Circular Dichroism Spectra of *Unsym-cis*(*O*) Isomers of (L-Alaninate-*N*-monoacetato)(diethylenetriamine)cobalt(III) Complexes

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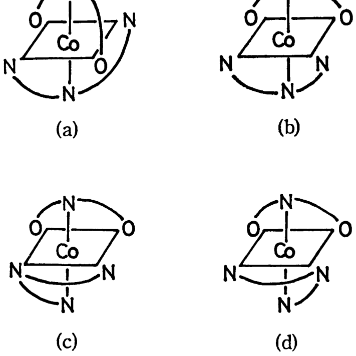
(Received May 10, 1975)

A couple of diastereomers, ΔΔΛ-*R*(*N*)–L(*C*) and ΔΛΛ-*R*(*N*)–L(*C*), of *unsym-cis*(*O*)-(L-alaninate-*N*-monoacetato)(diethylenetriamine)cobalt(III)(1+) complex was prepared and characterized from the circular dichroism spectra, which presented an example for the additivity between the circular dichroism contributions due to the configurational (ΔΔΛ and ΔΛΛ) and the vicinal (*R*(*N*)+L(*C*)) chiralities.

In a previous paper[1)] circular dichroism (CD) spectrum was reported for a *cis*(*O*)-[Co(L-alama)$(NH_3)_3$]$^+$ complex, where L-alama denotes L-alaninate-*N*-monoacetate(2-), which is an *O*,*N*,*O*-tridentate ligand. The present paper deals with the corresponding diethylenetriamine (dien) complex, *cis*(*O*)-[Co(L-alama)(dien)]$^+$. In a [Co(*O*,*N*,*O*-tridentato)(dien)]$^+$ type complex, four configurational isomers are possible as is seen in Fig. 1, neglecting the chirality which is produced by two meridionally coordinated non-planar tridentate ligands. In the *trans*(*O*) form the *O*,*N*,*O*-tridentate ligand spans in a meridional set of coordination sites, and in the remaining three *cis*(*O*) forms in a face of octahedron. Legg and Cooke[2)] prepared all three geometrical isomers, *trans*(*O*)(a), *sym-cis*(*O*)(b), and racemic *unsym-cis*(*O*)(c+d), of [Co(ida)(dien)]$^+$, where ida is a simple *O*,*N*,*O*-tridentate ligand iminodiacetate(2−). Recently Yoshikawa *et al.*[3)] reported optical resolution of the *unsym-cis*(*O*)-[Co(ida)(dien)]$^+$ by SE-sephadex column chromatography using an eluant containing tartar emetic.



(a) (b) (c) (d)

Fig. 1. Four possible isomers for a [Co(*O*,*N*,*O*-tridentato)(dien)]$^+$ type complex: (a) *trans*(*O*), (b) *sym-cis*(*O*), (c) ΔΔΛ-*unsym-cis*(*O*), and (d) ΔΛΛ-*unsym-cis*(*O*).

Since the ligand L-alama contains an asymmetric carbon atom, the isomers of cobalt(III) complex formed have two or more chiral centers, namely each one of asymmetric carbon (L) and nitrogen (*R* or *S*) atom, and in the case of *unsym-cis*(*O*) isomer a configurational chirality (ΔΔΛ or ΔΛΛ).[4)] Thus the *unsym-cis*(*O*)-[Co(L-alama)(dien)]$^+$ complex offers a useful couple of diastereomers for examination of additivity of the configurational and vicinal CD.

The present paper is concerned mainly to the *cis*(*O*) isomers, especially *unsym-cis*(*O*), and the *trans*(*O*) isomers are only briefly mentioned, because the stereochemistry of *trans*(*O*) isomers is rather complicated by possible existence of a new kind of chirality, which is produced by two meridionally coordinated non-planar tridentate ligands as in a established case of the optically resolved *mer*-[Co$(dien)_2$]$^{3+}$ complex.[5)] Heretofore none of the *trans*(*O*) isomers of [Co(*O*,*N*,*O*-tridentato)(dien)]$^+$ type complexes have been optically resolved.

Experimental

Preparations. *(1)* Unsym-cis*(O)-(Diethylenetriamine)-(iminodiacetato)cobalt(III) Perchlorate Monohydrate,* unsym-cis*(O)-[Co(ida)(dien)]*$ClO_4\cdot H_2O$: This was prepared by a modified method of Legg and Cooke.[2)] To a suspension of 5.4 g of [$CoCl_3$(dien)][6)] in 100 cm^3 of water was added a solution of 5.1 g of silver nitrate in 20 cm^3 of water. After the precipitated silver chloride was filtered off, to the filtrate was added a solution of 2.7 g of iminodiacetic acid which was neutralized in advance with potassium hydroxide. To the resulting mixture was added 3 g of charcoal and the mixture was constantly stirred at about 60 °C for three hours. After the reaction mixture had been cooled to room temperature, the charcoal was removed by filtration. The filtrate was poured into a column (35 mm×500 mm) containing strong-acid cation exchange resin (Dowex 50 W×8, 200—400 mesh, sodium form). After the column had been swept with water, the adsorbed band was eluted with 0.1 M aqueous solution of sodium perchlorate at a rate of 2.5 cm^3 per min. Three red bands were eluted. It had been already assigned from pmr spectra by Legg and Cooke that the first eluate contained *trans(O)* isomer, the second *sym-cis(O)* and the third *unsym-cis(O)*. So the third eluate was concentrated in a vacuum evaporator and a large amount of ethanol was added to the concentrated solution. The appeared complex was collected by filtration and recrystallized from a small amount of water by adding ethanol. The pure crystals were washed with ethanol and dried in air. Found: C, 23.76; H, 4.86; N, 13.69%. Calcd for [Co(ida)(dien)]$ClO_4\cdot H_2O = C_8H_{18}N_4O_8ClCo\cdot H_2O$: C, 23.39; H, 4.91; N, 13.64%.

(2) $(+)_{589}$-Unsym-cis*(O)-(diethylenetriamine)(iminodiacetato)cobalt(III) chloride monohydrate,* $(+)_{589}$-unsym-cis-*(O)-[Co(ida)(dien)]Cl*$\cdot H_2O$: Racemic *unsym-cis(O)*-[Co(ida)(dien)]$ClO_4\cdot H_2O$ (0.84 g) was dissolved in an appropriate amount of water. The solution was poured into a column containing strong-base anion exchange resin (Dowex 1×8, 200—400 mesh, chloride form) and the column was eluted with water. Silver acetate (0.34 g) was added to the eluate

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and the silver chloride resulted was filtered off. The filtrate was concentrated in a vacuum evaporator. A solution of 0.40 g of $(+)_{589}$-Na[Co(ox)$_2$(en)]$\cdot$4H$_2$O[7] in a minimum amount of water was added to the concentrated solution. The mixture was concentrated by stream of air at room temperature and then kept in a refrigerator. The less soluble diastereomer deposited as violet crystals, and they were collected by filtration and recrystallized from 15 cm^3 of warm water (40 °C). The pure diastereomer was washed with ethanol and dried in air. Yield: 0.31 g. Found: C, 26.18; H, 5.09; N, 12.94%. Calcd for *unsym-cis(O)*-[Co(ida)(dien)]$\cdot(+)_{589}$-[Co(ox)$_2$(en)]$\cdot$3H$_2$O=$C_{14}H_{26}N_6O_{12}Co_2\cdot 3H_2O$: C, 26.18; H, 5.02; N, 13.08%.

An aqueous solution of the diastereomer was poured into a column (Dowex 1×8, 200—400 mesh, chloride form) and was eluted with water. The eluate was concentrated in a vaccum evaporator and an appropriate amount of ethanol was added to the concentrated solution to obtain the optically active complex, $(+)_{589}$-*unsym-cis(O)*-[Co(ida)(dien)]Cl$\cdot$H$_2$O, which was washed with ethanol and dried in air. Found: C, 26.28; H, 6.09; N, 15.14%. Calcd for $(+)_{589}$-*unsym-cis(O)*-[Co(ida)(dien)]Cl$\cdot$H$_2$O=$C_8H_{18}N_4O_4ClCo\cdot H_2O$: C, 26.35; H, 6.08; N, 15.36%.

*(3) Isomers of (*L*-Alaninate-*N*-monoacetato)(diethylenetriamine)-cobalt(III) perchlorate, [Co(*L*-alama)(dien)]ClO$_4$:* These isomers were prepared by a similar procedure to that for (**1**) using L-alamaH$_2\cdot$HCl$\cdot$1/4H$_2$O[8] instead of idaH$_2$. The prepared isomers were separated by using a cation exchange column (30 mm×1300 mm) in a similar manner to that described in (1). Six red bands were eluted and they were numbered (i), (ii), ……, and (vi) in the order of elution. The yields for the isomers (v) and (vi) were very low. It was confirmed by the measurement of absorption spectra that the isomer (i) is a *trans(O)* isomer and the isomers (ii)—(vi) *cis(O)*. The eluates were separately concentrated in a vacuum evaporator and a large amount of ethanol was added to each of the concentrated solutions. The desired complex was collected by filtration and recrystallized from a small amount of water by adding ethanol and then dried in air. The isomer (v) was not obtained as solid salt because of its low yield, and some other isomers were contaminated with a small amount of sodium perchlorate as shown in the following analytical data. Found for isomer (i): C, 22.36; H, 4.50; N, 11.82%. Calcd for [Co(L-alama)(dien)]ClO$_4\cdot$1/2H$_2$O$\cdot$1/2NaClO$_4$=$C_9H_{20}N_4O_8ClCo\cdot 1/2H_2O\cdot 1/2NaClO_4$: C, 22.67; H, 4.44; N, 11.75%. Found for isomer (ii): C, 25.92; H, 5.13; N, 13.53%. Calcd for [Co(L-alama)(dien)]ClO$_4\cdot$1/2H$_2$O=$C_9H_{20}N_4O_8ClCo\cdot 1/2H_2O$: C, 26.01; H, 5.09; N, 13.48%. Found for isomer (iii): C, 25.35; H, 4.91; N, 13.34%. Calcd for [Co(L-alama)(dien)]ClO$_4\cdot$1/4H$_2$O$\cdot$1/10NaClO$_4$=$C_9H_{20}N_4O_8ClCo\cdot 1/4H_2O\cdot 1/10NaClO_4$: C, 25.53; H, 4.88; N, 13.23%. Found for isomer (iv): C, 26.31; H, 5.00; N, 13.52%. Calcd for [Co (L-alama) (dien)] ClO$_4\cdot$1/4H$_2$O=$C_9H_{20}N_4O_8ClCo\cdot 1/4H_2O$: C, 26.29; H, 5.03; N, 13.63%. Found for isomer (vi): C, 26.22; H, 5.03; N, 13.60%. Calcd for [Co(L-alama)(dien)] ClO$_4\cdot$1/4H$_2$O=$C_9H_{20}N_4O_8ClCo\cdot 1/4H_2O$: C, 26.29; H, 5.03; N, 13.63%.

*(4) Isomers of (Diethylenetriamine)(*L*-prolinate-*N*-monoacetato)-cobalt(III) Perchlorate, [Co(*L*-proma)(dien)]ClO$_4$:* The isomers were prepared and separated by a similar procedure to that described in (**1**) using L-promaH$_2$[8] instead of idaH$_2$. Two red bands were eluted; the absorption spectra indicated that the first eluate contained *trans(O)* isomer, and the second *cis(O)*. The first eluate was concentrated to dryness in a vacuum evaporator and then the sodium perchlorate in the residue was extracted with a large amount of ethanol. The desired complex was filtered and recrystallized from a small amount of water by adding ethanol. The second eluate was also concentrated in a vacuum evaporator and a large amount of ethanol was added to the concentrated solution. The obtained complex was filtered and recrystallized from a small amount of water by adding ethanol. Both the pure complexes were washed with ethanol and dried in air. Found for the *trans(O)* complex: C, 30.20; H, 5.19; N, 12.76%. Calcd for [Co(L-proma)(dien)]ClO$_4\cdot$1/4H$_2$O=$C_{11}H_{22}N_4O_8ClCo\cdot 1/4H_2O$: C, 30.22; H, 5.19; N, 12.81%. Found for the *cis(O)* complex: C, 30.28; H, 5.13; N, 12.90%. Calcd for [Co(L-proma)(dien)]ClO$_4$=$C_{11}H_{22}N_4O_8ClCo$: C, 30.53; H, 5.13; N, 12.95%.

Measurements. The electronic absorption spectra were measured by a Beckman DU spectrophotometer and a Shimadzu spectrophotometer UV-200. The CD spectra were recorded with a Jasco Model J-10 or J-20 spectropolarimeter with the CD attachment, or with a Roussel-Jouan Dichrograph. All the measurements were made in aqueous solutions at room temperature.

Results and Discussion

Visible and near ultraviolet absorption data of the present [Co^{III}(N)$_4$(O)$_2$] type complexes are shown in Table 1 and the typical absorption curves of a *cis-trans* couple are in Fig. 2. The isomers obtained are divided into two groups on the splitting pattern of the first absorption band. An isomer of the first group has a

TABLE 1. ABSORPTION MAXIMA OF THE [Co(*O,N,O*-tridentato)(dien)]$^+$ COMPLEXES (wave numbers are given in 10^3 cm^{-1})

Complex ion	$\sigma_{max}(\log\varepsilon_{max})$ I band	II band
unsym-cis(*O*)-[Co(ida)(dien)]$^+$	19.6(2.04)	28.2(2.11)
cis(*O*)-[Co(L-alama)(dien)]$^+$		
isomer ii, *sym-cis*(*O*)	20.5(1.87)	28.7(1.96)
isomer iii, *unsym-cis*(*O*)-R	19.3(2.05)	28.1(2.14)
isomer iv, *unsym-cis*(*O*)-R	19.4(2.06)	28.1(2.17)
isomer v, *cis*(*O*)	20.6(—)	28.7(—)
isomer vi, *cis*(*O*)	19.7(2.03)	28.1(2.12)
sym-cis(*O*)-*R*-[Co(L-proma)(dien)]$^+$	19.9(1.92)	28.4(1.99)
trans (*O*)-[Co(ida)(dien)]$^{+}$[2]	19.6(2.24)	27.8(2.28)
trans(*O*)-[Co(L-alama)(dien)]$^+$	19.9(2.28)	28.0(2.27)
trans(*O*)-*R*-[Co(L-proma)(dien)]$^+$	19.9(2.24)	27.4(2.31)

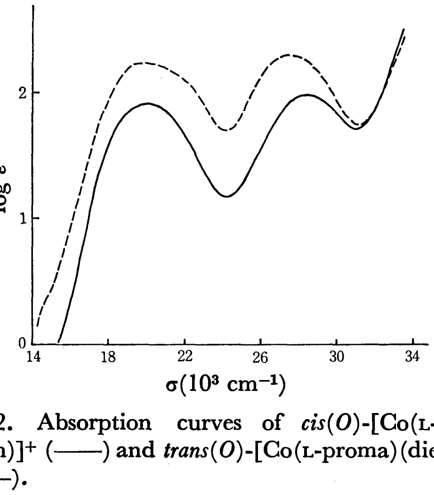

Fig. 2. Absorption curves of *cis*(*O*)-[Co(L-proma)(dien)]$^+$ (——) and *trans*(*O*)-[Co(L-proma)(dien)]$^+$ (----).

shoulder at higher energy side of the major peak, and the second group only a symmetrical major peak (Fig. 2). It is concluded, therefore, that an isomer of the first group has a *trans*(*O*) structure and that the second group a *cis*(*O*). It is worthwhile to note that the first absorption bands of the *trans*(*O*) isomers of this type complexes are more intense than those of the *cis*(*O*) ones; $\log \varepsilon_{\max}$ values are in a range of 2.24—2.28 for *trans*(*O*), while 1.87—2.06 for *cis*(*O*) (Table 1). The second absorption bands are also in the same trend, $\log \varepsilon_{\max}$=2.27—2.31 for *trans*(*O*), while 1.96—2.17 for *cis*(*O*).

In the [Co(L-alama)(dien)]$^+$ and [Co(L-proma)(dien)]$^+$ complexes, both the *cis*(*O*) and *trans*(*O*) isomers were obtained. Thus the L-alama and L-proma ligands take both the facial and meridional coordinations in the present dien complexes, in contrast to the corresponding triammine complexes, in which only the facial coordination occurred for both the ligands.[1)]

In the preparation of [Co(L-proma)(dien)]$^+$ complex, each one of *trans*(*O*) and *cis*(*O*) isomers was obtained. A molecular model examination shows that the formation of *unsym-cis*(*O*) isomers is almost impossible because of the repulsion between the pyrrolidine ring of the L-proma ligand and the ethylenediamine moiety of the dien ligand. It is assigned, therefore, that the *cis*(*O*) isomer obtained takes *sym-cis*(*O*) configuration. As for the configuration of the coordinated asymmetric nitrogen atom, the L-proma ligand takes only *R* configuration stereospecifically.[9)] Thus the two isomers obtained for the L-proma ligand are *trans*(*O*)-*R* and *sym-cis*(*O*)-*R* isomers.

One *trans*(*O*) and five *cis*(*O*) isomers were isolated for the [Co(L-alama)(dien)]$^+$ complex. Of the five *cis*(*O*) isomers the fifth eluate (isomer v) could not be examined by elemental analysis because of its extremely low yield, and then only the absorption spectrum was measured. Isomer vi was obtained in a lower yield than the earlier three isomers ii, iii, and iv. We have already found that for the coordinated asymmetric nitrogen atom of the L-alama ligand the *R* configuration is preferred to the *S* one; namely a repulsion exists in the L-alama ligand having the *S* asymmetric nitrogen atom, between the L-alaninate methyl group and a proton of the *N*-acetate chelate ring of the same ligand.[8)] Therefore, the predominant isomers ii, iii, and iv may be assigned to *R* configuration and the poorly yielded isomers v and vi to *S*. From the consideration of the CD curves (see below), it is concluded that the isomers iii and iv take actually *R* structure, but ambiguities remain to the nitrogen configurations of the isomers ii, v, and vi.

Table 2. CD Data of the *cis*(*O*)-[Co(*O*,*N*,*O*-tridentato)(dien)]$^+$ complexes (wave numbers are given in 10^3 cm^{-1})

Complex ion	$\sigma_{\text{ext}}(\Delta\varepsilon_{\text{ext}})$ I band	$\sigma_{\text{ext}}(\Delta\varepsilon_{\text{ext}})$ II band
$(+)_{589}$-Δ-*unsym-cis*(*O*)-[Co(ida)(dien)]$^+$	18.5(+1.57) 21.1(−1.16)	28.6(+0.28)
unsym-cis(*O*)-*R*-[Co(L-alama)-(dien)]$^+$		
isomer iv, $\Delta\Delta\Lambda$	18.4(+1.42) 21.2(−1.30)	28.7(+0.16)
isomer iii, $\Delta\Lambda\Lambda$	18.4(−1.97) 20.8(+1.34)	28.5(−0.63)
cis(*O*)-*R*-[Co(L-alama)-$(NH_3)_3$]$^+$ [1)]	18.1(−0.17) 19.8(+0.12) 21.9(−0.17)	28.4(−0.22)
sym-cis(*O*)-*R*-[Co(L-proma)-(dien)]$^+$	18.1(−0.05) 20.0(+0.37) 22.6(−0.07)	28.3(−0.34)
cis(*O*)-*R*-[Co(L-proma)-$(NH_3)_3$]$^+$ [1)]	17.9(−0.30) 19.9(+1.04)	28.1(−0.46)
sym-cis(*O*)-[Co(L-alama)(dien)]$^+$		
isomer ii	18.3(+0.02) 21.5(−0.38)	26.8(−0.14)

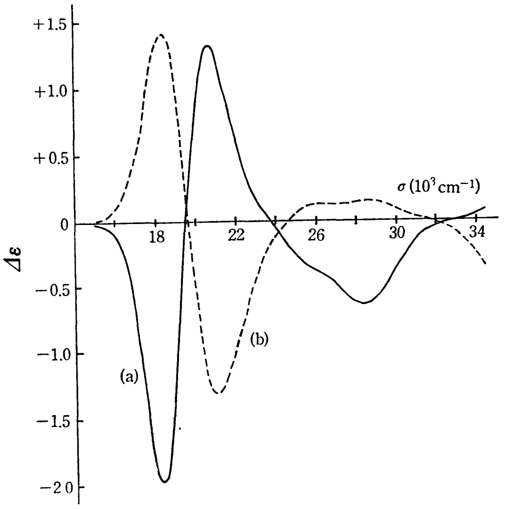

Fig. 3. CD curves of, (a) $\Delta\Lambda\Lambda$-*unsym-cis*(*O*)-*R*-[Co(L-alama)(dien)]$^+$ and (b) $\Delta\Delta\Lambda$-*unsym-cis*(*O*)-*R*-[Co(L-alama)(dien)]$^+$.

The CD data of *cis*(*O*) isomers are collected in Table 2. Of the three predominant *cis*(*O*) isomers of the L-alama complex, the isomer ii has much weaker CD intensity than the other two, iii and iv. The CD curve of isomer iii is almost a mirror image to that of the isomer iv as is seen in Fig. 3. These facts show that the isomer ii is *sym-cis*(*O*) type, while the isomers iii and iv *unsym-cis*(*O*).

If the configurational and vicinal CD are separable, the following additivity formulas are derived for the two *unsym-cis*(*O*)-*R* isomers as in other similar cases studied previously,[1,8)]

$$\Delta\varepsilon(\Delta\Delta\Lambda) = \Delta + R(N) + \mathrm{L}(C)$$

$$\Delta\varepsilon(\Delta\Lambda\Lambda) = \Lambda + R(N) + \mathrm{L}(C)$$

where $\Delta\varepsilon(\Delta\Delta\Lambda)$ and $\Delta\varepsilon(\Delta\Lambda\Lambda)$ are the CD of the isomer $\Delta\Delta\Lambda$ and $\Delta\Lambda\Lambda$, Δ and Λ the configurational contributions of Δ and Λ chiralities, $R(N)$ and $\mathrm{L}(C)$ the vicinal contributions of *R*-nitrogen and L-carbon chiralities, respectively. Since $\Delta = -\Lambda$, we have

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

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

$$R(N) + \mathrm{L}(C) = 1/2 \times \{\Delta\varepsilon(\Delta\Delta\Lambda) + \Delta\varepsilon(\Delta\Lambda\Lambda)\}$$

The partial contribution curves calculated under an assumption that the isomers iii and iv are $\Delta\Lambda\Lambda$-*R* and $\Delta\Delta\Lambda$-*R*, respectively, are shown in Fig. 4. The cal-

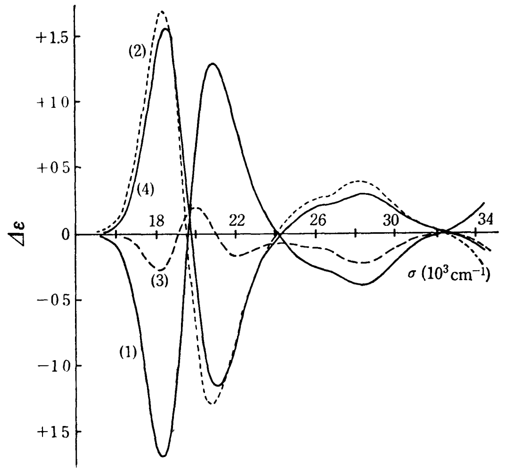

Fig. 4. CD curve analysis of *cis*(*O*)-[Co(L-alama)-(dien)]$^+$ complex: (1) Λ confirguational curve, 1/2× {Δε(iii)−Δε(iv)}; (2) Δ configurational curve, 1/2× {Δε(iv)−Δε(iii)}; (3) {*R*(*N*)+L(*C*)} vicinal curve, 1/2×{Δε(iii)+Δε(iv)}; and (4) observed CD curve of $(+)_{589}$-*unsym-cis*(*O*)-[Co(ida)(dien)]$^+$.

culated Δ configurational curve shows a positive and a negative CD band from lower energy side in the first absorption band region and agrees well with the observed CD curve of $(+)_{589}$-*unsym-cis*(*O*)-[Co(ida)-(dien)]$^+$, which has been assigned to ΔΔΛ configuration by previous authors.[3] Since the higher energy component of the first absorption band of the *cis*(*O*)-[Co(N)$_4$(O)$_2$]$^+$ type complex is related to the *E*(D$_{4h}$) parentage, the above assignment is along the line of a normal CD sign pattern for the first absorption band components.[10]

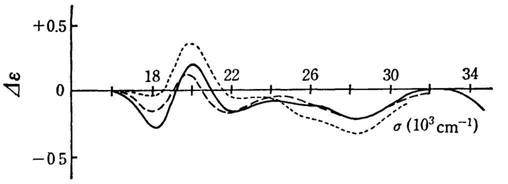

Fig. 5. CD curves of *cis*(*O*)-*R*-[Co(L-alama)(NH$_3$)$_3$]$^+$ (----)[1], *sym-cis*(*O*)-*R*-[Co(L-proma)(dien)]$^+$ (……), and vicinal effect curve of *unsym-cis*(*O*)-*R*-[Co(L-alama)-(dien)]$^+$ (——).

The calculated vicinal contribution *R*(*N*)+L(*C*) for the *unsym-cis*(*O*)-*R*-[Co(L-alama)(dien)]$^+$ diastereomers coincides well with the observed CD curve of *cis*(*O*)-*R*-[Co(L-alama)(NH$_3$)$_3$]$^+$ complex[1] (Fig. 5). In conclusion, the additivity rule is well applicable to the present complexes to separate the configurational and vicinal CD curves, and the CD curve analysis (Figs. 4 and 5) established the configurations of the two *unsym-cis*(*O*) isomers of [Co(L-alama)(dien)]$^+$; namely the isomer iii has *ΔΛΛ-R* configuration and the isomer iv *ΔΔΛ-R*. The observed CD curve of the *cis*(*O*)-*R*-[Co(L-proma)(dien)]$^+$ is also similar to the vicinal curves of L-alama complexes (Fig. 5). This shows that the *cis*(*O*)-*R*-[Co(L-proma)(dien)]$^+$ complex has actually the *sym-cis*(*O*) structure as predicted from molecular model consideration. The *sym-cis*(*O*)-[Co(L-alama)-(dien)]$^+$ complex (isomer ii) shows somewhat different CD (Table 2), and the asymmetric nitrogen configuration of this isomer is not clear at present.

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