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Preparation and Circular Dichroism of Six Isomers of Bis(L-alaninate-*N*-monoacetato)cobaltate(III) Complexes

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Six isomers, two *trans(N)* and four *cis(N)*, of bis(L-alaninate-*N*-monoacetato)cobaltate(III) ions have been synthesized as their sodium or potassium salts. The isomers have been separated by ion-exchange column chromatography and their geometrical and chiral configurations determined on the basis of their absorption and circular dichroism spectra in visible and near ultraviolet regions and of proton magnetic resonance spectra. The corresponding L-prolinate-*N*-monoacetate complex has also been studied. The asymmetry of the coordinated imino nitrogen has been discussed from the analysis of the CD curves.

L-Alanine-*N*-monoacetic acid is a derivative of iminodiacetic acid and a typical O,N,O-tridentate ligand of linear type which contains one asymmetric carbon atom. The nitrogen atom of this ligand, however, becomes asymmetric by coordination to a metal ion; the circular dichroism (CD) spectrum of the complex will then be supplied from two vicinal contributions produced by the asymmetric carbon and the asymmetric nitrogen. Some isomers of cobalt(III) complexes with iminodiacetate or *N*-methyliminodiacetate, which have neither asymmetric carbon nor nitrogen atom, have been prepared and characterized by their electronic absorption[1,2] and CD spectra[3] in visible and ultraviolet regions and by PMR spectra.[2,4] Of these complexes, *cis*(*N*) isomer of bis(iminodiacetato) complex has a chiral configuration, and the absolute configurations of the optical isomers have been determined from comparison of their CD bands with those of a stereospecifically formed complex ion, $(+)_{546}$-[Co{$(-)_{589}$-pdta}]$^-$.[5]

In the present paper, the preparation and separation of isomers of bis(L-alaninate-*N*-monoacetato)cobaltate(III) complex will be reported with those of the corresponding L-prolinate-*N*-monoacetate complex; the geometrical and chiral configurations of these complexes will be determined by their electronic absorption, CD, and PMR spectra. The additivity of three kinds of CD contributions, one from the configurational chirality and the other two from the vicinal chiralities of the asymmetric carbon and nitrogen atoms, will be discussed.

Experimental

(1) Preparation of Ligands. A solution of 45 g of L-alanine in 125 m*l* of 4 N lithium hydroxide was added to a solution of 47.3 g of monochloroacetic acid in 125 m*l* of 4 N lithium hydroxide. To this mixture 125 m*l* of 4 N lithium hydroxide was added drop by drop with vigorous stirring at 70—80°C. The pH of the mixture was maintained in the range 8—9 during the reaction. After the addition, the mixture was heated at 90°C for about 10 min. The reaction mixture was cooled to room temperature and 120 m*l* of concentrated hydrochloric acid was added to it. The solution was concentrated in a vacuum evaporator until it became syrupy. When it was kept in a refrigerator for 24 hr, white crystals were separated out, which were collected by filtration and then washed well with ethanol. These white crystals, the desired acid hydrochloride, were contaminated with a small amount of lithium chloride. They were recrystallized from warm water. The pure crystals were washed with ethanol and ether, and then dried in a vacuum desiccator. The yield was approximately 23 g. $[\alpha]^{25}_{D}=+3.0°$ (*c* 5.4, water).

Found: C, 31.84; H, 5.53; N, 7.41%. Calcd for L-alamaH$_2$·HCl·1/4H$_2$O=$C_5H_{10}NO_4Cl\cdot 1/4H_2O$: C, 31.93; H, 5.63; N, 7.45%.

L-Proline-*N*-monoacetic acid was also prepared by a similar procedure using L-proline instead of L-alanine. $[\alpha]^{17}_{D}=-54°$ (*c* 1.0, water).

Found: C, 48.66; H, 6.46; N, 7.98%. Calcd for L-promaH$_2$=$C_7H_{11}NO_4$: C, 48.55; H, 6.40; N, 8.09%.

*(2) Preparation of Isomeric Mixture of Lithium Bis(*L*-alaninate-*N*-monoacetato)cobaltate(III): Li[Co(*L*-alama)$_2$]·nH$_2$O.* A solution of 8.4 g of cobalt(II) chloride hexahydrate in 10 m*l* of water was added to a solution containing 13.6 g of L-alamaH$_2$·HCl·1/4H$_2$O whose pH had been previously adjusted to 7.3 with 4 N lithium hydroxide. To this solution 10 g of lead dioxide was added and the resulting mixture was mechanically stirred at about 30°C for 2 hr. The color of the solution turned from dark red to bluish violet. Thereafter the pH was adjusted to 6.5 with 4 N lithium hydroxide and the mixture was kept for 90 min at room temperature. An excess of lead dioxide was filtered off. A large amount of methanol-ether (1 : 2) mixture was added to the filtrate. The bluish violet deposit was filtered and washed with methanol-ether (1 : 2) mixture and ether, and then dried in a vacuum desiccator. The yield was approximately 11 g.

*(3) Separation of the Isomers of [Co(*L*-alama)$_2$]$^-$.* About 8 g of the lithium salt obtained in (2) was dissolved in an appropriate amount of water and passed through a column (25 mm × 1500 mm) containing strong anion exchange resin, Dowex 1×8 (200—400 mesh, chloride form). After the column had been swept with water, the adsorbed band was eluted with 0.07 N aqueous solution of potassium chloride or sodium perchlorate at a rate of 2.5 m*l* per min. Six colored bands, a brownish red one (i), a reddish purple one (ii), and four violet ones (iii), (iv), (v) and (vi), were eluted in this order. Isomers i and ii were confirmed to be ***trans(N)*** ones and iii, iv, v and vi the ***cis(N)*** ones, by measurement of their absorption spectra. Each eluate was concentrated to dryness in a vacuum evaporator. The resulting solid isomers were contaminated with a small amount of potassium chlo-

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[1] J. Hidaka, Y. Shimura, and R. Tsuchida, This Bulletin, **35**, 567 (1962).

[2] D. W. Cooke, *Inorg. Chem.*, **5**, 1141 (1966).

[3] C. W. Van Saun and B. E. Douglas, *ibid.*, **8**, 1145 (1969).

[4] J. I. Legg and D. W. Cooke, *ibid.*, **5**, 594 (1966).

[5] The following abbreviations are used for the ligands; "ida" for an iminodiacetate ion, "L-alama" L-alaninate-*N*-monoacetate ion, "L-proma" L-prolinate-*N*-monoacetate ion, "edta" ethylenediaminetetraacetate ion, and "pdta" propylenediaminetetraacetate ion.

TABLE 1. ANALYTICAL RESULTS (in %)

Elution order	Complex salt	$\Delta\varepsilon_{589}$	C Found	C Calcd	H Found	H Calcd	N Found	N Calcd
i	*trans*(*N*)-RR-Na[Co(L-alama)$_2$]·2.5H$_2$O	(−)0.26	28.68	28.79	4.60	4.59	6.62	6.72
ii	*trans*(*N*)-RS-Na[Co(L-alama)$_2$]·2.5H$_2$O	(+)0.05	28.58	28.79	4.62	4.59	6.70	6.72
iii	*Δ-cis*(*N*)-RR-K[Co(L-alama)$_2$]·4H$_2$O	(−)4.62	26.42	26.09	4.93	4.82	6.14	6.09
iv	*Δ-cis*(*N*)-RS-K[Co(L-alama)$_2$]·3H$_2$O	(−)2.84	27.66	27.16	4.54	4.58	6.01	6.33
v	*Λ-cis*(*N*)-RR-K[Co(L-alama)$_2$]·4H$_2$O	(+)0.66	26.39	26.09	4.89	4.82	5.95	6.09
vi	*Λ-cis*(*N*)-RS-K[Co(L-alama)$_2$]·3H$_2$O	(+)1.75	27.09	27.16	4.67	4.58	6.32	6.33
—	*trans*(*N*)-RR-K[Co(L-proma)$_2$]·3H$_2$O	(+)0.06	33.92	34.01	4.88	4.89	5.66	5.67

ride, and were treated as follows. An aqueous solution of silver perchlorate was added drop by drop to the solution containing the crude complex and the precipitated silver chloride was filtered off. The complex desired was obtained by adding ethanol to the filtrate. The complex crystals were washed with water-ethanol (1 : 2) mixture and ethanol, and then dried in a vacuun desiccator. Isomers i and ii were isolated as sodium salts, while iii∼vi as potassium salts. Analytical results are given in Table 1.

*(4) Preparation and Separation of Potassium Bis(*L*-prolinate-*N*-monoacetato)cobaltate(III):* *K[Co(*L*-proma)$_2$]·nH$_2$O.* This was prepared and separated by a similar procedure to that for L-alama complex, using L-promaH$_2$ instead of L-alamaH$_2$·HCl·1/4H$_2$O. Two colored bands, a violet one and a brownish red one, were eluted in this order with 0.07 N aqueous solution of potassium chloride. The violet isomer was unstable in solution; the CD of the violet eluate decayed out with time. The violet isomer was not obtained in solid state, but the absorption and CD spectra of the solution suggested that this is the *cis(N)* isomer. The brownish red isomer was isolated as potassium salt trihydrate (Table 1), and was confirmed to be the *trans(N)* isomer by measurement of the absorption spectrum.

(5) Measurements. The electronic absorption spectra of the complexes were measured with a Beckman DU spectrophotometer. The CD spectra were recorded with a Roussel-Jouan dichrograph and a JASCO Model ORD/UV-5 spectrophotometer. All measurements were made in aqueous solutions at room temperature. The PMR spectra of the complexes in deuterium oxide were measured with a Japan Electron Optics 3H-60 spectrometer.

Results and Discussion

It has veen well established that the *trans*(*N*) and *cis*(*N*) isomers of a [Co^{III}(O)$_4$(N)$_2$]$^-$ type complexes can be identified from the splitting pattern of their first absorption bands in the visible region.[6,7] As is seen in Fig. 1 and Table 2, the first absorption bands of the two earlier eluates (isomers i and ii) of [Co(L-alama)$_2$]$^-$ and of the stable eluate of [Co(L-proma)$_2$]$^-$ exhibit a sub-peak (or shoulder) at the longer wavelength side of the major peak. On the contrary, on the absorption curves of the four later eluates (isomers iii, iv, v and vi) of [Co(L-alama)$_2$]$^-$, a vague shoulder is observed at the shorter wavelength side of the major peak. This indicates that the former group is *trans*(*N*) isomer and the latter *cis*(*N*).

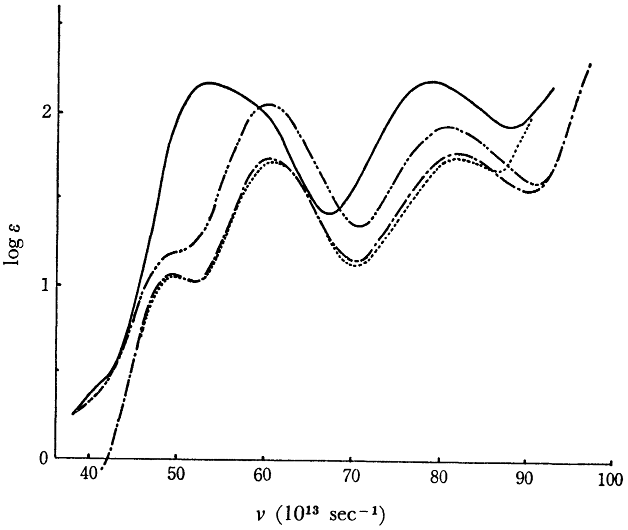

Fig. 1. Absorption curves of *trans*(*N*)-RR-[Co(L-alama)$_2$]$^-$ (—-—-), *trans*(*N*)-RS-[Co(L-alama)$_2$]$^-$ (———---), *trans*(*N*)-[Co(ida)$_2$]$^-$ (----) and *Δ-cis*-(*N*)-RR-[Co(L-alama)$_2$]$^-$ (——).

The *cis*(*N*) isomers of [Co(L-alama)$_2$]$^-$ exhibit two CD extrema in the first absorption band region as shown in Table 3. Of the four isomers the earlier eluted two isomers (iii and iv)show a negative and a positive CD band listing from longer wavelength side, whereas isomers v and vi show a positive and a negative band in the corresponding region. The absolute configuration of the isomer of *cis(N)*-[Co(ida)$_2$]$^-$, which was obtained from the less soluble diastereoisomer with (−)$_{546}$-[Co(en)$_2$(ox)]$^+$, has been assigned to be *Δ*[8] by Van Saun and Douglas,[3] and the first absorption band of this complex shows a positive and a negative CD band listing from longer wavelength side. The *Λ*-(−)$_{546}$ isomer of [Co(edta)]$^-$ also shows a similar Cotton effect pattern in this region.[3,9] Since each of the *cis(N)* isomers in the present work has a C_2 or pseudo-C_2 symmetry, it is expected that the effective crystal field in these complexes is quite similar to those in the ida and edta complexes. Therefore it is concluded that the *cis*(*N*) isomers iii and iv have a *Δ* configuration and the isomers v and vi a *Λ* configuration.

In the parent complex, [Co(ida)$_2$]$^-$, four isomers are

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[6] a) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967); b) *Inorg. Chem.*, **9**, 719 (1970).

[7] a) N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, This Bulletin, **42**, 1583 (1969); b) *ibid.*, **43**, 1737 (1970).

[8] Absolute configurations of the complexes are designated by the IUPAC tentative rule: *Inorg. Chem.*, **9**, 1 (1970).

[9] B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

TABLE 2. ABSORPTION MAXIMA OF $[Co(O,N,O\text{-tridentate})_2]^-$ TYPE COMPLEXES

Complex ion	I Band		II Band		Ref.
	ν_{max}	$(\log \varepsilon_{max})$	ν_{max}	$(\log \varepsilon_{max})$	
trans(*N*)-RR-$[Co(L\text{-alama})_2]^-$	49.6	(1.08)	82.6	(1.77)	
	60.6	(1.74)			
trans(*N*)-RS-$[Co(L\text{-alama})_2]^-$	*ca.* 50	(1.2)	81.5	(1.91)	
	60.4	(2.05)			
trans(*N*)-RR-$[Co(L\text{-proma})_2]^-$	*ca.* 50	(1.1)	81.3	(1.86)	
	59.3	(1.79)			
trans(*N*)-$[Co(ida)_2]^-$	50.0	(1.06)	83.3	(1.75)	(1)
	61.2	(1.72)			
Δ-*cis*(*N*)-RR-$[Co(L\text{-alama})_2]^-$	53.3	(2.22)	78.8	(2.21)	
Δ-*cis*(*N*)-RS-$[Co(L\text{-alama})_2]^-$	53.5	(2.15)	79.2	(2.15)	
Λ-*cis*(*N*)-RR-$[Co(L\text{-alama})_2]^-$	53.2	(2.17)	78.4	(2.15)	
Λ-*cis*(*N*)-RS-$[Co(L\text{-alama})_2]^-$	53.5	(2.15)	78.7	(2.10)	
cis(*N*)-$[Co(ida)_2]^-$	53.4	(2.18)	79.0	(2.13)	(1)

Frequencies are given in 10^{13} sec^{-1}.

TABLE 3. CD DATA

Complex ion		I Band		II Band	
		ν_{ext}	$(\Delta\varepsilon_{ext})$	ν_{ext}	$(\Delta\varepsilon_{ext})$
trans(*N*)-RR-$[Co(L\text{-alama})_2]^-$	(i)	48.4	(−0.32)	78.9	(+0.08)
		59.7	(−1.11)		
trans(*N*)-RS-$[Co(L\text{-alama})_2]^-$	(ii)	49.2	(+0.06)	80.0	(+0.18)
		61.2	(−1.04)		
trans(*N*)-RR-$[Co(L\text{-proma})_2]^-$		48.6	(+0.14)	80.1	(−0.20)
		58.6	(−1.72)		
Δ-*cis*(*N*)-RR-$[Co(L\text{-alama})_2]^-$	(iii)	50.9	(−4.62)	*ca.* 74	(−1.0)
		58.6	(+4.57)	80.5	(−1.44)
Δ-*cis*(*N*)-RS-$[Co(L\text{-alama})_2]^-$	(iv)	51.2	(−2.86)	*ca.* 74	(−0.5)
		58.8	(+2.74)	81.9	(−0.83)
Λ-*cis*(*N*)-RR-$[Co(L\text{-alama})_2]^-$	(v)	52.4	(+0.71)	*ca.* 74	(+0.2)
		60.1	(−1.56)	77.9	(+0.21)
Λ-*cis*(*N*)-RS-$[Co(L\text{-alama})_2]^-$	(vi)	51.6	(+1.78)	*ca.* 74	(+0.4)
		59.9	(−2.90)	77.7	(+0.61)

Frequencies are given in 10^{13} sec^{-1}.

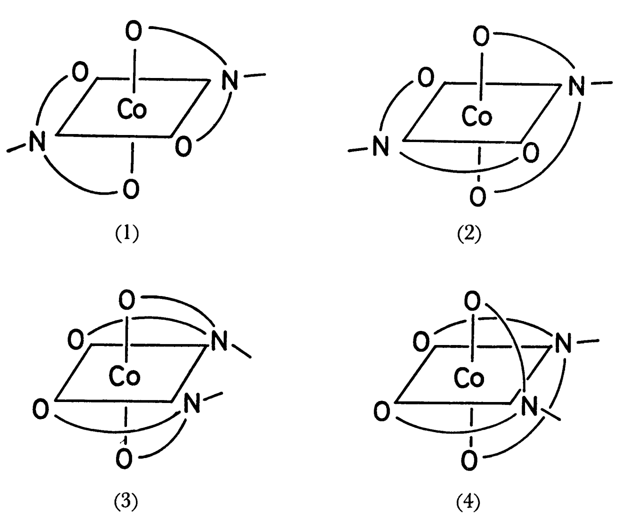
(1) (2)
(3) (4)

Fig. 2. Four possible isomers for a $[Co(O,N,O\text{-tridentate})_2]$ type complex: (1) facial-*trans*(*N*), (2) meridional-*trans*(*N*), (3) Λ-*cis*(*N*) and (4) Δ-*cis*(*N*).

possible as is seen in Fig. 2; so far the meridionally coordinating *trans(N)* isomer (2) is unknown. Such a meridional form of ida has been found only in a mixed complex with diethylenetriamine, $[Co(ida)(dien)]^+$.[4] A molecular model examination shows that the Δ-*cis(N)* isomer of L-proma complex can not exist because of serious steric hindrance between two pyrrolidine rings in the complex. We obtained an unstable violet colored eluate, which shows an absorption spectrum of *cis(N)*-$[Co(O)_4(N)_2]^-$ type and a CD spectrum similar to those of isomers v and vi of L-alama complex (with Λ configuration). The molecular model of the Λ isomer of $[Co(L\text{-proma})_2]^-$ shows that the pyrrolidine ring of one ligand makes a rather short contact to the acetate methylene in another ligand, and that this may be the reason for the instability of this isomer. The stable *trans(N)*-$[Co(L\text{-proma})_2]^-$ may be type (1) isomer in Fig. 2.

When L-alama coordinates to a cobalt(III) ion, the nitrogen atom of the ligand is optically activated (as having R or S configuration). Accordingly three isomers, RR, RS, and SS, are possible for each of the bis(L-alama) complexes of *trans(N)*, *Δ-cis(N)* and *Λ-cis(N)* form. In the case of L-proma complex, the ligand cannot coordinate to take the S configuration of nitrogen atom; then only the RR isomer is expected for each of the *trans(N)* and *Λ-cis(N)* L-proma complexes. In fact, only one isomer was obtained by ion-exchange column chromatography for each of the *trans(N)* and *cis(N)* complexes. It has already been established that L-prolinate shows a complete stereospecific coordination of this kind; L-prolinate itself fixes the absolute configuration of the asymmetric nitrogen center to the S configuration.[10,11]

Experimentally only two isomers of possible three isomers were obtained for the *trans(N)* bis(L-alama) complex by ion-exchange column chromatography. If the nitrogen center takes S configuration, a repulsion exists between an alaninate methyl group of a coordinated L-alama ligand and a proton of the glycinate ring of the same ligand as is seen in Fig. 3(b). There is no such a repulsion in the R-form coordination (Fig. 3(a)). From this viewpoint, it is possible to assume tentatively that the two *trans(N)* isomers of bis(L-alama) complex obtained are the RR and RS forms of the type (1) isomer in Fig. 2.

The PMR spectra of the *trans(N)* bis(L-alama) complexes, i and ii, are shown in Fig. 4. The proton signals of *trans(N)* bis(L-alama) complexes consist of a group of AX$_3$ pattern due to $>$CH–CH$_3$ and another group of AB pattern due to –CH$_2$–. Only one set of AX$_3$ and AB patterns is expected for the RR or SS isomer and two sets for the RS isomer, since the former has C_2 symmetry and the latter C_1. As shown in Fig. 4, isomer i showed a doublet (at 1.73 ppm) in the region of methyl protons, whereas isomer ii showed two doublets (at 1.65 and 1.78 ppm) in this region. This behavior supports the view that isomer i is RR and isomer ii RS form. This was also confirmed by the result in the region of methylene and methine protons (3—5 ppm): the PMR spectrum of isomer i exhibited a pair of quartets, whereas that of isomer ii was complicated.

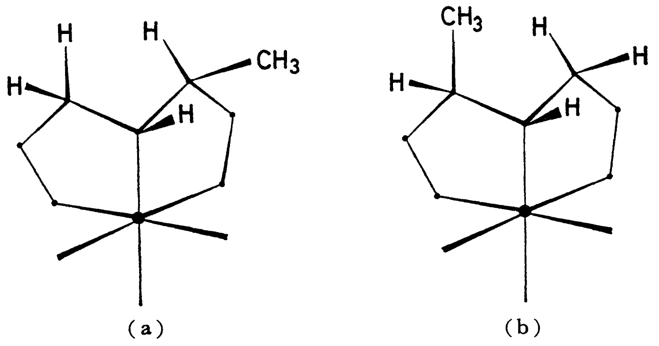

Fig. 3. Two possible configurations of the L-alama^{2-} ligand facially coordinated to a cobalt atom: (a) R from with regard to the asymmetric nitrogen atom, and (b) S form.

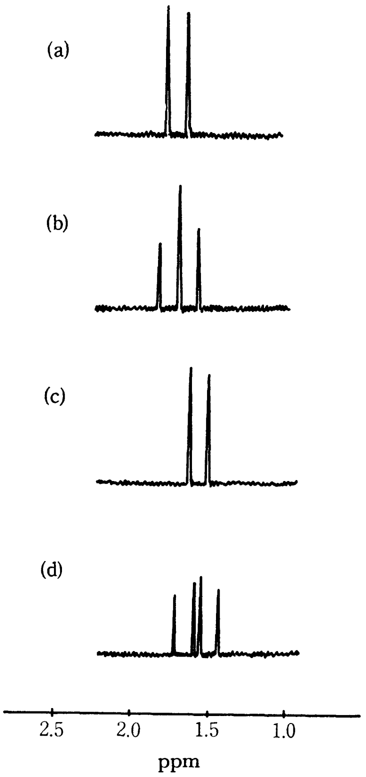

Fig. 4. The PMR spectra of bis(L-alama) complexes in D$_2$O. (a) isomer i (RR), (b) isomer ii (RS), (c) isomer v (RR) and (d) isomer iv (RS).

A similar conclusion was also obtained for the PMR spectra of the isomers of *cis(N)* bis(L-alama) complex. Isomer iv showed two doublets (at 1.48 and 1.66 ppm) due to two methyl groups and isomer v a doublet (at 1.56 ppm) (Fig. 4). The poor yields of isomers iii and vi did not allow measurement of the PMR spectra. However, the absorption maximum and CD extremum data in Tables 2 and 3 suggest that isomer iii corresponds to isomer v (RR) and isomer vi to iv (RS). Thus, if the possibility of the SS configuration is excluded, the four isomers obtained of *cis(N)*-[Co(L-alama)$_2$]$^-$ are assigned as follows: iii to Δ-RR, iv to Δ-RS, v to Λ-RR, and vi to Λ-RS.

It has been reported for several cobalt(III) complexes that the configurational and vicinal contributions to CD are separable and almost additive.[6b,12–14] The CD data and curves of the present complexes are shown in Table 3 and Figs. 5 and 6. The CD curve of a *cis(N)* isomer consists of a configurational contribution (Δ or Λ) and two vicinal ones due to the asymmetric nitrogen (R or S) and carbon (L) atoms. This assumption leads to the following additivity formulas:

$$\Delta\varepsilon(\text{iii}) = \Delta + 2\text{R} + 2\text{L} \qquad (1)$$

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[10] T. Yasui, J. Hidaka, and Y. Shimura, *J. Amer. Chem. Soc.*, **87**, 2762 (1965); T. Yasui, This Bulletin, **38**, 1746 (1965).

[11] D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, and A. M. Sargeson, *Chem. Commun.*, **1969**, 583.

[12] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965); B. E. Douglas, *ibid.*, **4**, 1813 (1965); J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967); S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969); C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, **4**, 3 (1970).

[13] J. Hidaka and Y. Shimura, This Bulletin, **40**, 2312 (1967); K. Yamasaki, J. Hidaka, and Y. Shimura, *ibid.*, **42**, 119 (1969).

[14] K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Letters*, **4**, 351 (1968).

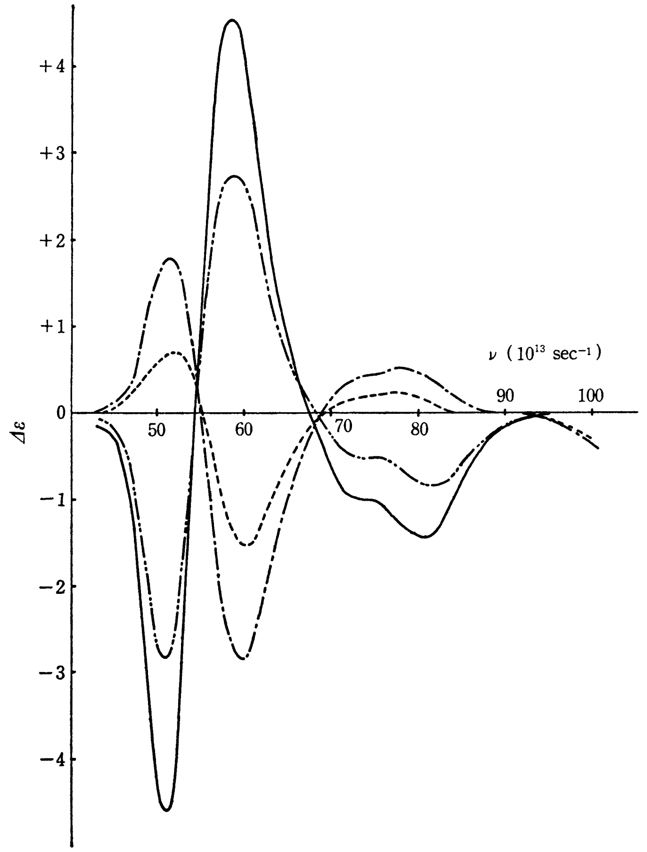

Fig. 5. CD curves of *cis*(*N*)-[Co(L-alama)$_2$]$^-$ isomers: Δ-*cis*(*N*)-RR (——), Δ-*cis*(*N*)-RS (————), Λ-*cis*(*N*)-RR (----) and Λ-*cis*(*N*)-RS (———).

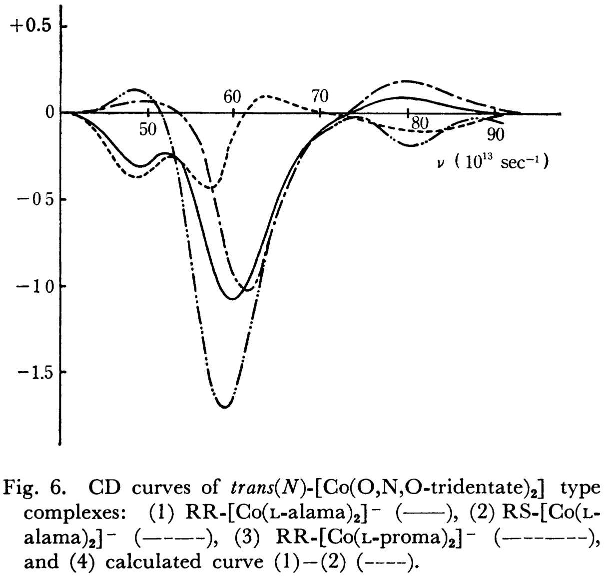

Fig. 6. CD curves of *trans*(*N*)-[Co(O,N,O-tridentate)$_2$] type complexes: (1) RR-[Co(L-alama)$_2$]$^-$ (——), (2) RS-[Co(L-alama)$_2$]$^-$ (———), (3) RR-[Co(L-proma)$_2$]$^-$ (————), and (4) calculated curve (1)−(2) (----).

$$\Delta\varepsilon(\text{iv}) = \Delta + 2\text{L} \tag{2}$$

$$\Delta\varepsilon(\text{v}) = \Lambda + 2\text{R} + 2\text{L} \tag{3}$$

$$\Delta\varepsilon(\text{vi}) = \Lambda + 2\text{L} \tag{4}$$

where, of course, there exists the relation, $\Delta = -\Lambda$. Thus we have

$$\Lambda = 1/2 \times \{\Delta\varepsilon(\text{v}) - \Delta\varepsilon(\text{iii})\}$$

$$= 1/2 \times \{\Delta\varepsilon(\text{vi}) - \Delta\varepsilon(\text{iv})\} \tag{5}$$

$$2\text{R} = \Delta\varepsilon(\text{iii}) - \Delta\varepsilon(\text{iv}) = \Delta\varepsilon(\text{v}) - \Delta\varepsilon(\text{vi}) \tag{6}$$

$$2\text{L} = 1/2 \times \{\Delta\varepsilon(\text{iv}) + \Delta\varepsilon(\text{vi})\} \tag{7}$$

The curves of configurational Λ, vicinal 2R, and vicinal 2L can be calculated by applying Eqs. (5)—(7) to the observed CD curves of *cis(N)* isomers. The calculated curves are shown in Fig. 7.

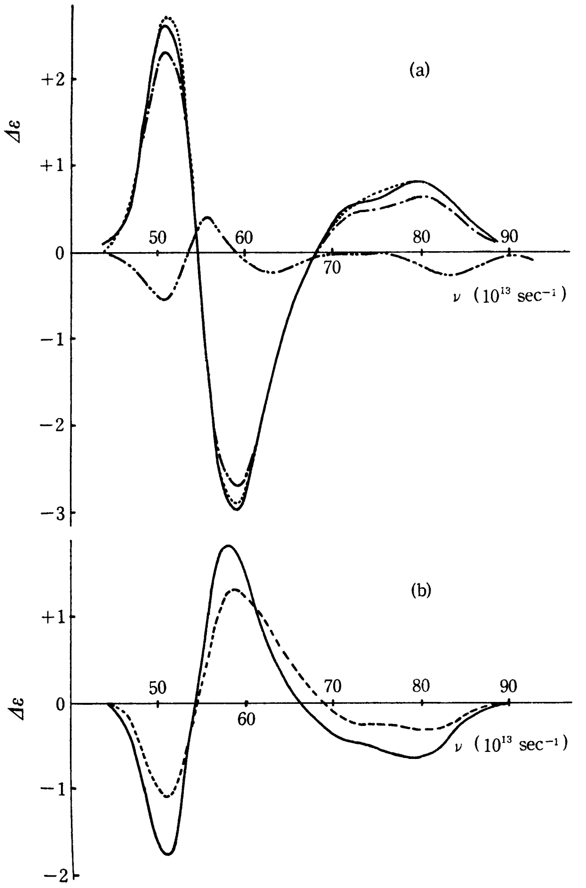

Fig. 7. Curve analyses of *cis*(*N*)-[Co(L-alama)$_2$]$^-$ complexes: (a) Λ configurational and 2L vicinal (carbon atom) curves; 1/2×{Δε(v)−Δε(iii)} (——), 1/2×{Δε(vi)−Δε(iv)} (———) and 1/2×{Δε(iv)+Δε(vi)} (————). Observed CD curve of Λ-*cis*(*N*)-[Co(ida)$_2$]$^-$ (----). (b) 2R vicinal curves (nitrogen atom); Δε(iii)−Δε(iv) (——) and Δε(v)−Δε(vi) (----).

The calculated configurational curve Λ (Fig. 7a), agrees well with the curve of Λ-*cis(N)*-[Co(ida)$_2$]$^-$ by Van Saun and Douglas.$^{3)}$ As shown in Fig. 7b, there is also a rather good correspondence between the vicinal 2R curve which was calculated from a pair of Δ-*cis(N)* isomers and that from a pair of Λ-*cis(N)* isomers. This also supports the assignment of the configurations of the nitrogen atoms, which was made from the visible absorption and PMR spectra.

The CD spectra of the *trans(N)* bis(L-alama) isomers are also treated in a similar manner. In this case, however, there is no configurational contribution. Therefore the calculated curve, Δε(i)—Δε(ii), represents the vicinal contribution 2R (Fig. 6).