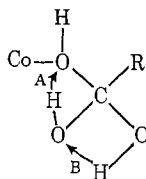


actually involved, such an intermediate is a useful high-energy reference state to which the stabilities of the two activated complexes for reaction can be compared. In the equilibrium distribution for the assumed high-energy intermediate composed of the cobalt complex, H_2O , and H^+ each of the oxygens presumably bears a proton



The entities CH_3^+ (or $C_2H_5^+$) and $Co(NH_3)_5^{3+}$ can both be regarded as Lewis acids, and it is interesting to compare their effects in promoting addition of water to the carbonyl double bond. It is likely that proton redistribution reactions (shown by the arrows A and B) in the intermediate are rapid compared to C–O bond rupture, and thus, except for a minor statistical factor, each time water is added to the carboxyl oxygen, exchange or aquation (hydrolysis) follows. On this basis, the sum of the exchange rate and aquation or hydrolysis rate will be taken as a measure of the rate of hydration of the carbonyl group. The vibrational frequencies of the carboxyl group as observed¹⁹ in the infrared spectrum suggest that the contrast in bond order for the two C–O bonds in a carbon ester is much

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greater than in a cobalt ester, so that the π bond is much more completely localized in the carbonyl oxygen for the carbon ester. It is to be expected that addition to the double bond will take place the more readily the more completely the π bond is localized, and on this basis the sum of the exchange and aquation rates is expected to be greater for the carbon than for the cobalt ester. This relationship holds for the k_0 paths for $(CH_3)_2C_2O_4$ compared to $Co(NH_3)_5C_2O_4H^{2+}$, despite the fact that we are dealing with upper limits on the rates of aquation by C–O bond cleavage for the cobalt esters. (Most of the reaction, it has already been concluded, proceeds by Co–O bond rupture.) It also holds for the k_h paths for the trifluoroacetate and formate cases, but it does not hold for the k_h path when binoxalate is the ligand. The remarkably high value of k_h for carbonyl exchange for the latter system seems quite anomalous, particularly in comparison with the trifluoroacetate and formate systems. The unusual exchange lability of the adjacent carbonyl in the binoxalate case may be a consequence of participation in the activation by the proton on the remote carboxyl. This proton is in addition to that added from solution in making up the activated complex.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE, OSAKA UNIVERSITY, TOYONAKA, OSAKA, JAPAN

Absorption and Circular Dichroism Spectra of Oxalatobis(aminoacidato)cobaltate(III) Complexes

BY NOBUKO MATSUOKA, JINSAI HIDAKA, AND YOICHI SHIMURA

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Oxalatobis(L-serinato)cobaltate(III) complex has been prepared and completely separated into the six configurationally optically active isomers by an ion-exchange chromatographic method and isolated as their potassium salts: they are Δ - and Λ -*trans*(N)-Co(ox)(L-ser)₂⁻, Δ - and Λ -C₂-*cis*(N)-Co(ox)(L-ser)₂⁻, and Δ - and Λ -C₁-*cis*(N)-Co(ox)(L-ser)₂⁻. These isomers have been characterized by their absorption and circular dichroism spectra in the visible wavelength region being compared with the data of the corresponding three isomers of oxalatobis(glycinato)cobaltate(III) complex, of which the C₂-*cis*(N) and C₁-*cis*(N) isomers have been newly resolved. The additivity of configurational and vicinal contributions to the optical activity has been substantiated.

Introduction

Amino acid complexes of cobalt(III) have been recognized as interesting in relation to the electronic absorption and circular dichroism (CD) spectra and to the stereospecificity of the complexes.¹⁻¹¹ In a

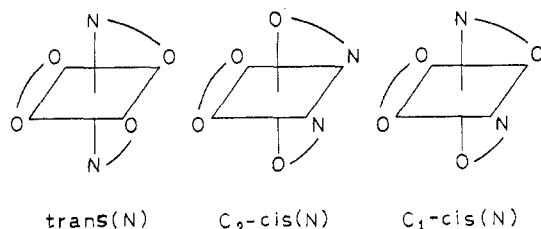
previous paper dealing with the preparation of mixed amino acid complexes,¹² we characterized the three geometrical isomers (*trans*(N), C₂-*cis*(N), and C₁-*cis*-

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TABLE I
 ANALYTICAL RESULTS (%)

Elution order	Complex	$\Delta\epsilon_{546}$	C		H		N	
			Calcd	Found	Calcd	Found	Calcd	Found
i	$\Delta(-)_{546}\text{-trans(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 3\text{H}_2\text{O}$	(+) 1.98	21.44	21.38	4.05	3.90	6.25	6.10
ii	$\Lambda(+)_{546}\text{-trans(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 3.5\text{H}_2\text{O}$	(-) 1.60	21.01	21.24	4.19	3.90	6.13	6.08
iii	$\Delta(-)_{546}\text{-C}_2\text{-cis(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 2.5\text{H}_2\text{O}$	(+) 3.12	21.87	21.96	3.90	3.66	6.38	6.13
vi	$\Lambda(+)_{546}\text{-C}_2\text{-cis(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 2.5\text{H}_2\text{O}$	(-) 2.94	21.87	21.58	3.90	3.60	6.38	6.15
v	$\Delta(-)_{546}\text{-C}_1\text{-cis(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 1.5\text{H}_2\text{O}$	(+) 2.28	22.81	22.97	3.59	3.39	6.65	6.52
iv	$\Lambda(+)_{546}\text{-C}_1\text{-cis(N)-K[Co(ox)(L-ser)}_2\text{]}\cdot 2\text{H}_2\text{O}$	(-) 2.68	22.33	22.31	3.75	3.72	6.51	6.22

Figure 1.—Geometrical isomers of Co(ox)(gly)_2^- .

(N)¹³ of oxalatobis(glycinato)cobaltate(III) complex (Figure 1) on the basis of their electronic absorption and nmr spectra and of the reaction processes of derivation. Of these isomers only the *trans*(N) form has been optically resolved.⁶

The present paper is concerned with the complete separation of six isomers of oxalatobis(L-serinato)cobaltate(III) and with their electronic absorption and CD spectra, with which are compared those of the optically active *trans*(N)-, *C*₂-*cis*(N)-, and *C*₁-*cis*(N)-oxalatobis(glycinato)cobaltate(III) ions.

Experimental Section

Potassium Oxalatobis(L-serinato)cobaltate(III).—The preparation of the complex and the separation of the isomers were carried out by a method similar to that used for the corresponding glycinato complex.¹²

A solution containing 4.3 g of cobalt(II) chloride hexahydrate in 10 ml of water was added to a mixed solution of 5 g of potassium oxalate and 5 g of L-serine in 20 ml of water. Three grams of lead dioxide was gradually added to the mixed solution on a water bath. The resulting mixture was mechanically stirred at 60° for about 30 min, whereupon the solution became violet. After having been allowed to stand at room temperature, the reaction mixture was filtered a few times repeatedly to remove an excess of lead dioxide. The filtrate was kept in a refrigerator overnight to complete the separation of the precipitate. After the precipitate had been filtered off, a large amount of methanol was added to the filtrate. The crude product deposited was filtered and washed with a small amount of water-methanol (1:1) mixture and with methanol and dried in air. The red-violet product obtained was the mixture of *trans*(N), *C*₂-*cis*(N), and *C*₁-*cis*(N) isomers. The yield was approximately 5.5 g.

Separation of Isomers.—Five grams of the red-violet product was dissolved in 30 ml of water and the solution was poured into a column (30 mm × 900 mm) containing strong anion-exchange resin (Dowex 1 × 10, 100–200 mesh, chloride form). A small quantity of nonelectrolyte complexes, *mer*- and *fac*-Co(L-ser)₃, was eluted when the column was flushed with water. The adsorbed band was eluted with a 0.07 *N* aqueous solution of potassium chloride at a rate of 0.7 ml/min. By elution with the potassium chloride solution, six colored bands—(i) a pale violet one, (ii) a violet one, (iii) a pale violet-red one, (iv) a red one, (v) another red one, and (vi) another pale violet-red one—were eluted in this order. The group eluted at first consisted of

bands i and ii which were separated from the others. After a long gap from the two bands, bands iii and iv were eluted successively but distinguishably from each other. Band v was broad and well separated from bands iv and vi. The last band (vi) was sharp but thin in its color. The two early eluted bands, the pale violet and violet ones, were determined by the measurements of their visible absorption spectra to be *trans*(N)-Co(ox)(L-ser)₂⁻ and the remaining four reddish bands which appeared in progression were determined to be *cis*(N) isomers. The six eluates were separately evaporated to dryness at 30° with a vacuum evaporator. Each of the crude products obtained was dissolved in as little water as possible and an appropriate amount of silver acetate was added to the solution. After the resulting mixture had been vigorously shaken for 10 min, the silver chloride precipitated was filtered off and washed with a small amount of ice water. The filtrate and washing were combined and a large volume of methanol (about five times that of the aqueous solution) was added to the solution to precipitate the complex. Each of the complexes was recrystallized from water by adding methanol. The analytical data are shown in Table I.

After the six isomers of Co(ox)(L-ser)₂⁻ had been eluted with 0.07 *N* potassium chloride solution, a narrow dark blue band with a trace of green layer remained in the column. The dark blue band was eluted with 0.27 *N* potassium chloride solution and separated into two adsorbed bands. By comparing their absorption and CD spectra with those of optical isomers of Co(ox)₂(L-ala)₂²⁻,⁷ the earlier eluted band was confirmed to be $\Delta\text{-Co(ox)}_2\text{(L-ser)}_2^-$ and the later eluted one to be $\Lambda\text{-Co(ox)}_2\text{(L-ser)}_2^-$. The remaining green layer was considered to be the Co(ox)₃³⁻ complex.

Resolution of Sodium Oxalatobis(glycinato)cobaltate(III).—The three geometrical isomers, *trans*(N)-, *C*₂-*cis*(N)-, and *C*₁-*cis*(N)-Na[Co(ox)(gly)₂], were prepared and separated by the same procedures as described in the previous paper.¹²

(+)₅₄₆-*trans*(N)-Na[Co(ox)(gly)₂].—For the resolution of this complex, (-)₅₄₆-[Co(ox)(en)₂]I was used as the resolving agent.⁸

(+)₅₄₆-*C*₂-*cis*(N)-Na[Co(ox)(gly)₂].—In a solution of 0.70 g of strychnium sulfate pentahydrate in 30 ml of water *C*₂-*cis*(N)-Na[Co(ox)(gly)₂] (0.15 g) was dissolved. When the resulting solution had been cooled in an ice bath for 1 hr, the diastereomer began to crystallize. The diastereomer was filtered and washed with a water-ethanol mixture and with ethanol and then dried in air. The diastereomer was dissolved in a solution containing a little excess of sodium iodide with stirring well. After the least soluble strychnium iodide which precipitated had been filtered off, an appropriate amount of ethanol (99%) was gradually added to the filtrate. The violet (+)₅₄₆-*C*₂-*cis*(N)-Na[Co(ox)(gly)₂] crystallized out soon after. The product was recrystallized from water by adding ethanol: $\Delta\epsilon_{546} = -1.62$.

(-)₅₄₆-*C*₁-*cis*(N)-Na[Co(ox)(gly)₂].—*C*₁-*cis*(N)-Na[Co(ox)(gly)₂] (0.15 g, 0.0016 mol) was dissolved in 20 ml of aqueous solution of strychnium sulfate pentahydrate (0.35 g, 0.0008 mol). The resulting solution was cooled in an ice bath. The diastereomer began to separate almost at once. The first fraction was removed after a few hours. The diastereomer was washed with a water-ethanol mixture and with ethanol and then dried in air.¹⁴ The diastereomer was dissolved in a solution containing a little excess of sodium iodide. After the strychnium iodide which

(13) The prefixes *C*₁ and *C*₂ represent the symmetry of each the complex.

(14) From the results of CD measurements, it was found that the complex obtained from the first fraction is the most optically active.

precipitated had been removed, the filtrate was employed for the CD measurement; $\Delta\epsilon_{546} = +1.02$. The concentration of complex in this solution was estimated from the intensity of visible absorption band referring to the quantitative curve of the corresponding racemic complex.

Measurements.—The electronic absorption spectra were measured by a Beckman DU spectrophotometer. CD spectra were recorded with a Roussel-Jouan Dichrographe and RD curves with a Yanagimoto recording spectropolarimeter, Model-185. All measurements were made in aqueous solutions at room temperature.

Results and Discussion

Spectral and Structural Assignments.—Though a large number of isomers are expected for the oxalatobis-(serinato)cobaltate(III) complex, if we confine the absolute configuration of the ligand serine as L type (Figure 2), only six isomers are possible, namely, Δ -

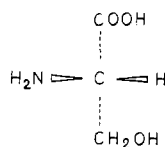


Figure 2.—The absolute configuration of L-serine.

and Δ -*trans*(N), Δ - and Λ -*C*₂-*cis*(N), and Δ - and Λ -*C*₁-*cis*(N) isomers, any couple of which is not the antipodal one, and in fact these six isomers were separated easily by anion-exchange chromatography.

The first (lowest energy) absorption band of a *trans*-(N)-Co(O)₄(N)₂ type complex is known to show much greater splitting than that of the corresponding *cis* isomer.^{6,12,15,18} Of the six L-serinato isomers obtained the two *trans* ones are well characterized by the splitting of their first absorption bands (Table II, Figures 3

TABLE II
ABSORPTION DATA OF *trans*(N)-Co(O)₄(N)₂ TYPE OF COMPLEXES

Complex ion	Band I		Band II		Ref
	$\bar{\nu}_{\text{max}}$	ϵ_{max}	$\bar{\nu}_{\text{max}}$	ϵ_{max}	
<i>trans</i> (N)-Co(ox)(gly) ₂ ⁻	Ca. 16,700	50.1	25,830	170	
	18,870	100			
<i>trans</i> (N)-Co(ox)(L-ala) ₂ ⁻	Ca. 16,700	50.1	25,970	174	6
	18,930	102			
Δ - <i>trans</i> (N)-Co(ox)(L-ser) ₂ ⁻	Ca. 16,700	45.7	25,970	159	
	19,030	93.3			
Λ - <i>trans</i> (N)-Co(ox)(L-ser) ₂ ⁻	Ca. 16,700	56.2	25,970	162	
	19,030	91.2			
<i>trans</i> (N)-Co(ox)(β -ala) ₂ ⁻	Ca. 16,000	57.5	26,300	132	6
	18,830	100			
<i>trans</i> (N)-Co(ada) ₂ ⁻	Ca. 16,700	11.5	27,770	56.2	15
	20,400	52.5			

and 4). From their CD spectra in the first absorption band region, it is possible to assign an absolute configuration, Δ (C₂) for the earlier eluted (-)₅₄₆-*trans* isomer (i) and Λ (C₂) for the later eluted (+)₅₄₆-*trans* isomer (ii), as in the case of oxalatobis(glycinato)cobaltate(III) complex.¹² The assignment of absolute configuration based on the major CD band in the first absorption band region can be applied also for the other four isomers, which were shown by their absorption measurements to be of the *cis* form (Table

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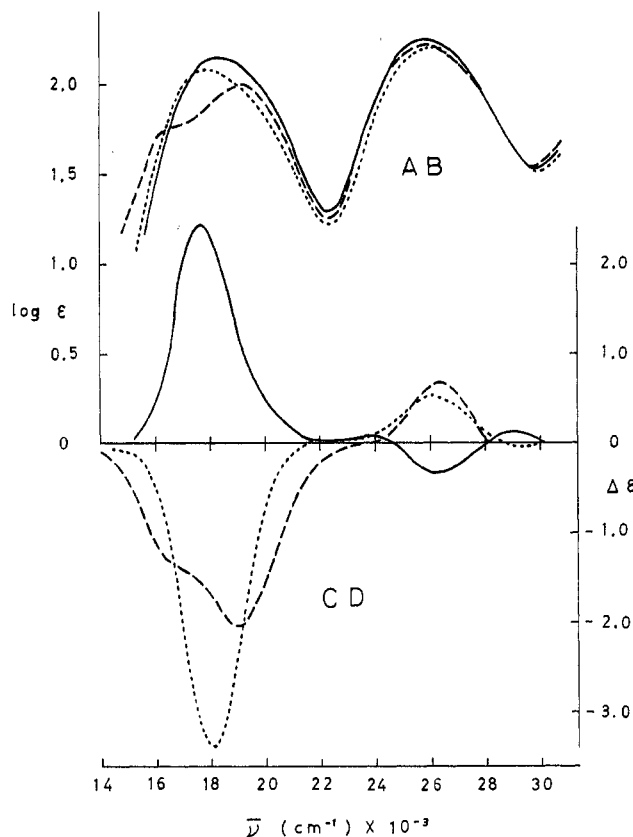


Figure 3.—Absorption (AB) and CD curves of three isomers of Co(ox)(gly)₂⁻: — — —, *trans*(N) isomer; · · · · ·, *C*₂-*cis*(N) isomer; — — —, *C*₁-*cis*(N) isomer.

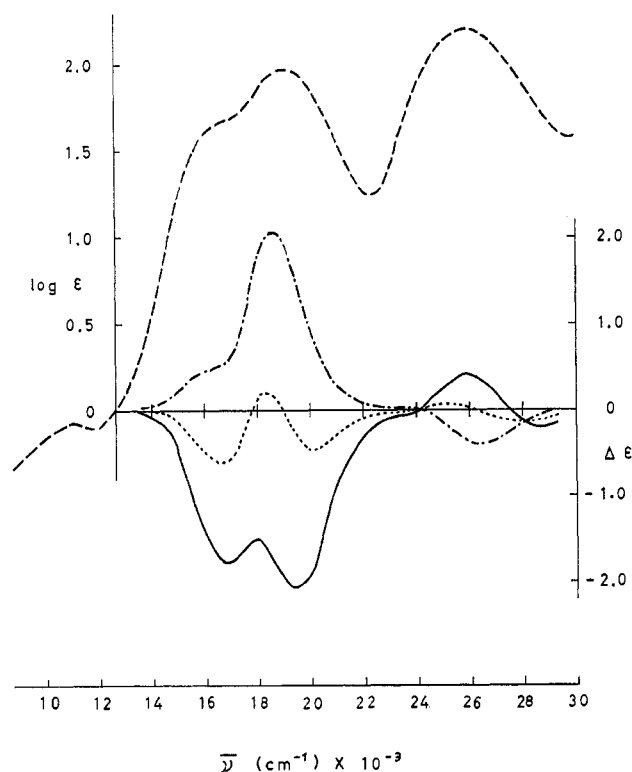


Figure 4.—Absorption (— — —) and CD (— · — ·) curves of Δ -(-)₅₄₆-*trans*(N)-Co(ox)(L-ser)₂⁻. CD (— — —) curve of Λ -(+)₅₄₆-*trans*(N)-Co(ox)(L-ser)₂⁻. Vicinal-effect (2L) curve (· · · · ·) of *trans*(N)-Co(ox)(L-ser)₂⁻.

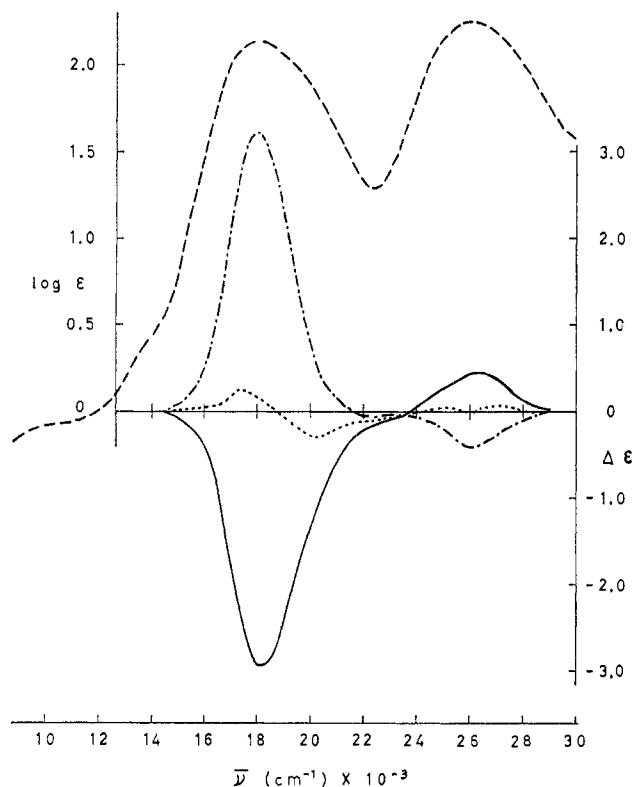


Figure 5.—Absorption (— — —) and CD (— · — ·) curves of Δ -(-)₅₄₆- C_2 -*cis*(N)-Co(ox)(L-ser)₂⁻. CD (—) curve of Δ -(+)₅₄₆- C_2 -*cis*(N)-Co(ox)(L-ser)₂⁻. Vicinal-effect (2L) curve (· · · ·) of C_2 -*cis*(N)-Co(ox)(L-ser)₂⁻.

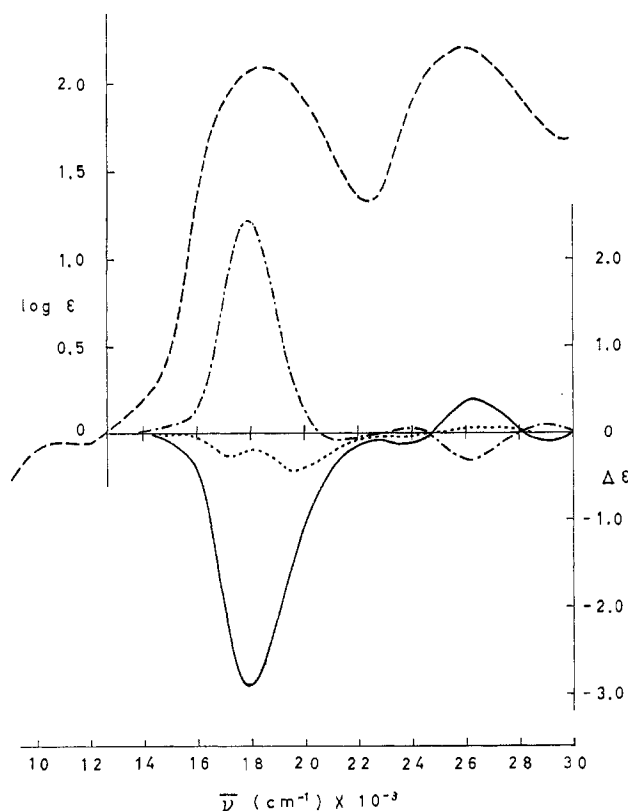


Figure 6.—Absorption (— — —) and CD (— · — ·) curves of Δ -(-)₅₄₆- C_1 -*cis*(N)-Co(ox)(L-ser)₂⁻. CD (—) curve of Δ -(+)₅₄₆- C_1 -*cis*(N)-Co(ox)(L-ser)₂⁻. Vicinal-effect (2L) curve (· · · ·) of C_1 -*cis*(N)-Co(ox)(L-ser)₂⁻.

TABLE III
ABSORPTION DATA OF *cis*(N)-Co(O)₄(N)₂ TYPE OF COMPLEXES

Complex ion	Band I		Band II		Ref
	$\bar{\nu}_{\max}$	ϵ_{\max}	$\bar{\nu}_{\max}$	ϵ_{\max}	
C_2 - <i>cis</i> (N)-Co(ox)(gly) ₂ ⁻	17,830	120	25,900	159	
C_1 - <i>cis</i> (N)-Co(ox)(gly) ₂ ⁻	18,330	141	25,770	174	
Δ - C_2 - <i>cis</i> (N)-Co(ox)(L-ser) ₂ ⁻ (iii)	18,000	138	26,070	178	
Δ - C_2 - <i>cis</i> (N)-Co(ox)(L-ser) ₂ ⁻ (vi)	18,000	118	25,970	148	
Δ - C_1 - <i>cis</i> (N)-Co(ox)(L-ser) ₂ ⁻ (v)	18,470	123	25,900	159	
Δ - C_1 - <i>cis</i> (N)-Co(ox)(L-ser) ₂ ⁻ (iv)	18,500	146	25,870	195	
<i>cis</i> (N)-Co(ada) ₂ ⁻	17,800	151	26,330	135	15
Co(edta) ⁻	18,630	324	26,030	229	15

III and Figures 5 and 6). Thus the absolute configuration of the *cis* forms iii and v is Δ (C_2) and that of the *cis* forms iv and vi is Λ (C_2).

Now, these *cis* isomers are classified into two groups on the basis of their absorption maxima, though their absorption curves are quite similar to each other on the whole. Namely, the two of them show their first absorption bands at 18,000 cm^{-1} and the other two isomers at 18,470 or 18,500 cm^{-1} . In the case of the isomers of oxalatobis(glycinato)complex, we pointed out that the first absorption maximum of the C_2 isomer locates at lower energy than that of the C_1 isomer¹² (Table III and Figure 3). Consequently it is possible to assign the geometrical and configurational structures for all of the four *cis* isomers of the L-serinato complex. The conclusion is clearly supported by their CD curves. In the second absorption band region (-)₅₄₆- C_1 - and (+)₅₄₆- C_2 -*cis*(N)-Co(ox)(gly)₂⁻, of which the structures have been determined by the nmr spectra,¹² show three and two CD bands, respectively (Table IV and Figure 3). The same relationship exists also in the CD curves of L-serinato isomers (Figures 5 and 6).

Douglas and his coworkers^{1,2} concluded that the vicinal and the configurational effects of the complex which has two chiral centers, one around the ligand (vicinal chirality) and the other around the central metal ion (configurational chirality), are separable and reasonably additive on the CD curves. This additivity rule is also true for the complexes here studied (Figures 4-6). The vicinal CD due to the two coordinated L-serinate ligands, $\Delta\epsilon(2L)$, and the configurational CD, $\Delta\epsilon(\Delta)$ or $\Delta\epsilon(\Lambda)$, have been calculated by applying the following relations to the observed CD curves, $\Delta\epsilon(\Delta_{2L})$ and $\Delta\epsilon(\Lambda_{2L})$, of Δ - and Λ -Co(ox)(L-ser)₂⁻

$$\Delta\epsilon(2L) = \frac{1}{2} \{ \Delta\epsilon(\Delta_{2L}) + \Delta\epsilon(\Lambda_{2L}) \}$$

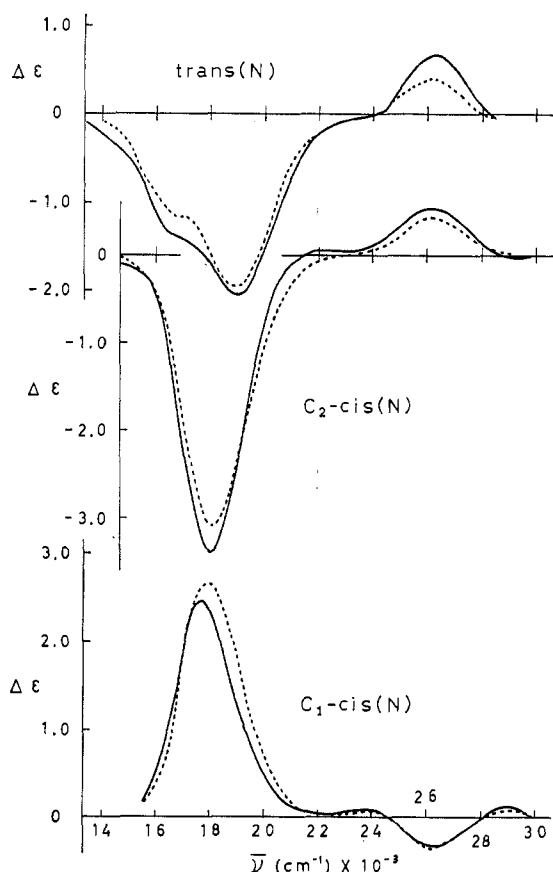
$$\Delta\epsilon(\Delta) = \frac{1}{2} \{ (\Delta\epsilon(\Delta_{2L}) - \Delta\epsilon(\Lambda_{2L})) \}$$

$$\Delta\epsilon(\Delta) + \Delta\epsilon(\Lambda) = 0$$

The calculated configurational curves from the data of the L-serinato complexes well coincide with the observed curves for the corresponding glycinato complexes (Figure 7). This coincidence means that the configurational chirality has almost identical conditions in the L-serinato and the glycinato complexes. Therefore, it can be considered that the chelate ring of the L-serinato complex takes nearly planar conformation

TABLE IV
 CD DATA OF OXALATOBIS(GLYCINATO)COBALTATE(III) AND OXALATOBIS(L-SERINATO)COBALTATE(III) COMPLEXES

Complex ion	Band I		Band II	
	$\bar{\nu}_{\text{ext}}$	$\Delta\epsilon_{\text{ext}}$	$\bar{\nu}_{\text{ext}}$	$\Delta\epsilon_{\text{ext}}$
$\Lambda-(+)_{{}_{546}}\text{-trans(N)-Co(ox)(gly)}_2^-$	Ca. 16,700	-1.4	26,170	+0.69
	18,770	-2.07		
$\Delta-(-)_{{}_{546}}\text{-trans(N)-Co(ox)(L-ser)}_2^-$	Ca. 16,700	+0.45	26,500	-0.41
	18,670	+2.08		
$\Lambda-(+)_{{}_{546}}\text{-trans(N)-Co(ox)(L-ser)}_2^-$	16,670	-1.79	25,970	+0.39
	19,370	-2.06	28,770	-0.19
$\Lambda-(+)_{{}_{546}}\text{-C}_2\text{-cis(N)-Co(ox)(gly)}_2^-$	18,030	-3.39	25,970	+0.52
	Ca. 22,500	+0.04		
$\Delta-(-)_{{}_{546}}\text{-C}_2\text{-cis(N)-Co(ox)(L-ser)}_2^-$	18,000	+3.24	26,100	-0.41
	22,430	-0.05		
$\Lambda-(+)_{{}_{546}}\text{-C}_2\text{-cis(N)-Co(ox)(L-ser)}_2^-$	18,170	-2.76	26,230	+0.42
	$\Delta-(-)_{{}_{546}}\text{-C}_1\text{-cis(N)-Co(ox)(gly)}_2^-$	17,700	+2.48	23,930
Ca. 22,300		+0.04	26,300	-0.32
$\Delta-(-)_{{}_{546}}\text{-C}_1\text{-cis(N)-Co(ox)(L-ser)}_2^-$	17,970	+2.46	29,000	+0.10
	21,570	-0.06	24,170	+0.05
$\Lambda-(+)_{{}_{546}}\text{-C}_1\text{-cis(N)-Co(ox)(L-ser)}_2^-$	18,000	-2.91	26,230	-0.33
			29,070	+0.09
			24,100	-0.09
			26,330	+0.38
			29,170	-0.08


 Figure 7.—Configurational-effect curves of three geometrical isomers of Co(ox)(L-ser)_2^- (-----) and observed curves of the corresponding geometrical isomers of Co(ox)(gly)_2^- (—).

like that of the glycinate complex, regardless of the additional group $-\text{CH}_2\text{OH}$.

Judging from the effective symmetry of the *cis* isomers, it may be reasonable to expect that the first absorption band splits into at least two components,

but in appearance no splitting is observed. In the corresponding region, however, the vicinal CD curves of the C_1 - and C_2 -*cis*-L-serinate isomers show two components: two (-) components in the C_1 -*cis* isomer and (+) and (-) components in the C_2 -*cis* isomer. The vicinal-effect curve of the *trans* isomer shows three components in the first absorption band region. It has been pointed out that the CD curve due to the vicinal effect shows the split components of the electronic transition more clearly than that due to the configurational effect.^{1,17}

Each of the three vicinal curves is quite characteristic for each of the geometrical isomers (Figures 4-6). The configurational CD curves of C_2 -*cis*(N)- and C_1 -*cis*(N)- Co(ox)(L-ser)_2^- are rather similar in their shapes in the first absorption band region, but the intensities are different (Figure 7).

Separation of the Isomers.—It has been generally recognized that the *trans* isomer is eluted before the *cis* one because of its smaller dipole moment.¹⁸ This was realized also in the present work. In the glycinate complex, the C_1 -*cis* isomer was eluted earlier than the C_2 -*cis* one; similar behavior was reported in the case of bis(glycinate)ethylenediaminecobalt(III) complex.^{12,19} The elution order of four *cis* isomers of the L-serinate complex, however, somewhat deviates from this general pattern; namely, the order is $\Delta\text{-C}_2$, $\Lambda\text{-C}_1$, $\Delta\text{-C}_1$, and $\Lambda\text{-C}_2$. Molecular models reveal that a hydrogen-bond interaction between $-\text{OH}$ of one L-serinate and $-\text{NH}_2$ of another L-serinate ligand in a complex ion decreases in the order $\Delta\text{-C}_2 > \Lambda\text{-C}_1 > \Delta\text{-C}_1 = \Lambda\text{-C}_2$. It may be significant that this order runs parallel to the elution order.

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