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Absorption Spectra and Circular Dichroisms of Metal Complexes. II. Preparation and Structure of Isomers of L-Aminoalcohol Cobalt(III) Complexes

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Seven new optically active complexes of *fac*-Δ- and *fac*-Λ-$[Co_2(L\text{-amoH})_3(L\text{-amo})_3]^{3+}$ type have been prepared, where L-amoH and L-amo denote L-aminoalcohol and L-aminoalcoholate ion, respectively. The geometrical and the absolute configuration around the metal ion of these complexes have been determined on the basis of their absorption and circular dichroism (CD) spectra. The complexes are monomeric tervalent complex ions in acid solution. In organic solvents and in crystalline states, they seem to have a dimeric structure with face-to-face O···H···O hydrogen bonds between three OH groups of the triprotonated $[Co(L\text{-amoH})_3]^{3+}$ and three oxygen atoms of the deprotonated $[Co(L\text{-amo})_3]^0$.

Although many examples of the stereospecific coordination of optically active diamines or amino acids to metal ions have been reported,[1] no work has been done concerning the complex containing optically active aminoalcohols. Yoneda and Kida[2] prepared the ethanolamine cobalt(III) complex, in which the ethanolamine coordinates to the cobalt ion as a bidentate ligand to form a five membered ring. Since the conformation of chelated ethanolamine will be a gauche form, the coordination of optically active aminoalcohols, such as L-alaninol, to the metal ion is expected to be stereospecific, as in the case of complex formation from *l*-propylenediamine and cobalt(III) ion.[3] In this paper we report the stereospecific preparation of some optically active cobalt(III) complexes of L-alaninol, -leucinol, -isoleucinol and -prolinol, and assign the geometrical and the absolute configuration of these complexes on the bases of an analysis of their absorption spectra and circular dichroism curves.

Experimental

Ligands. The optically active aminoalcohols, L-alaninol, -leucinol, -isoleucinol and -prolinol were prepared by reducing the corresponding L-amino-acid ethyl esters[4] with lithium aluminum hydride according to the method described by Karrer *et al.*[5] The aminoalcohols were distilled freshly before the use for preparation.

Preparation of the Complexes.[*2] 1) *fac*-Δ-$[Co_2(L\text{-alanoH})_3(L\text{-alano})_3](ClO_4)_3 \cdot 2H_2O$. A mixture containing 4.0 g of $[Co(OH_2)(NH_3)_5](ClO_4)_3$ and 2.0 g of L-alaninol in 100 m*l* of water was heated on a water bath at 90°C with frequent stirring for an hour. After cooling down to the room temperature, the dark reddish violet solution was filtered to remove $[Co(NH_3)_6](ClO_4)_3$ produced during the reaction. The filtrate was evaporated gradually on a water bath at 60°C to about 20 m*l* and kept at room temperature for two or three days. The reddish violet crystals deposited gradually were filtered off and washed with ethanol and ether. The crude complex was recrystallized from 0.1 N perchloric acid solution by adding a mixture of ethanol and ether (1 : 1) and then cooling it in a refrigerator. This complex is soluble in water, methanol and perchloric acid but insoluble in ethanol and ether. The aqueous solution decomposed gradually and gave a dark brown solution.

Found: C, 24.00; H, 6.21; N, 9.46%. Calcd for $C_{18}H_{55}N_6O_{20}Cl_3Co_2 = [Co_2(L\text{-alanoH})_3(L\text{-alano})_3](ClO_4)_3 2H_2O$: C, 24.02; H, 6.16; N, 9.33%.

An attempt to prepare the corresponding bromide or sulfate was unsuccessful because of their large solubilities in accessible solvents.

2) *fac*-Δ-$[Co_2(L\text{-leunoH})_3(L\text{-leuno})_3]_2(SO_4)_3 \cdot 3H_2O$. The crude complex was obtained by warming a mixture containing 3.4 g of L-leucinol and 2.9 g of $[Co(OH_2)_2(NH_3)_4](SO_4)_3 \cdot 3H_2O$ in 25 m*l* of water at 70°C for three hours. Recrystallization was made as follows; to the 2 N sulfuric acid solution of crude complex was

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1) See for example, J. H. Dunlop and R. D. Gillard, "Stereoselectivity in Coordination Compounds" in "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, New York (1966), Vol. 9, pp. 184—215.

2) H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960).

3) F. P. Dwyer, F. L. Garvan and A. Schulman, *ibid.*, **81**, 290 (1959).

4) E. Fischer, *Ber.*, **34**, 433 (1901); G. Hillmann, *Z. Naturforschg.*, **1**, 682 (1946).

[*2] The following abbreviations are used; L-alaninol = L-alanoH, L-leucinol = L-leunoH, L-isoleucinol = L-isoleunoH, L-prolinol = L-prolinoH.

5) P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948).

added dropwise with stirring 1 N sodium hydroxide solution until the pH value of the solution reached 6. After a while, the precipitates, which might be a Λ-type leucinol complex contained in the crude complex, were removed by filtration. The desired Δ-type complex was obtained by adding more 1 N sodium hydroxide solution to the filtrate to pH 8. This procedure was repeated to give a constant CD curve. The pure complex is insoluble in water, ethanol and ether, but fairly soluble in dilute sulfuric acid, and more in a mixture of concentrated sulfuric acid and methanol (1 : 1).

Found: C, 43.84; H, 10.38; N, 8.52%. Calcd for $C_{36}H_{89}N_6O_{13}S_{3/2}Co_2 = [Co_2(\text{L-leunoH})_3(\text{L-leuno})_3](SO_4)_{3/2}H_2O$: C, 44.12; H, 9.15; N, 8.57%.

3) *fac*-Λ-$[Co_2(\text{L-leunoH})_3(\text{L-leuno})_3]Br_3$. The crude complex was obtained by a procedure similar to that used for the Δ-leucinol complex, with 2.0 g of L-leucinol and 2.2 g of $[Co(OH_2)(NH_3)_5]Br_3$. The product was dissolved in a mixture of 47% hydrobromic acid and methanol (1 : 1), and 1 N sodium hydroxide solution was added dropwise to the solution to pH 1. The precipitate was recrystallized repeatedly by the above method to obtain a constant CD curve. The pure complex is insoluble in water and methanol, but slightly soluble in concentrated hydrobromic acid and fairly so in a mixture of concentrated hydrobromic acid and methanol (1 : 1).

Found: C, 40.63; H, 8.31; N, 7.78%. Calcd for $C_{36}H_{87}N_6O_6Br_3Co_2 = [Co_2(\text{L-leunoH})_3(\text{L-leuno})_3]Br_3$: C, 40.88; H, 8.29; N, 7.94%.

4) *fac*-Δ-$[Co_2(\text{L-isoleunoH})_3(\text{L-isoleuno})_3]_2(SO_4)_3 \cdot 7H_2O$ and *fac*-Λ-$[Co_2(\text{L-isoleunoH})_3(\text{L-isoleuno})_3]Br_3 \cdot 3H_2O$. These complexes were prepared by recrystallizing the crude products which were obtained by the procedures similar to those for the corresponding L-leucinol complexes.

Found: C, 39.65; H, 9.17; N, 7.45%. Calcd for $C_{36}H_{101}N_6O_{19}S_{3/2}Co_2 = [Co_2(\text{L-isoleunoH})_3(\text{L-isoleuno})_3](SO_4)_{3/2} \cdot 7H_2O$: C, 39.73; H, 9.36; N, 7.72%.

Found: C, 38.88; H, 8.00; N, 7.47%. Calcd for $C_{36}H_{93}N_6O_9Br_3Co_2 = [Co_2(\text{L-isoleunoH})_3(\text{L-isoleuno})_3]Br_3 \cdot 3H_2O$: C, 38.89; H, 8.43; N, 7.56%.

5) A mixture of *fac*-Δ- and *fac*-Λ-$[Co_2(\text{L-prolinoH})_3(\text{L-prolino})_3](ClO_4)_3$. A mixture containing 2.0 g of L-prolinol and 2.3 g of $[Co(OH_2)_2(NH_3)_4](ClO_4)_3$ in 40 m*l* of water was evaporated gradually with frequent stirring on a water bath at 60°C to about 20 m*l*, and kept at room temperature for a day. The reddish purple crystals were a mixture of *fac*-Δ- and *fac*-Λ-L-prolinol complex.

Separation of Δ- and Λ-Isomer. The product was dissolved in a mixture of 60% perchloric acid and methanol (1 : 1), and filtered once. The crude Λ-complex was precipitated by adjusting the pH of the filtrate to 1 with 2 N sodium hydroxide solution. Pure Λ-complex was obtained by recrystallizing these precipitates repeatedly by the same method until the CD exhibited identical curves.

To the filtrate which was made free from the Λ-complex was added more 2 N sodium hydroxide solution slowly and the pH of the solution was adjusted to about 4. The precipitate was filtered off and recrystallized by the same method repeatedly to have a constant CD curve. Both the *fac*-Δ- and the *fac*-Λ-complex were insoluble in water and methanol, but fairly soluble in acetone and dilute perchloric acid and more in a mixture of 60% perchloric acid and methanol (1 : 1).

Found: *fac*-Δ isomer, C, 31.26; H, 6.38; N, 7.23%. Calcd for $C_{30}H_{77}N_6O_{25}Cl_3Co_2 = [Co_2(\text{L-prolinoH})_3(\text{L-prolino})_3](ClO_4)_3 \cdot 7H_2O$, C, 31.40; H, 6.76; N, 7.32%.

Found: *fac*-Λ isomer, C, 34.17; H, 6.21; N, 7.79%. Calcd for $C_{30}H_{67}N_6O_{20}Cl_3Co_2 = [Co_2(\text{L-prolinoH})_3(\text{L-prolino})_3](ClO_4)_3 \cdot 2H_2O$, C, 34.07; H, 6.39; N, 7.95%.

Measurements. Visible and ultraviolet absorption spectra were obtained by Hitachi recording spectrophotometer Model 124. The CD curves were recorded with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. All the measurements were made at room temperature, 15—20°C.

Results and Discussion

Numerical data for the absorption and the CD bands of the complexes are given in Table 1. Figures 1—5 show the absorption and the CD spectra of the complexes prepared here.

Yoneda and Kida[2] reported that the ratio of cobalt to anion in the crystalline ethanolamine cobalt(III) complex salts was always 2 : 3, and assumed that the complex should be regarded as a double salt involving two different cations, $[Co\,eta_2\,eta']^{2+}$ and $[Co\,eta\,eta'_2]^{+}$ (eta $= NH_2CH_2CH_2OH$, eta' $= NH_2CH_2CH_2O^-$) bonded with each other through O–H–O hydrogen bonds. All the aminoalcohol complexes prepared here have the same molar ratio as that of the ethanolamine complex.

Configuration of the Isomers. Since the donor atoms of an aminoalcohol are nitrogen and

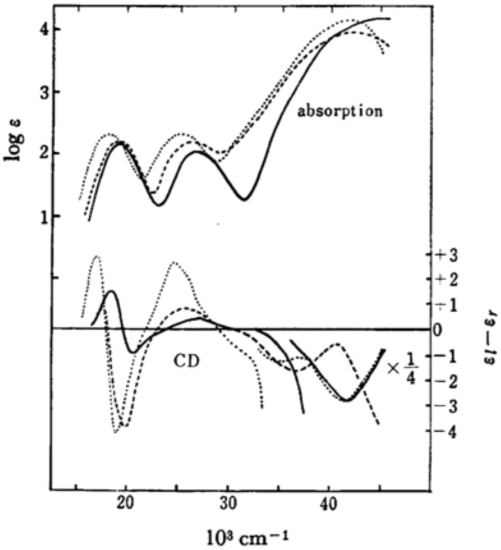

Fig. 1. Absorption and circular dichroism curves of L-alaninol complex.
—— in 30% $HClO_4$
---- in absolute methanol
...... in a mixture (1 : 1, v/v) of methanol and 0.1 N aq. NaOH soln.
log ε and $\varepsilon_l - \varepsilon_r$ are converted into per one mole of cobalt

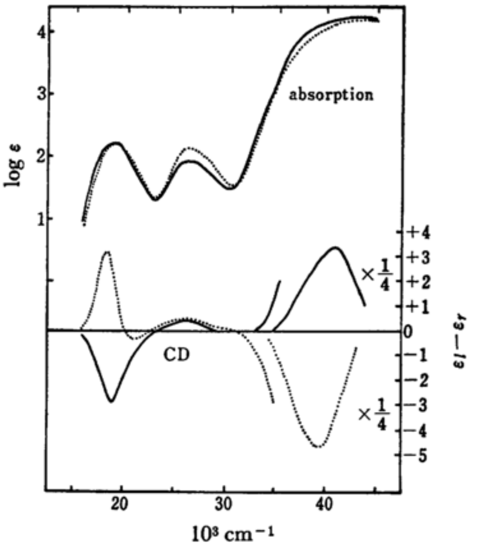

Fig. 2. Absorption and circular dichroism curves of L-leucinol complexes in 60% $HClO_4$-methanol (1 : 1).
······ *fac-Δ* isomer —— *fac-Λ* isomer
log ε and $\varepsilon_l-\varepsilon_r$ are converted into per one mole of cobalt.

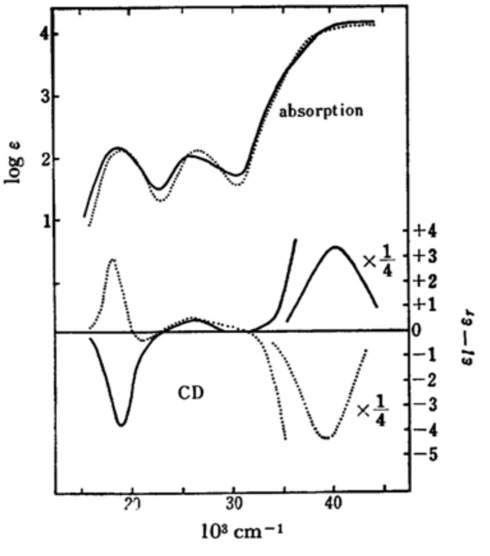

Fig. 3. Absorption and circular dichroism curves of L-isoleucinol complexes in 60% $HClO_4$-methanol (1 : 1).
······ *fac-Δ* isomer —— *fac-Λ* isomer
log ε and $\varepsilon_l-\varepsilon_r$ are converted into per one mole of cobalt.

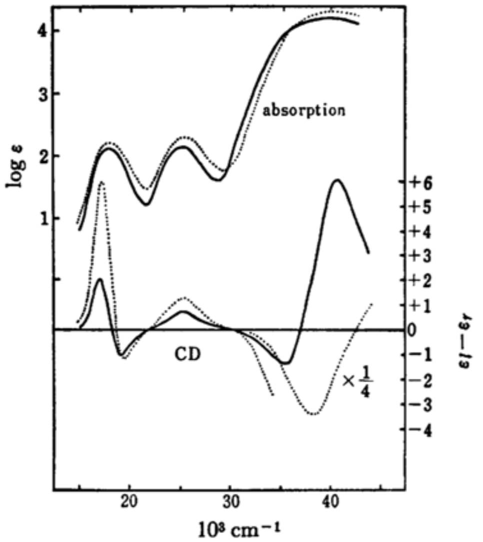

Fig. 4. Absorption and circular dichroism curves of L-prolinol complexes in 60% $HClO_4$-methanol (1 : 1).
······ *fac-Δ* isomer —— *fac-Λ* isomer
log ε and $\varepsilon_l-\varepsilon_r$ are converted into per one mole of cobalt.

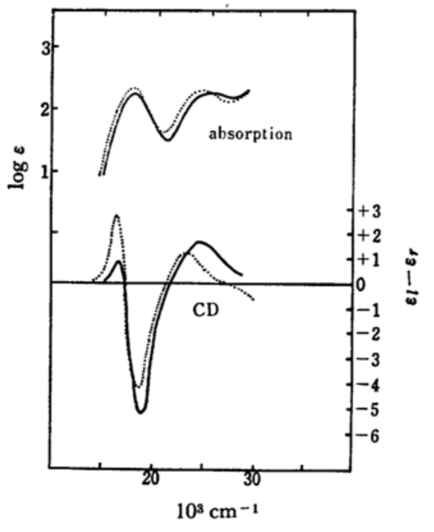

Fig. 5. Absorption and circular dichroism curves of L-prolinol complexes in acetone.
······ *fac-Δ* isomer —— *fac-Λ* isomer
log ε and $\varepsilon_l-\varepsilon_r$ are converted into per one mole of cobalt.

oxygen, two geometrical isomers, facial (*fac*) and meridional (*mer*), are possible, and each of these isomers has its optical enantiomer, $\Delta(C_2)$ or D and $\Lambda(C_2)$ or L. The geometrical isomers can be distinguished from their absorption spectra; the first band of the *mer* form, having a lower symmetry (C_1), should split to a much greater extent than that of the *fac* form, having a higher symmetry (C_3).⁶⁾

As Figs. 1—4 show, the first bands of all the complexes exhibit always nearly symmetrical curves

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6) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956); F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

TABLE 1. NUMERICAL DATA FOR ABSORPTION (AB) AND CIRCULAR DICHROISM (CD)

fac-complex ion	I Band				II Band				C. T. Band	
	AB		CD		AB		CD		CD	
	ν_{max}	log ε	ν_{max}	$\varepsilon_l-\varepsilon_r$	ν_{max}	log ε	ν_{max}	$\varepsilon_l-\varepsilon_r$	ν_{max}	$\varepsilon_l-\varepsilon_r$
Δ-[Co_2(L-alanoH)$_3$ (L-alano)$_3$]$^{3+}$	19.2$^{a)}$	2.14	18.1 20.6	+1.54 −0.84	27.0	2.04	26.2	+0.45	41.8	−11.10
	18.9$^{b)}$	2.22	17.7 19.8	+0.77 −3.92	25.9	2.19	25.3	+0.86	36.5 40.9	− 6.38 − 2.30
	17.9$^{c)}$	2.32	16.9 19.1	+2.87 −4.16	25.0	2.33	24.6	+2.65	35.7^{sh} 41.5	− 5.20 −11.40
Δ-[Co_2(L-leunoH)$_3$ (L-leuno)$_3$]$^{3+}$	19.2$^{a)}$	2.18	18.3 20.8	+3.15 −0.34	26.9	2.14	25.6	+0.52	39.4	−18.58
Λ-[Co_2(L-leunoH)$_3$ (L-leuno)$_3$]$^{3+}$	18.9$^{a)}$	2.20	18.9	−2.89	26.7	1.93	26.3	+0.38	41.7	+13.55
Δ-[Co_2(L-isoleunoH)$_3$ (L-isoleuno)$_3$]$^{3+}$	19.2$^{a)}$	2.15	18.3 20.8	+2.93 −0.36	26.9	2.10	25.6	+0.51	39.2	−17.29
Λ-[Co_2(L-isoleunoH)$_3$ (L-isoleuno)$_3$]$^{3+}$	18.9$^{a)}$	2.22	18.9	−3.73	26.6	2.03	26.2	+0.45	40.3	+13.40
Δ-[Co_2(L-prolinoH)$_3$ (L-prolino)$_3$]$^{3+}$	18.1$^{a)}$	2.25	17.3 19.4	+5.99 −1.25	25.4	2.35	25.2	+1.27	38.0	−13.9
	17.8$^{d)}$	2.35	16.7 18.9	+2.84 −4.59	24.6	2.31	24.7	+0.91		
Λ-[Co_2(L-prolinoH)$_3$ (L-prolino)$_3$]$^{3+}$	18.1$^{a)}$	2.11	17.2 19.2	+2.05 −1.04	25.3	2.16	25.3	+0.79	35.6 40.7	− 1.45 + 6.10
	18.0$^{d)}$	2.20	16.5 18.5	+0.88 −5.32	25.9	2.31	23.5	+1.06		

ν in 10^3 cm^{-1}; sh shoulder; C. T. charge transfer

a) in 5 N $HClO_4$; b) in absolute methanol; c) in a mixture (1 : 1, v/v) of methanol and 0.1 N aq. NaOH soln.; d) in acetone

log ε and $\varepsilon_l-\varepsilon_r$ are converted into per one mole of cobalt.

and no indication of splitting in the solvents used here. These facts indicate that all the complexes have the *fac* configuration around the cobalt(III) ion. The shift of the first and the second absorption bands of the alaninol and the prolinol complex in the different solvents may be related to the deprotonation of the hydroxo group in coordinated aminoalcohols (Figs. 1 and 5). This can be compared to the relation between aquo and hydroxo cobalt(III) complexes in acid and alkaline solutions.

The absolute configuration of the complexes can be assigned safely from their CD spectra. The CD curve of the L-alaninol complex in acid exhibits one strong positive and one weak negative peak in the first band region (Fig. 1). Such a pattern is characteristic of the Δ-type complex with trigonal symmetry and is very similar to those of such complexes of known absolute configuration as *fac*-Δ-[Co(L-alanine)$_3$]$^{7)}$ or Δ-[Co(L-pn)$_3$]$^{3+}$ (pn=propylenediamine)$^{8)}$. Since the complex ion in acid will exist as a monomeric protonated tris-alaninol complex, we conclude that the complex ion is of *fac*-Δ type around the cobalt(III) ion. The sulfates of L-leucinol and L-isoleucinol complex show CD curves similar to that of *fac*-Δ L-alaninol complex and can be assigned to the *fac*-Δ type, too (Figs. 2 and 3). The CD curves of the bromides of L-leucinol and L-isoleucinol complex, on the other hand, exhibit only a strong negative peak at *ca.* 19000 cm^{-1}, and are very similar to that of Λ-[Co(D-pn)$_3$]$^{3+}$.$^{8)}$ Therefore, we have assigned these bromides to the *fac*-Λ-configuration.

Figure 4 shows that both isomers of the L-prolinol complex give very different CD spectra from those of the above complexes in the first band region. Both appear to be typical of the Δ-type complex, although the CD intensity of one isomer is exceptionally large. Since both the isomers have been assigned to the *fac* form from their absorption spectra, they should be diastereomeric with each other. In order to determine the absolute configuration of these isomers, the CD in

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7) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965); E. Larsen and S. F. Mason, *J. Chem. Soc., (A)*, **1966**, 313; J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, **1965**, 6531; R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966); M. G. B. Drew, J. H. Dunlop, R. D. Gillard and D. Rogers, *Chem. Commun.*, **1966**, 42.

8) A. J. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 49; H. Iwasaki and Y. Saito, This Bulletin, **39**, 92 (1966).

the ultraviolet region seems to give a useful information. From the CD spectra of the alaninol, leucinol and isoleucinol complexes in the ultraviolet region, it will be recognized that the Δ-type complex in acid exhibits a strong negative CD band at *ca.* 39000 cm^{-1}, while the Λ-type complex a positive CD band at *ca.* 40000 cm^{-1} with a smaller intensity than that for the Δ-type complex. Such a relation was also observed in the CD spectra of Δ- and Λ-[Co(L-pn)$_3$]$^{3+}$.[9] On this empirical observation, the isomer which was separated below pH 1 could be assigned to the Λ-type, and the other isomer which precipitated at a higher pH to the Δ-type, as may be seen in Fig. 4. These CD bands may correspond to the charge transfer transition between the coordinated aminoalcohol and the cobalt(III) ion.

The higher CD intensity of Δ-prolinol complex or anomalous CD appearance of Λ-prolinol complex in the first band region as compared with those of the other aminoalcohol complexes could be explained by considering the vicinal effect of asymmetric nitrogen atoms of L-prolinols. The donor nitrogen atom of L-prolinol coordinated as a bidentate ligand becomes an asymmetric atom, and is forced to take a configuration antipodal to that of the similarly coordinated D-prolinol. The same CD behavior was observed in some L-proline complexes.[10] In the Λ-complex of L-prolinol, a negative CD band due to the Λ-configurational effect would be partly compensated by the strong vicinal effect of such an asymmetric nitrogen atom with positive CD sign. The high CD intensity of the Δ-complex of L-prolinol can be explained by the same consideration.

The Δ- and the Λ-isomer of each L-aminoalcohol complex are not enantiomeric with each other, but diastereomeric. If we assume that the stable conformation of the L-aminoalcohol, which has a similar skeletal structure to that of L-(+)$_D$-pn, is δ-gauche form, the Δ- and the Λ-tris-L-aminoalcohol complex should have the "lel" and the "ob" structure, respectively.[11] The *lel* complex is said to be more stable than the *ob* complex.[11] However, except for the case of L-alaninol complex, the reaction of L-aminoalcohols and cobalt(III) ammine complexes gave always both the *lel* and the *ob* complex of *fac*-type. The formation ratio of these isomers seemed to depend on the kind of outer-anion of starting cobalt(III) complexes, and might be related to the solubility of aminoalcohol complexes produced. More detailed study would be needed to elucidate the stereoselective coordination of such complicated ligands as L-leucinol or L-prolinol. In the case of L-alaninol complex, only a stable *lel* isomer was separated from the reaction mixture.

Attempts to prepare the other geometrical isomers, the meridional complexes, were unsuccessful. This might be related to the difficulty in forming a dimeric structure bonded with the O–H–O or N–H–O hydrogen bonding discussed later.

The higher CD intensity of charge transfer bands of the Δ-complexes than those of the Λ-complexes would be caused by a superposition of two CD bands with the same negative sign resulting from the Δ-configurational effect and the vicinal effect of L-aminoalcohols in δ-conformation. A weak negative CD band at 35600 cm^{-1} of the Λ-prolinol complex might be an imaginary minimum which appeared depending on the relation between the positive CD curve of the Λ-configuration and the negative CD curve of the δ-vicinal effect. The vicinal effect of coordinated L-pn in δ-conformation gave also a negative CD band for the charge transfer band in cobalt(III) complexes.[9]

Corresponding to the second absorption bands, both diastereomers give weak positive CD peaks. However, detailed discussion can not be made at the present stage because their origin is uncertain.

CD Spectra in Organic Solvents and in Alkaline Solutions. As is seen in Fig. 1, the CD curves of L-alaninol complex in methanol and in alkaline solution are very different from that in acid solution. The absorption spectra indicate that no substantial change of the complex itself such as decomposition or isomerization occur, but the complexes containing deprotonated L-alaninols will be present in these solvents as stated before. Therefore, such a big change in CD curves might be caused by a special interaction between the two kinds of complex in methanol or alkaline solution. Mason and Norman[12] reported that the CD curve of Δ-[Co en$_3$]$^{3+}$ (en=ethylenediamine) changes remarkably by forming an ion-pair between the complex ion and the phosphate ion, and that the complex ion and the phosphate ion might have a preferred mutual orientation in the ion-pair. The change of CD in the L-alaninol complex is much more remarkable than that in the ethylenediamine complex. A most probable structure of such an aggregate between the L-alaninol complex ions and molecules in methanol will be a dimeric form with face-to-face O···H···O hydrogen bonding between three OH groups of the triprotonated [Co(L-alanoH)$_3$]$^{3+}$ and three oxygen atoms of the deprotonated [Co(L-alano)$_3$]^0. The dimeric structure would also hold in the solid state as indicated by the chemical analysis. The same discussion could be made for the change on CD curves of L-prolinol complexes in acetone (Fig. 5).

In alkaline solutions, all alcoholic protons would be removed and the dimeric form would have O···H···N hydrogen bonding between three

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

[10] T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.*, **78**, 2762 (1965); This Bulletin, **38**, 2025 (1965); T. Yasui, *ibid.*, **38**, 1746 (1965).

[11] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

oxygen atoms of a complex molecule and the three amino groups of another molecule.

As in the case of the Δ-[Co en$_3$]$^{3+}$-phosphate system,[12] the change in CD of the first band in methanol and in alkaline solution might be related to the appearance of a new CD band at *ca.* 36000 cm^{-1}, which originates probably in a charge transfer transition relating to the bridging hydrogen bonding in the aggregate. The absorption spectra in these solvents indicate also the appearance of new absorption bands due to such a transition in the range between 20000 to 40000 cm^{-1}. At present, however, it is almost impossible to interpret the behavior of CD curves of the aggregates in these solvents.

Molecular models of the aggregates show that the O···H···O hydrogen bonding seems to be formed more easily between the Λ(*ob*)-complexes than that between Δ-(*lel*)-complexes, when we assume a tetrahedral angle for ∠Co–O–H and a linear O···H···O hydrogen bonding. Together with the different stabilities between the *lel* and the *ob* form,[11] two different dimeric forms, Δ-Δ and Λ-Λ, might have different stabilities, and consequently different solubilities. Therefore, the two isomers, *fac*-Δ- and *fac*-Λ- complex of each L-leucinol, L-isoleucinol and L-prolinol could be isolated by the solubility differences in solutions with different pH values.

We wish to thank the Ministry of Education for the financial support granted to this research.

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[12] R. Larsson, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, *(A)*, **1966**, 301.