Preparation and Circular Dichroism Spectra of Bis(amino-acidato)ethylenediaminecobalt(III) Complexes

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Cis(O) and *trans(O)* complexes of bis(L-serinato)ethylenediaminecobalt(III) ion have been prepared and completely separated into six possible isomers by ion-exchange column chromatography. These isomers have been assigned to *Λ-trans(O)*, *Λ-trans(O)*, *Λ-C_2-cis(O)*, *Λ-C_1-cis(O)*, *Λ-C_1-cis(O)* and *Λ-C_2-cis(O)* in the elution order, on the basis of their absorption and circular dichroism spectra. *Trans(O)*- and *C_1-cis(O)*-bis(glycinato)ethylenediaminecobalt(III) complexes have been resolved into their optically active isomers, and *trans(O)*-bis(L-alaninato)-ethylenediaminecobalt(III) ion has been prepared and separated into two configurationally active isomers. The absorption and circular dichroism data of six isomers of $[Co(L\text{-}ser)_2en]^+$, two isomers of $[Co(L\text{-}ala)_2en]^+$ and two isomers of $[Co(gly)_2en]^+$ have been discussed in being compared with those of the corresponding isomers of oxalatobis(L-serinato)cobaltate(III) complex.

Recently a number of reports[1-8] have been presented for the stereochemistry of cobalt(III) complexes with α-aminoacidato ligand and these studies have mainly been developed on the basis of their absorption and circular dichroism (CD) spectra. In a previous paper,[7] we reported the spectral and stereochemical properties of six isomers of oxalatobis(L-serinato)cobaltate(III) complex, with which are compared those of the corresponding isomers of oxalatobis(glycinato)cobaltate(III) complex. It is interesting to compare the results for such $[Co(O)_4(N)_2]$ type complexes with those for $[Co(O)_2(N)_4]$ type complexes. The present work is concerned with the absorption and CD spectra of six isomers of bis(L-serinato)-ethylenediaminecobalt(III) complex and optical isomers of *trans(O)*- and *C_1-cis(O)*-bis(glycinato)-ethylenediaminecobalt(III) complexes, all of which belong to a general type, $[Co(O)_2(N)_4]$. This may be the first study reported for the CD of bis(amino-acidato)ethylenediaminecobalt(III) type complexes.

Experimental

1) Resolution of Bis(glycinato)ethylenediaminecobalt(III) Iodide. By using an aqueous solution of sodium perchlorate as an eluting agent, we obtained three kinds of racemic perchlorates, *trans(O)*, *C_1-cis(O)* and *C_2-cis(O)*, of this complex, more easily than by using the potassium bromide solution as in a previous paper.[9] A large excess of sodium iodide was added to the concentrated solution of each the perchlorate; then the corresponding racemic iodides deposited. When the crystallization was not easy, they were obtained by adding an appropriate amount of ethanol to the solution. The red crystals were filtered off, washed with ethanol-water mixture and ethanol, and dried in air.

$(+)_{589}$-trans(O)-[Co(gly)$_2$en]I·H_2O. An aqueous suspension of 2.0 g (0.0048 mol) of racemic *trans(O)* iodide[10] was stirred well with 0.8 g (0.0048 mol) of silver acetate. The resulted yellow precipitate of silver iodide was removed. To the filtrate, 1.0 g (0.0024 mol) of $(-)_{546}$-K[Co(edta)]·$2H_2O$ was added, and a small amount of insoluble material formed was filtered out. From this solution the reddish violet diastereomer was obtained by concentrating it in a vacuum desiccator, and was recrystallized from aqueous solution by adding acetone. Pure crystals were filtered, washed with acetone-water mixture and acetone, and dried in air. Then the diastereomer was converted to iodide by dissolving it in a small amount of water and by adding an excess of sodium iodide. The red crystals deposited were filtered, washed with ethanol and dried in air.

$(+)_{589}$-C_1-cis(O)-[Co(gly)$_2$en]I·$2H_2O$. Racemic *C_1-cis(O)* iodide (2.6 g, 0.006 mol) and silver acetate (1.2 g, 0.007 mol) were stirred well in 20 m*l* of water. After the silver iodide formed was removed, a saturated solution of 1.0 g (0.003 mol) of potassium antimony(III) L-tartrate 1½-hydrate was added to the filtrate. The red crystals of diastereomer deposited when the solution was evaporating in a vacuum desiccator. If a colorless compound was formed before deposition of the diastereomer, it was removed. The red crystals were filtered, washed with ethanol-water mixture and ethanol, and dried in air. To a concentrated solution of the diastereomer a large excess of sodium iodide was dissolved and the solution was cooled in an ice-bath. The optically active iodide was recrystallized from water by adding ethanol. The red crystals were filtered, washed with ethanol-water mixture and dried in air.

2) Preparation and Separation of Two Isomers of trans(O)-*Bis(L-alaninato)ethylenediaminecobalt(III) Perchlorate.* To a solution of 12.0 g (0.05 mol) of cobalt(II) chloride hexahydrate in 40 m*l* of water, a mixed solution of 9.0 g (0.10 mol) of L-alanine and 3.0 g (0.05 mol) of ethylenediamine in 50 m*l* of water was added. The resulting solution was oxidized by mechanical stirring with 10 g of lead dioxide at 70°C for about 20 min, and cooled to room temperature. After removing a bulky insoluble material, a large amount of acetone was added to the filtrate. The supernatant was decanted out and the residual dark-red oil was dissolved in a small amount of water. Insoluble material was filtered out and the filtrate was poured into a column (30 mm × 900 mm) containing strong anion-exchange resin (Dowex 50 W × 8, 200~400 mesh, hydrogen form). The neutral

1) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).
2) T. Yasui, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 2417 (1966); T. Yasui, J. Fujita, and Y. Shimura, *ibid.*, **42**, 2081 (1969).
3) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).
4) J. Hidaka and Y. Shimura, This Bulletin, **40**, 2312 (1967).
5) M. Shibata, H. Nishikawa, and Y. Nishida, *Inorg. Chem.*, **7**, 9 (1968).
6) Y. Kojima and M. Shibata, *ibid.*, **9**, 238 (1970).
7) N. Matsuoka, J. Hidaka, and Y. Shimura, *ibid.*, **9**, 719 (1970).
8) T. Yasui and B. E. Douglas, *ibid.*, **10**, 97 (1971).
9) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967).

species was swept out with water. By eluting with 0.1 N $NaClO_4$ solution, the adsorbed bands were gradually separated to a violet, two kinds of dark-red, and a broad red bands in this order. From the measurements of the visible absorption spectra of eluants, it was confirmed that the species in the violet band was *mer*-$[Co(O)_3(N)_3]^+$ type by-product, and that complexes in the dark red bands were two kinds of isomers of *trans(O)*-$[Co(L\text{-ala})_2en]^+$, and that one in the red band was a mixture of isomers of C_1- and C_2-*cis(O)*-$[Co(L\text{-ala})_2en]^+$. As for the *trans* isomers it was also shown that the earlier eluted species was $(-)_{589}$-isomer and the later eluted $(+)_{589}$-isomer, by measurements of their ORD. The eluates of the two *trans(O)* isomers were independently concentrated in a vacuum evaporator, and the obtained crystals were filtered, washed with ethanol-water mixture and ethanol, and dried in air.

3) Preparation and Separation of Six Isomers of Bis(L-serinato)ethylenediaminecobalt(III) Complexes. A solution containing 12.0 g (0.05 mol) of cobalt(II) chloride hexahydrate in 30 m*l* of water was mixed with a solution of 3.0 g (0.05 mol) of ethylenediamine and 10.5 g (0.10 mol) of L-serine in 40 m*l* of water. The resulting brown solution was mechanically stirred with 20 g of lead dioxide at 70°C for about 30 min; then the solution became violet-red. The solution was cooled to room temperature and kept in a refrigerator overnight. After the bulky insoluble material precipitated was filtered out, ethanol-ether mixture was added to the filtrate, until an oily substance settled and the supernatant became colorless. The supernatant was decanted out and dark red oil was dissolved in a small amount of water. If an insoluble compound was formed, it was filtered out. The resulting solution was poured into a column (30 mm × 150 mm) containing strong cation exchange resin (Dowex 50W × 8, 200~400 mesh, hydrogen form), and the violet and pink neutral species, which were *mer*- and *fac*-$[Co(L\text{-ser})_3]$ respectively, were swept out with water. By elution with $NaClO_4$ aqueous solution (0.02 N in the first stage, then 0.05, 0.1, 0.2, and 0.5 N in the later stage of elution, successively) at a rate of 3 m*l*/min, the adsorbed bands were gradually separated into several violet and blue violet bands, two dark red bands, and four red bands in this order. Of the last four red bands the first and the fourth bands were of faint color as compared with the other two. It was confirmed from the measurements of absorption spectra and ORD that there were some by-products in the violet and blue violet bands. There were $(+)_{589}$-*trans(O)*- and $(-)_{589}$-*trans(O)*-$[Co(L\text{-ser})_2en]^+$ isomers in the two dark red bands in the elution order, and $(+)_{589}$-C_2-*cis(O)*-, $(-)_{589}$-C_1-*cis(O)*, $(+)_{589}$-C_1-*cis(O)*- and $(-)_{589}$-C_2-*cis(O)*-$[Co(L\text{-ser})_2en]^+$ isomers in the four red bands in the elution order. In top region of the column, brownish red bands of some higher charged complexes stayed. Each eluate of six isomers was concentrated to less than 50 m*l* in a vacuum evaporator at 30°C, and the perchlorate or iodide was crystallized from the concentrated solution as follows.

$(+)_{589}$-trans(O)-$[Co(L\text{-}ser)_2en]ClO_4$. To the concentrated eluate containing this isomer, about two times volume of ethanol was added. Red needles deposited. This was recrystallized from water by adding ethanol. Yield: 0.5 g.

$(-)_{589}$-trans(O)-$[Co(L\text{-}ser)_2en]I$. This isomer did not deposit by adding ethanol to the concentrated eluate. So that an appropriate amount of ether was added to the mixture of the eluate and ethanol. Then an oily substance was separated, and it was dissolved in a methanol-water mixture. To solution ether was added once more. If the substance formed was oily again, this treatment was repeated until crystals began to appear. Thus a crude perchlorate was obtained. By adding an excess of sodium iodide (solid) and an appropriate amount of ethanol to an aqueous solution of the crude perchlorate, the red crystals of iodide were deposited. The pure crystals were filtered, washed with ethanol-water mixture and ethanol, and dried in air. Yield: 0.6 g.

$(+)_{589}$-C_2-cis(O)-$[Co(L\text{-}ser)_2en]I$. A saturated aqueous solution of potassium iodide was added to the concentrated eluate until a white precipitate of potassium perchlorate was no more produced, and then the precipitate was filtered out. To remove of iodine formed in the solution, following procedure was carried out. To a mixture of the filtrate and a little amount of ethanol, an appropriate amount of ether was added until two layers were formed. The resultant was transferred into a separatory funnel and was shaken well. A yellow ether layer, in which iodine dissolved, was removed, and the red aqueous solution containing the complex was more several times shaken with ether, until the ether layer became nearly colorless. Then the red solution was kept in a refrigerator overnight. The crystals deposited were filtered and washed well with methanol until impure colorless crystals were washed away. The crude complex was recrystallized from water by adding ethanol and ether. The red crystals were filtered, washed with ethanol-water mixture and ethanol, and dried in air. Yield: 0.07 g.

$(-)_{589}$-C_1-cis(O)-$[Co(L\text{-}ser)_2en]I$. By adding a large amount of ethanol and ether to the concentrated eluate, the dark red oily substance was separated. The supernatant was decanted out, and the oily substance was stirred well with a large amount of ethanol until it became powdery. After kept in a refrigerator overnight, the red powder was filtered, washed with ethanol-water mixture and ethanol, and dried in air. When a small amount of acetone was added to an aqueous solution of the crude compound, a red crystalline substance was formed. After filtering out this substance, an excess of sodium iodide and ethanol were added to the mother liquor. Then the complex iodide deposited as red crystals. It was filtered, washed with ethanol-water mixture and ethanol, and dried in air. Yield 0.2 g.

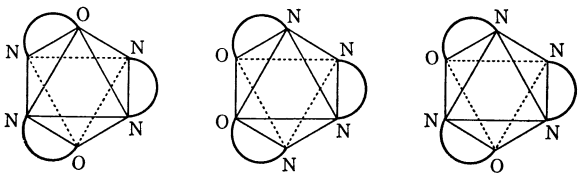
$(+)_{589}$-C_1-cis(O)-$[Co(L\text{-}ser)_2en]ClO_4$. A crude perchlorate was prepared by a similar method to that used for the isolation of $(-)_{589}$-C_1-*cis(O)*-isomer. It was recrystallized from water by adding acetone. The red crystals were filtered, washed with acetone-water mixture and acetone, and dried in air. Yield: 0.2 g.

$(-)_{589}$-C_2-cis(O)-$[Co(L\text{-}ser)_2en]I \cdot 2H_2O \cdot 1/2serH$. This complex was isolated as pinkish red crystals from a concentrated sixth eluate by the same method as that used for the isolation of $(+)_{589}$-C_2-*cis(O)*-isomer. Yield: 0.04 g.

4) Measurements. The electronic absorption spectra were measured with a Beckman DU spectrophotometer. The CD spectra were recorded on a Roussel-Jouan Dichrograph and the ORD curves were checked with a Yanagimoto recording spectropolarimeter, Model-185. All measurements were made in aqueous solutions at room temperature.

Results and Discussion

Three geometrical isomers, *trans(O)*, C_2-*cis(O)*, and C_1-*cis(O)*, are possible for the bis(glycinato)-ethylenediaminecobalt(III) complex (Fig. 1). Of these isomers, *trans(O)* and C_1-*cis(O)* isomers were optically resolved with $(-)_{546}$-K[Co(edta)] and



trans(O) *C_2-cis(O)* *C_1-cis(O)*

Fig. 1. The three geometrical isomers of *Λ*-$[Co(gly)_2en]^+$.

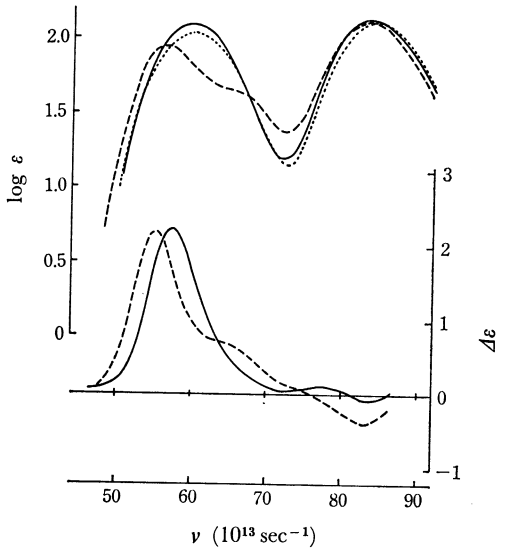


Fig. 2. Absorption and CD curves of $(+)_{589}$-*trans(O)* (----) and $(+)_{589}$-*C_1-cis(O)*-$[Co(gly)_2en]^+$ (——); and absorption curve of *C_2-cis(O)*-$[Co(gly)_2en]^+$ (……).

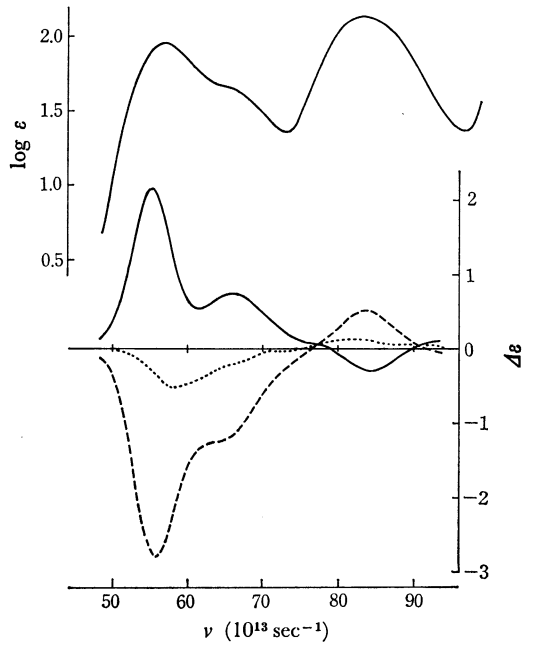


Fig. 3. Absorption and CD curves of $(+)_{589}$-*trans(O)*-[Co(L-ser)$_2$en]$^+$ (——); CD curve of $(-)_{589}$-*trans(O)*-[Co(L-ser)$_2$en]$^+$ (----); and vicinal effect (2L) curve of *trans(O)*-[Co(L-ser)$_2$en]$^+$ (……).

potassium antimony(III) L-tartrate, respectively, as resolving agents. Their absorption and CD curves are shown in Fig. 2 with the absorption curve of the

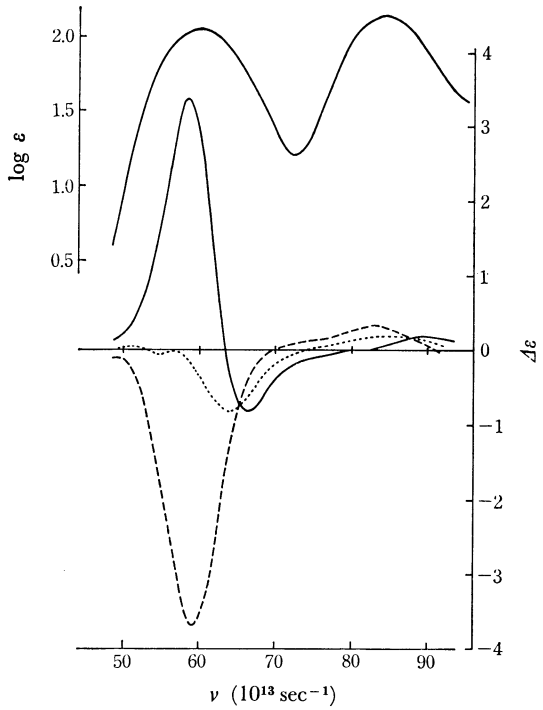


Fig. 4. Absorption and CD curves of $(+)_{589}$-*C_2-cis(O)*-[Co(L-ser)$_2$en]$^+$ (——); CD curve of $(-)_{589}$-*C_2-cis(O)*-[Co(L-ser)$_2$en]$^+$ (----); and vicinal effect (2L) curve of *C_2-cis(O)*-[Co(L-ser)$_2$en]$^+$ (……).

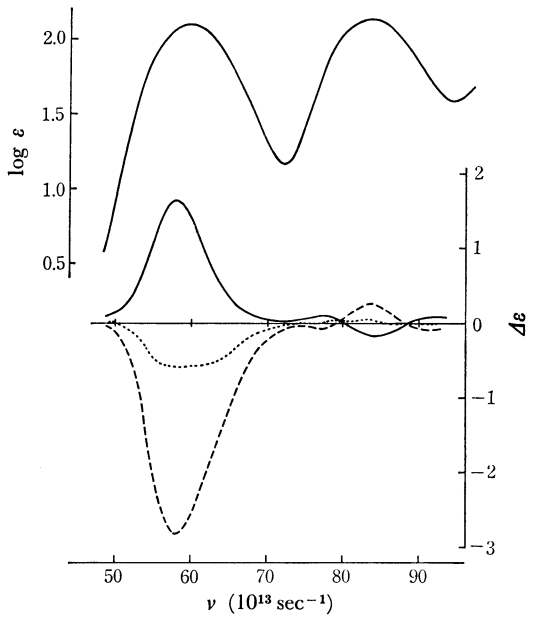


Fig. 5. Absorption and CD curves of $(+)_{589}$-*C_1-cis(O)*-[Co(L-ser)$_2$en]$^+$ (——); CD curve of $(-)_{589}$-*C_1-cis(O)*-[Co(L-ser)$_2$en]$^+$ (----); and vicinal effect (2L) curve of *C_1-cis(O)*-[Co(L-ser)$_2$en]$^+$ (……).

C_2-cis(O) isomer. The six possible isomers of the bis(L-serinato)ethylenediaminecobalt(III) complex, *Δ*- and *Λ-trans(O)*, *Δ*- and *Λ-C_2-cis(O)* and *Δ*- and *Λ-C_1-cis(O)*, were completely separated by ion-exchange column chromatography. Their absorption and CD curves are shown in Figs. 3—5 and the curves of *trans(O)* isomers of bis(L-alaninato)ethylene-

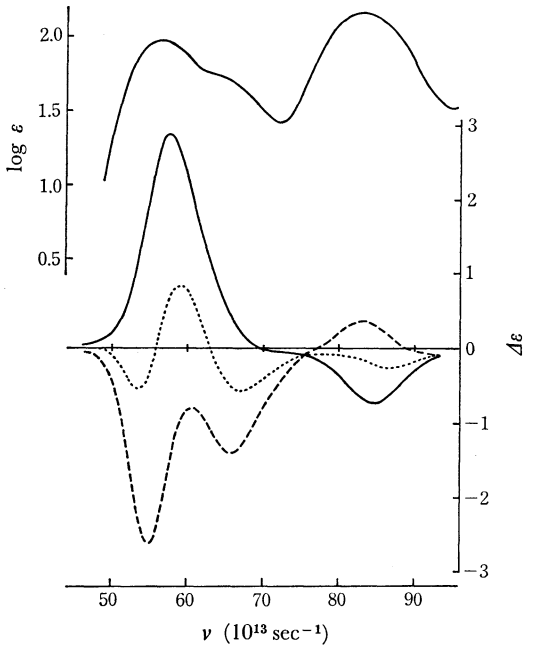


Fig. 6. Absorption and CD curves of $(+)_{589}$-*trans(O)*-[Co(L-ala)$_2$en]$^+$ (——); CD curve of $(-)_{589}$-*trans(O)*-[Co(L-ala)$_2$en]$^+$ (----); and vicinal effect (2L) curve of *trans(O)*-[Co(L-ala)$_2$en]$^+$ (·····).

diaminecobalt(III) complex in Fig. 6. The analytical data of the isomers obtained in this work are summarized in Table 1 and the spectral data in Tables 2 and 3.

Characterization of Isomers. The isomers from the first and second eluates in column chromatography of bis(L-serinato) complex can be assigned confidently to the *trans(O)* structure from the remarkable splitting of their first absorption bands (Fig. 3 and Table 2).[9] The isomers from the remaining four eluates are of *cis(O)* structure because of the symmetrical pattern of their first absorption bands (Figs. 4 and 5 and Table 2) and of the ion-exchange chromatographic behavior as described in "Experimental section." In a previous work,[9] we found that the second absorption band maximum of the C_2-*cis(O)* isomer of bis(glycinato)-ethylenediamine complex locates at higher energy than that of the C_1-*cis(O)* isomer and that the $\log(D_I/D_{II})$ value in the C_2-*cis(O)* isomer is larger in absolute value than that in the C_1-*cis(O)* isomer, where D_I and D_{II} are the optical densities at the absorption maxima of the first and the second absorption bands, respectively. The C_1-*cis(O)* and C_2-*cis(O)* structures of the bis(glycinato) complexes have been confirmed by PMR.[9] The second absorption bands of the present four *cis(O)* isomers are at 84.3, 83.3, 83.6, and 85.1×10^{13} sec^{-1} for the 3rd, 4th, 5th, and 6th eluates, respectively. From these values, it is assumed that the isomers from the 3rd and 6th eluates are C_2-*cis(O)* and the 4th and 5th C_1-*cis(O)*. This assignment brings about that the log (D_I/D_{II}) value is −0.09 for each of the two C_2-*cis(O)* isomers, −0.02 for one C_1-*cis(O)* (from 4th eluate) and −0.04 for another C_1-*cis(O)* isomer (from 5th eluate).

It is well known that the absolute configuration of the cobalt(III) complexes with chelated α-aminoacidato ligands can be assigned from the sign of major CD band in the first absorption band region, *i.e.*, the Δ[12] complex has (−) major CD band and the Λ one (+).[7] The assignment was supported by Dabrowiak and Cooke[11] from their PMR study on several α-aminoacidato complexes including *trans(O)*-[Co(L-ala)$_2$en]$^+$. Therefore each of the $(+)_{589}$-isomers in the present work has Λ-configuration and each of the $(-)_{589}$-isomers Δ-configuration (Figs. 2—6 and Table 3). According-

Table 1. Analytical data of [Co(aminoacidato)$_2$en]X type complexes

Complex	Found			Calcd		
	C	H	N	C	H	N
trans(O)-[Co(gly)$_2$en]ClO$_4$	19.48	4.45	15.07%	19.66	4.40	15.28%
$(+)_{589}$-*trans(O)*-[Co(gly)$_2$en][Co(edta)]	30.76	4.86	13.49	31.18	4.91	13.64
$(+)_{589}$-*trans(O)*-[Co(gly)$_2$en]I·H$_2$O	17.46	4.49	13.55	17.49	4.40	13.60
C_1-*cis(O)*-[Co(gly)$_2$en]ClO$_4$·2H$_2$O	18.02	4.91	13.79	17.90	5.01	13.92
C_1-*cis(O)*-[Co(gly)$_2$en]I·2H$_2$O	17.06	4.78	12.96	16.76	4.69	13.03
$(+)_{589}$-C_1-*cis(O)*-[Co(gly)$_2$en]I·2H$_2$O	16.78	4.74	12.82	16.76	4.69	13.03
C_2-*cis(O)*-[Co(gly)$_2$en]ClO$_4$	19.37	4.32	14.82	19.66	4.40	15.28
C_2-*cis(O)*-[Co(gly)$_2$en]I	18.28	4.05	14.82	18.29	4.09	15.28
$(+)_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	24.12	5.12	14.47	24.35	5.11	14.20
$(-)_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	24.24	5.11	13.98	24.35	5.11	14.20
$(+)_{589}$-*trans(O)*-[Co(L-ser)$_2$en]ClO$_4$	22.42	4.89	13.01	22.52	4.72	13.13
$(-)_{589}$-*trans(O)*-[Co(L-ser)$_2$en]I	20.71	4.45	12.11	21.16	4.44	12.34
$(+)_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]ClO$_4$	23.21	4.90	13.02	22.52	4.72	13.13
$(-)_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]I	21.18	4.46	12.12	21.16	4.44	12.34
$(+)_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I	21.30	4.57	12.15	21.16	4.44	12.34
$(-)_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I·2H$_2$O·1/2 serH	21.23	5.12	11.41	21.03	5.11	11.61

10) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 1257 (1966).
11) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, **92**, 1097 (1970).
12) Absolute configurations are designated by the IUPAC tentative rule: *Inorg. Chem.*, **9**, 1 (1970).

TABLE 2. ABSORPTION DATA OF [Co(aminoacidato)$_2$en]$^+$ TYPE COMPLEXES

Complex	I-Band		II-Band		Ref.
	ν_{max}[a]	(log ε_{max})	ν_{max}[a]	(log ε_{max})	
trans(O)-[Co(gly)$_2$en]I·H$_2$O	56.6	(1.94)	83.3	(2.12)	9
	ca. 66	(*ca.* 1.64)			
C_2-*cis(O)*-[Co(gly)$_2$en]Br·H$_2$O	59.8	(2.04)	84.0	(2.11)	9
C_1-*cis(O)*-[Co(gly)$_2$en]Br·3H$_2$O	59.9	(2.09)	83.1	(2.13)	9
Λ-(+)$_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	56.4	(1.97)	83.1	(2.17)	
	ca. 66	(*ca.* 1.70)			
Δ-(−)$_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	56.6	(1.98)	82.9	(2.13)	
	ca. 66	(*ca.* 1.67)			
Λ-(+)$_{589}$-*trans(O)*-[Co(L-ser)$_2$en]ClO$_4$	56.7	(1.95)	83.1	(2.13)	
	ca. 66	(*ca.* 1.64)			
Δ-(−)$_{589}$-*trans(O)*-[Co(L-ser)$_2$en]I	56.7	(1.95)	83.3	(2.13)	
	ca. 66	(*ca.* 1.70)			
Λ-(+)$_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I	60.0	(2.05)	84.3	(2.14)	
Δ-(−)$_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I·2H$_2$O·1/2 serH	60.1	(2.10)	85.1	(2.19)	
Λ-(+)$_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]ClO$_4$	59.9	(2.11)	83.6	(2.15)	
Δ-(−)$_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]I	60.0	(2.12)	83.3	(2.14)	

a) In the unit of 10^{13} sec^{-1}.

TABLE 3. CIRCULAR DICHROISM DATA OF [Co(aminoacidato)$_2$en]$^+$ TYPE COMPLEXES

Complex	I-Band		II-Band	
	ν_{ext}[a]	($\Delta\varepsilon_{ext}$)	ν_{ext}[a]	($\Delta\varepsilon_{ext}$)
Λ-(+)$_{589}$-*trans(O)*-[Co(gly)$_2$en]I·H$_2$O	55.3	(+2.19)	83.3	(−0.32)
	ca. 66	(+0.64)		
Λ-(+)$_{589}$-C_1-*cis(O)*-[Co(gly)$_2$en]I·2H$_2$O	57.1	(+2.21)	77.4	(+0.11)
			83.8	(−0.08)
Λ-(+)$_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	57.7	(+2.88)	84.7	(−0.74)
Δ-(−)$_{589}$-*trans(O)*-[Co(L-ala)$_2$en]ClO$_4$	54.8	(−2.63)	83.3	(+0.36)
	65.7	(−1.40)		
Λ-(+)$_{589}$-*trans(O)*-[Co(L-ser)$_2$en]ClO$_4$	55.1	(+2.13)	84.3	(−0.30)
	65.7	(+0.75)		
Δ-(−)$_{589}$-*trans(O)*-[Co(L-ser)$_2$en]I	55.7	(−2.81)	84.3	(+0.51)
	63.8	(−1.26)		
Λ-(+)$_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I	58.4	(+3.38)	89.6	(+0.18)
	66.2	(−0.83)		
Δ-(−)$_{589}$-C_2-*cis(O)*-[Co(L-ser)$_2$en]I·2H$_2$O·1/2 serH	59.2	(−3.67)	83.3	(+0.33)
Λ-(+)$_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]ClO$_4$	58.0	(+1.64)	77.9	(+0.09)
			84.3	(−0.18)
			92.3	(+0.08)
Δ-(−)$_{589}$-C_1-*cis(O)*-[Co(L-ser)$_2$en]I	58.0	(−2.84)	77.5	(−0.08)
			84.0	(+0.24)
			91.5	(−0.11)

a) In the unit of 10^{13} sec^{-1}.

ly, it is concluded that the six L-serinato isomers obtained are *Λ-trans(O)*, *Δ-trans(O)*, *Λ*-C_2-*cis(O)*, *Δ*-C_1-*cis(O)*, *Λ*-C_1-*cis(O)*, and *Δ*-C_2-*cis(O)* in the elution order, which agrees also with that found in the case of [Co(ox)(L-ser)$_2$]$^-$.

The iodide of *Δ*-C_2-*cis(O)*-[Co(L-ser)$_2$en]$^+$ isomer was isolated with L-serine (Table 1). This fact suggests that the coordinated L-serinate ion is partly freed from the coordination sphere in the isolation process. This suggestion is supported from the fact that the yield of C_2-*cis(O)* isomer was considerably low in comparison with that of C_1-*cis(O)* isomer in the case of [Co(gly)$_2$en]$^+$ or [Co(L-ser)$_2$en]$^+$ and that the optical resolution of C_2-*cis(O)*-[Co(gly)$_2$en]$^+$ was unsuccessful because of the partial decomposition. Similar low yields were also reported for the C_2-*cis(O)*-isomers of bis(glycinato)(D-propylenediamine)cobalt(III)[6] and bis(L-hydrogenaspartato)(D-propylenediamine)cobalt(III)[13] complexes. Though it seems from these facts that the C_2-*cis(O)* structure is less stable than the

13) Y. Kojima and M. Shibata, *ibid.* **10**, 2382 (1971).

C_1-cis(O) structure, further studies should be carried out for substantiation of this remark.

Circular Dichroism Spectra. In the first absorption band region, the *trans(O)* isomer shows two CD bands of same sign whose dominant peak is in the lower energy side. This agrees well with the pattern, which is predicted from the CD spectra of the *trans(N)* oxalatobis(α-aminoacidato) complexes.[4,7] It appears that, of the *trans(O)* isomers here studied, *Λ-trans(O)*-[Co(L-ala)$_2$en]$^+$ somewhat deviates from the group behavior in CD (Fig. 6). It has been known that the configurational and vicinal contributions to CD are almost separable and additive for the cobalt(III) complexes with optically active α-aminoacidato ligands.[1,7] From this viewpoint, the following relationships were applied for the CD curves of L-serinato and L-alaninato isomers.

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

Each calculated configurational curve agrees with the observed curve of the corresponding glycinato isomer (Fig. 7). For this reason, there is nothing strange about the CD curve of *Λ-trans(O)*-[Co(L-ala)$_2$en]$^+$, whose configurational CD also consists of two bands in the first absorption band region.

The CD patterns of C_1- and *C_2-cis(O)* isomers are not so distinctive in the first absorption band region (Figs. 4, 5 and 7). In the second absorption band region, however, the CD pattern of the *C_1-cis(O)* isomer differs significantly from that of the *C_2-cis(O)* isomer. That is, the *C_1-cis(O)* isomer shows well split three CD bands whose signs are +, −, and +, listing from lower energy for the *Λ* isomer (Figs. 2 and 5), whereas the *C_2-cis(O)* and *trans(O)* isomers show one or two CD bands in appearance. The same relationship was also observed for the CD spectra of the C_1 and C_2 isomers of oxalatobis(α-aminoacidato) complexes.[7] These facts suggest that the CD pattern in the second band region favorably reflects the symmetry of the complex ion.

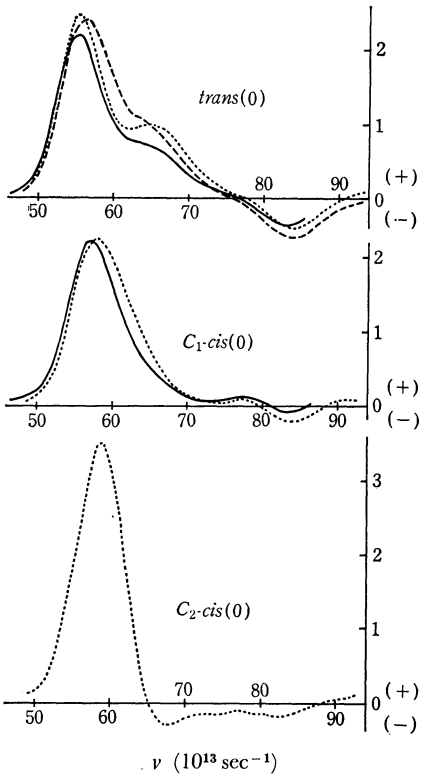


Fig. 7. Configurational effect curve of *Λ-trans(O)*-, *Λ-C_1*- and *Λ-C_2-cis(O)*-[Co(L-ser)$_2$en]$^+$ (·····) and *trans(O)*-[Co(L-ala)$_2$en]$^+$ (----); and observed curves of *Λ-trans(O)*- and *Λ-C_1-cis(O)*-[Co(gly)$_2$en]$^+$ (——).