vicinal CD in these *trans* type complexes, which contain L-aminoacidato ligands, may be summarized as follows: the $\mathrm{A_{2g}(D_{4h})}$ transition has a negative CD component and the $\mathrm{E_g(D_{4h})}$ splits into two CD components with opposite signs, by lowering the molecular symmetry. Hawkins has proposed an empirical rule for the vicinal effects of aminoacidato ligands: "In tetragonal or rhombic complexes, amino acids with the L configuration impose a negative Cotton effect on the transition with $\mathrm{A_{2g}(D_{4h})}$ parentage and give rise to two nondegenerate transitions of opposite sign corresponding to the $\mathrm{E_g(D_{4h})}$ band".[9] This is just the case for the present *trans* type complexes. The $\mathrm{E_g(D_{4h})}$ component of $[\mathrm{Co(L\text{-}prol)_2ox}]^-$ does not appear split. The strong positive intensity of this component may be related to the existence of asymmetric (S) nitrogen atoms of the coordinated L-prolinate ligands.

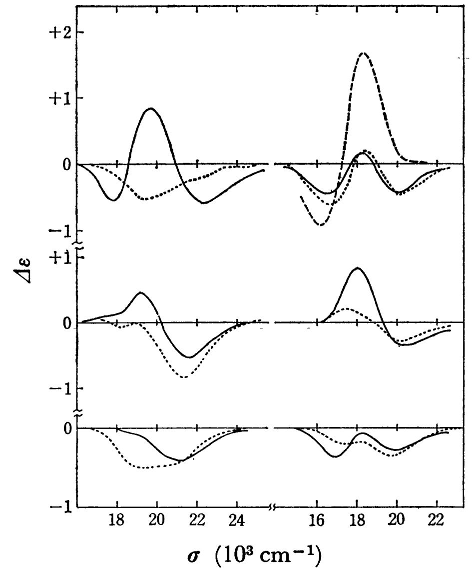

Fig. 7. Vicinal CD curves of $[\mathrm{Co(L\text{-}amac)_2en}]^+$ (left) and $[\mathrm{Co(L\text{-}amac)_2ox}]^-$ (right), for *trans* (upper), $\mathrm{C_2}$-*cis* (middle) and $\mathrm{C_1}$-*cis* (lower) isomers.
——: L-alaninato complexes; ----: L-serinato complexes; — — —: L-prolinato complex.

The vicinal CD curves of the $\mathrm{C_2}$-*cis*(*O*) isomers of $[\mathrm{Co(L\text{-}ala)_2en}]^+$, $[\mathrm{Co(L\text{-}ala)_2ox}]^-$ and $[\mathrm{Co(L\text{-}ser)_2ox}]^-$ have two bands, whose signs are positive and negative from lower energy side, while those of all the $\mathrm{C_1}$-*cis* isomers have two (or one in appearance) negative bands. It is interesting that the same pattern is observed in both types of complex, $\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(L\text{-}amac)_2en}]^+$ and $\mathrm{C_2}$-*cis*(*N*)-$[\mathrm{Co(L\text{-}amac)_2ox}]^-$, because the order of the energies of their $\mathrm{A_{2g}(D_{4h})}$ and $\mathrm{E_g(D_{4h})}$ transitions are reversed.

The vicinal CD curves of *trans*(*O*)- and $\mathrm{C_2}$-*cis*(*O*)-$[\mathrm{Co(L\text{-}ser)_2en}]^+$ deviate from the ordinary patterns. A molecular model examination indicates that an intramolecular hydrogen-bond is possible for the Λ-isomers of these two complexes: a hydrogen-bond is possible between two L-serinato ligands for the Λ-*trans*(*O*) isomer, and two hydrogen-bonds between an L-serinato and an ethylenediamine ligand for the Λ-$\mathrm{C_2}$-*cis*(*O*) isomer. Such hydrogen-bond interactions may more or less fix the conformation of chelate ring or restrict the internal rotation of the substituent group on the α-carbon atom, and thus be responsible for the anomalous vicinal CD.

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