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Circular Dichroism and Absolute Configuration of Triammine(sarcosinate-*N*-monopropionato)cobalt(III) Chloride and Several Analogues

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cis(O)- and *trans(O)*-Triammine(sarcosinate-*N*-monopropionato)cobalt(III) salts, which have an asymmetrically coordinated nitrogen atom, were prepared and the *cis(O)* isomer was optically resolved through its diastereomeric salt with $(+)_{546}$-(ethylenediaminetetraacetato)cobaltate(III) anion. The less soluble diastereomeric salt produced $(+)_{546}$-*cis(O)* isomer of the triammine cation, and its absolute configuration (*R*) was established from circular dichroism spectrum, referring to the stereochemistry of the several analogous triammine complexes stereospecifically formed, which contain L-alaninate- and L-prolinate-*N*-monocarboxylate ligands, where the carboxylate stands for acetate or propionate. Two diastereomeric isomers, *R*(N)–L(C) and *S*(N)–L(C), were synthesized for the *cis(O)*-(L-alaninate-*N*-monopropionato)triamminecobalt(III) perchlorate salt.

In previous papers,[1,2] the stereochemistry was studied for cobalt(III) complexes with several *O,N,O*-tridentate ligands such as L-alaninate-*N*-monoacetate (L-alama^{2-})[1] and L-prolinate-*N*-monopropionate (L-promp^{2-}).[2] Most of these *O,N,O*-tridentate ligands contain an asymmetric carbon atom, and the cobalt(III) complexes formed have two or more kinds of chiral centers, namely each one of asymmetric carbon (L) and nitrogen (*R* or *S*) atoms per one ligand, and in some cases a configurational chirality (Δ or Λ). The additivity of the two or more kinds of circular dichroism (CD) contributions was discussed, but the lack of an appropriate model complex which contains only one asymmetric nitrogen atoms prevented us from thorough elucidation. The present paper deals with such a model complex newly synthesized, triammine(sarcosinate-*N*-monopropionato)cobalt(III) cation. The ligand sarcosinate-*N*-monopropionate (sarmp^{2-}) forms a five- and a six-membered chelate rings by coordination of an α-aminocarboxylate foot and an *N*-propionate one, respectively. This allowed the existence of two geometrical isomers, *cis(O)* and *trans(O)*, of the triammine complex.

The optical resolution of the *cis(O)* isomer was made successfully and the absolute configuration was established from the consideration of the CD spectrum, referring to the stereochemistry and CD spectra of analogous triammine complexes with L-alama^{2-}, L-alamp^{2-} (L-alaninate-*N*-monopropionate), L-proma^{2-} (L-prolinate-*N*-monoacetate), and L-promp^{2-}. The conclusion coincides with that obtained by an X-ray crystal structure study of the diastereomer, $(+)_{546}$-*cis(O)*-$[\mathrm{Co(sarmp)(NH_3)_3}]\cdot(+)_{546}$-$[\mathrm{Co(edta)}]\cdot\mathrm{H_2O}$, of which a preliminary report has been presented recently.[3]

Experimental

Preparation of Ligands. (1). L-alanine-*N*-monoacetic, L-proline-*N*-monoacetic and L-proline-*N*-monopropionic acids were described in the previous papers.[1,2]

(2) L-Alanine-N-monopropionic Acid. A solution of 41 g (0.46 mol) of L-alanine in 92 ml of 5 M potassium hydroxide was mixed with the solution of 50 g (0.46 mol) of 3-chloropropionic acid in 92 ml of 2.5 M potassium hydroxide, and 92 ml of 7.5 M potassium hydroxide was added drop by drop to the mixture with vigorous stirring at 80—85 °C on an oil bath. The mixture was maintained in the pH range 8—9 during the reaction. The reaction mixture was further stirred for about 15 min, cooled to 40 °C, and 119 ml (1.44 mol) of 70% perchloric acid was added to it. The potassium perchlorate resulted was filtered off. The filtrate was concentrated in a vacuum evaporator at 40 °C. The solution concentrated was neutralized with 18 g (0.45 mol) of sodium hydroxide in 20 ml of water. The white deposit was filtered, and recrystallized from warm water. The crystals were washed with ethanol and ether, and then dried in a vacuum desiccator. Yield 33 g. $[\alpha]^{20}_{\mathrm{D}}=+3.2°$ (*c.* 2.47, water). Found: C, 43.93; H, 6.89; N, 8.54%. Calcd for L-alampH$_2$=$\mathrm{C_6H_{11}NO_4}$: C, 44.72; H, 6.88; N, 8.69%.

(3). Sarcosine-*N*-monopropionic acid was prepared by the procedure similar to that in (2), and more soluble in water than the other acids. Found: C, 43.49; H, 6.82; N, 8.43%. Calcd for sarmpH$_2\cdot$1/4H$_2$O=$\mathrm{C_6H_{11}NO_4}\cdot$1/4H$_2$O: C, 43.50; H, 7.00; N, 8.46%.

Preparation and Separation of Complexes. A solution of 8.9 g (0.17 mol) of ammonium chloride and 9.9 ml (0.15 mol) of 28% aqueous ammonia in 40 ml of water was mixed with a solution of the *O,N,O*-tridentate acid (0.042 mol) neutralized by sodium hydroxide in 20 ml of water. To this was added a solution of 10 g (0.042 mol) of cobalt(II) chloride hexahydrate in 10 ml of water. The molar ratio among $\mathrm{Co^{2+}}$, *O,N,O*-tridentate ligand, $\mathrm{NH_3}$, and $\mathrm{NH_4^+}$ takes 1 : 1 : 3.5 : 4. Ten grams of lead dioxide was added to the mixture, and this was stirred at about 40—50 °C for an hr. The color of the solution turned from dark red to reddish violet. After having been allowed to stand at room temperature for 30 min, the reaction mixture was filtered to remove an excess of lead dioxide, and the filtrate was kept in a refrigerator. A small amount of yellow deposit, $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$, was filtered off. The filtrate was poured into a column (35 mm × 500 mm) containing strong-acid cation exchange resin (Dowex 50WX8 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 ml per min.

(4) trans(O)- *and* cis(O)-*[Co(L-promp)(NH$_3$)$_3$]ClO$_4$.* The complexes were already reported.[2] A great portion of the complex obtained consisted of the *cis(O)* isomer, and the *trans(O)* one occurred in a trace amount.

(5) trans(O)-*[Co(sarmp)(NH$_3$)$_3$]ClO$_4$ and* cis(O)-*[Co(sarmp)-(NH$_3$)$_3$]Cl.* Two colored bands, violet one (i)

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[1] K. Okamoto, J. Hidaka, and Y. Shimura, This Bulletin, **44**, 1601 (1971).

[2] K. Okamoto, J. Hidaka, and Y. Shimura, *ibid.*, **46**, 475 (1973).

[3] K. Okamoto, T. Tsukihara, J. Hidaka, and Y. Shimura, *Chem. Lett.*, **1973**, 145.

in a small amount and red one (ii) in a large amount, were eluted in this order. These eluates were separately concentrated in a vacuum evaporator and a large amount of ethanol was added to the concentrated solution. The desired complex was collected by filtration and recrystallized from a small amount of water by adding ethanol. It was confirmed by absorption measurements that the eluate (i) contained *trans(O)*-[Co(sarmp)$(NH_3)_3$]$^+$ and the eluate (ii) *cis(O)* one. The pure complexes were obtained as perchlorate salts. The *cis(O)* perchlorate was dissolved in a small amount of water and the solution was poured into a column containing strong-base anion exchange resin (Dowex 1-X8, 200—400 mesh, chloride form). The column was eluted with water and an appropriate amount of acetone was added to the eluate. In this procedure, the *cis(O)* perchlorate was converted into the chloride salt and washed with acetone and then dried in a vacuum desiccator.

(6) cis(O)-[*Co(ida)*$(NH_3)_3$]*ClO*$_4$. Two colored bands, a reddish violet one (i) in a small amount and a red one (ii) in a large amount, were eluted in this order. It was identified by absorption measurements and analytical results that the eluate (i) was a by-product containing two iminodiacetate ligands and the eluate (ii) was *cis(O)*-[Co(ida)$(NH_3)_3$]$^+$. The eluate (ii) was treated as in (5) and the desired complex was obtained as perchlorate salt.

(7) cis(O)-[*Co(*L*-proma)*$(NH_3)_3$]*ClO*$_4$. Two colored bands, violet one (i) in a small amount and red one (ii) in a large amount, were eluted in this order. From the absorption measurements, the eluate (i) was confirmed to be a by-product as in (6) and the eluate (ii) *cis(O)*-[Co(L-proma)$(NH_3)_3$]$^+$. The eluate (ii) was treated as in (5).

(8) cis(O)-[*Co(*L*-alama)*$(NH_3)_3$]*ClO*$_4$. Only one red band was eluted and the desired complex was obtained by adding a large amount of ethanol to the concentrated eluate and recrystallized from a small amount of water by adding ethanol. Two kinds of crystals were obtained and it was confirmed that one was *cis(O)*-[Co(L-alama)$(NH_3)_3$]$ClO_4\cdot 1/2H_2O\cdot 1/4C_2H_5OH$ and the other *cis(O)*-[Co(L-alama)-$(NH_3)_3$]$ClO_4\cdot 3/4H_2O$, from their absorption and NMR spectra and by elemental analysis (see Table 1).

(9) trans(O)-[*Co(*L*-alamp)*$(NH_3)_3$]*ClO*$_4$, R- *and* S-cis(O)-[*Co(*L*-alamp)*$(NH_3)_3$]*ClO*$_4$. By elution, a reddish purple band (i) in a large amount and two adjacent red bands (ii) and (iii) in small amounts were obtained. By absorption measurements, it was confirmed that the eluate (i) contained *trans(O)*-[Co(L-alamp)$(NH_3)_3$]$^+$ and the eluates (ii) and (iii) *cis(O)*-[Co(L-alamp)$(NH_3)_3$]$^+$. These eluates were separately concentrated in a vacuum evaporator. The perchlorate of *trans(O)* isomer was precipitated by concentrating the eluate (i) and recrystallized from a small amount of water by adding ethanol. The perchlorates of *cis(O)* isomers ii (*R*) and iii (*S*) were obtained by adding a large amount of ethanol to the concentrated eluates (ii) and (iii), respectively. The isomer iii was recrystallized from ethanol and obtained as hygroscopic crystals. These pure complexes were washed with ethanol and dried in a vacuum desiccator.

Optical Resolution of Complex.

(10) $(+)_{546}$-cis(O)-[*Co(sarmp)*$(NH_3)_3$]*Cl.* Silver acetate (0.30 g) was added to a solution of 0.54 g of racemic *cis(O)*-[Co(sarmp)$(NH_3)_3$]Cl in a minimum amount of water and the silver chloride resulted was filtered off. A solution of 0.375 g of $(+)_{546}$-K[Co(edta)]$\cdot 2H_2O$[4] in a minimum amount of water was added to the filtrate. The mixture was concentrated by stream of air at room temperature and then kept in a refrigerator overnight. The violet crystals deposited as the less soluble diasteromer were collected by filtration (yield: 95 mg) and recrystallized from a small amount of water by adding ethanol. The pure diastereomer was washed with ethanol and dried in a vacuum desiccator. An aqueous solution of the diastereomer was poured into a column containing strong-base anion exchange resin (Dowex 1-X8, 200—400 mesh, chloride form) and the column was washed with water. An appropriate amount of acetone was added to the eluate to obtain the desired complex. The optically active $(+)_{546}$-*cis(O)*-[Co(sarmp)-$(NH_3)_3$]Cl was washed with acetone and dried in a vacuum desiccator. $\Delta\varepsilon_{546}=+0.35$.

The analytical results for the cobalt(III) complexes obtained are shown in Table 1.

Measurements. The electronic absorption spectra were measured by a Beckman DU spectrophotometer and Shimadzu spectrophotometer UV-200. The CD spectra were recorded with a JASCO Model J-10 or J-20 spectropolarimeter with a CD attachment or by Roussel-Jouan Dichrograph. A Yanagimoto spectropolarimeter, Model 185, was used to examine the eluates from the chromatographic column. All the measurements were made in aqueous solution at room temperature.

The infrared spectra were measured with a JASCO DS-402G spectrophotometer with NaCl prism using KBr disk samples. The proton nuclear magnetic resonance spectra of the complexes were recorded with a Japan Electron Optics JNM-4H 100 spectrometer operating at 100 MHz, in D_2O solutions. Measurements were carried out using *t*-butanol as an internal standard. All the signals lie at a lower field than that of the standard. The chemical shifts are referred to NaTMS (sodium trimethylsilylpropanesulfonate) as zero; *t*-butanol resonate at 1.234 ppm down field of NaTMS.

Results and Discussion

Visible Absorption Spectra. The present triammine complexes which belong to a $[Co^{III}(O)_2(N)_4]$ type are divided into two groups on the characteristics of splitting of their first d–d absorption bands. The first group has a shoulder at higher energy side of the major peak which is located at $18.3—19.0\times10^3\ cm^{-1}$, and the second group a vague shoulder at lower energy side of the major peak, $19.3—19.9\times10^3\ cm^{-1}$ (Fig. 1 and Table 2). By referring to a general theory of the splitting pattern of first absorption bands of cobalt(III) complexes,[5,6] it is concluded that the first group (including L-alamp, L-promp, and sarmp complexes) has *trans(O)* structure with a meridionally coordinated *O,N,O*-tridentate ligand and the second (including ida, L-alama, and L-proma complexes and another set of L-alamp, L-promp, and sarmp ones) has *cis(O)* structure with a facially coordinated *O,N,O*-tridentate ligand. The ligands ida, L-alama, and L-proma form two five-membered chelate rings by coordination and the ligands L-alamp, L-promp, and sarmp form each one of five- and six-membered chelate ring with an α-aminocarboxylate part and an *N*-propionate foot, respectively. Thus the inclusion of the six-membered

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[4] F. P. Dwyer and F. L. Garvan, "Inorg. Syntheses," Vol. 6, p. 192 (1960).

[5] H. Yamatera, This Bulletin, **31**, 95 (1958); C. E. Schäffer and C. K. Jørgensen, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **34**, No. 13 (1965).

[6] N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967).

TABLE 1. ANALYTICAL DATA

Complex	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
trans(*O*)-[Co(L-alamp)$(NH_3)_3$]ClO_4·1/2H_2O	19.08	18.63	5.07	5.08	14.84	14.72
trans(*O*)-[Co(sarmp)$(NH_3)_3$]ClO_4·1/2H_2O·1/4$NaClO_4$	17.65	17.96	4.69	4.74	13.72	13.92
cis(*O*)-[Co(ida)$(NH_3)_3$]ClO_4·1/4H_2O	13.92	13.97	4.24	4.33	16.24	16.23
cis(*O*)-[Co(L-alama)$(NH_3)_3$]ClO_4·3/4H_2O	16.31	16.35	4.79	4.82	15.22	15.27
cis(*O*)-[Co(L-alama)$(NH_3)_3$]ClO_4·1/2H_2O·1/4C_2H_5OH	17.60	17.22	4.97	4.93	14.94	15.26
cis(*O*)-[Co(L-proma)$(NH_3)_3$]ClO_4·1/4H_2O	21.83	22.17	4.84	4.82	14.55	14.43
cis(*O*)-[Co(L-alamp)$(NH_3)_3$]ClO_4·H_2O (isomer ii)	18.63	18.47	5.21	5.20	14.49	14.27
cis(*O*)-[Co(L-alamp)$(NH_3)_3$]ClO_4·H_2O (isomer iii)	18.63	18.35	5.21	5.01	14.49	14.51
cis(*O*)-Co(sarmp)$(NH_3)_3$]Cl	23.66	23.34	5.96	5.97	18.39	18.19
$(+)_{546}$-*cis*(*O*)-[Co(sarmp)$(NH_3)_3$]Cl·H_2O	22.36	22.29	6.25	6.28	17.37	17.24

TABLE 2. ABSORPTION MAXIMA OF [Co(*O*,*N*,*O*-tridentato)$(NH_3)_3$]$^+$ IONS

Complex ion	I band		II band	
	$\tilde{\nu}_{max}$	(log ε_{max})	$\tilde{\nu}_{max}$	(log ε_{max})
trans(*O*)-[Co(L-alamp)$(NH_3)_3$]$^+$	19.0	(2.24)	27.7	(2.14)
trans(*O*)-[Co(L-promp)$(NH_3)_3$]$^+$	18.5	(2.23)	27.1	(2.24)
trans(*O*)-[Co(sarmp)$(NH_3)_3$]$^+$	18.3	(2.17)	27.0	(2.20)
cis(*O*)-[Co(ida)$(NH_3)_3$]$^+$	19.9	(2.00)	28.3	(2.13)
cis(*O*)-[Co(L-alama)$(NH_3)_3$]$^+$	19.8	(1.96)	28.2	(2.09)
cis(*O*)-[Co(L-proma)$(NH_3)_3$]$^+$	19.4	(1.99)	28.5	(2.06)
cis(*O*)-*R*-[Co(L-alamp)$(NH_3)_3$]$^+$	19.8	(2.07)	27.7	(2.07)
cis(*O*)-*S*-[Co(L-alamp)$(NH_3)_3$]$^+$	19.9	(2.02)	27.6	(2.02)
cis(*O*)-[Co(L-promp)$(NH_3)_3$]$^+$	19.3	(1.94)	27.5	(2.00)
cis(*O*)-[Co(sarmp)$(NH_3)_3$]$^+$	19.3	(1.97)	27.3	(2.02)

The wave numbers are given in 10^3 cm^{-1}.

TABLE 3. CD DATA OF [Co(*O*,*N*,*O*-tridentato)$(NH_3)_3$]$^+$ IONS

Complex ion	I band		II band	
	$\tilde{\nu}_{ext}$	($\Delta\varepsilon_{ext}$)	$\tilde{\nu}_{ext}$	($\Delta\varepsilon_{ext}$)
trans(*O*)-*R*-[Co(L-alamp)$(NH_3)_3$]$^+$	17.2	(−0.06)	27.8	(+0.08)
	19.0	(+0.28)		
	21.4	(−0.81)		
trans(*O*)-*R*-[Co(L-promp)$(NH_3)_3$]$^+$	17.2	(−0.64)	27.2	(−0.09)
	19.0	(+0.92)		
	21.3	(−0.10)		
cis(*O*)-*R*-[Co(L-alama)$(NH_3)_3$]$^+$	18.1	(−0.17)	28.4	(−0.22)
	19.8	(+0.12)		
	21.9	(−0.17)		
cis(*O*)-*R*-[Co(L-proma)$(NH_3)_3$]$^+$	17.9	(−0.30)	28.1	(−0.46)
	19.9	(+1.04)		
cis(*O*)-*R*-[Co(L-alamp)$(NH_3)_3$]$^+$ (isomer ii)	18.4	(+0.38)	27.4	(−0.18)
	21.2	(−0.39)		
cis(*O*)-*S*-[Co(L-alamp)$(NH_3)_3$]$^+$ (isomer iii)	17.3	(+0.08)	27.8	(+0.34)
	19.5	(−0.22)		
cis(*O*)-*R*-[Co(L-promp)$(NH_3)_3$]$^+$	18.7	(+0.66)	27.4	(−0.18)
$(+)_{546}$-*cis*(*O*)-*R*-[Co(sarmp)$(NH_3)_3$]$^+$	19.2	(+0.52)	27.8	(−0.14)

The wave numbers are given in 10^3 cm^{-1}.

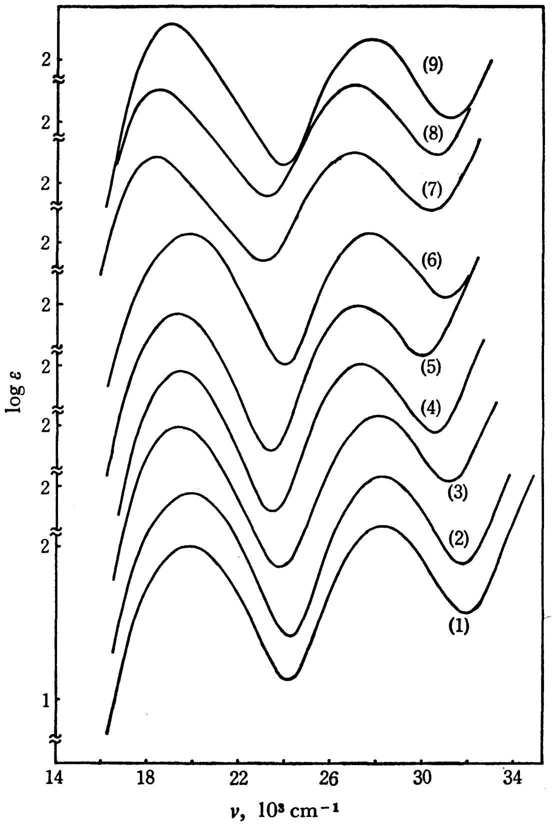

Fig. 1. Absorption curves of [Co(*O*,*N*,*O*-tridentato)$(NH_3)_3$]$^+$ complexes: (1) ida *cis*(*O*), (2) L-alama *cis*(*O*), (3) L-proma *cis*(*O*), (4) sarmp *cis*(*O*), (5) L-promp *cis*(*O*), (6) L-alamp *cis*(*O*)-*R*, (7) sarmp *trans*(*O*), (8) L-promp *trans*(*O*), and (9) L-alamp *trans*(*O*).

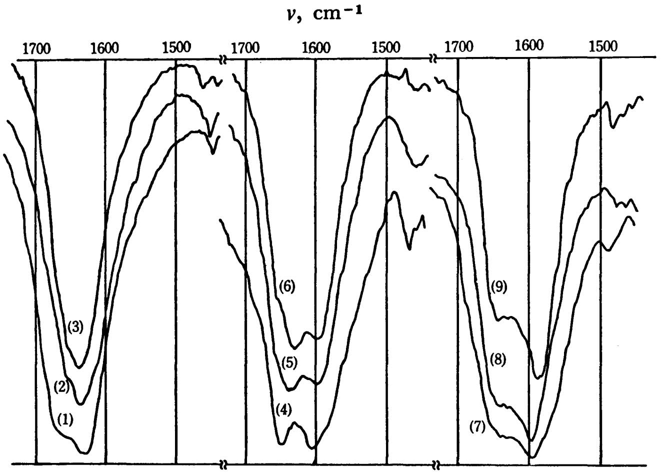

Fig. 2. Infrared curves in antisymmetric C=O stretching band region: (1) ida *cis*(*O*), (2) L-alama *cis*(*O*), (3) L-proma *cis*(*O*), (4) sarmp *cis*(*O*), (5) L-alamp *cis*(*O*)-*R*, (6) L-promp *cis*(*O*), (7) sarmp *trans*(*O*), (8) L-alamp *trans*(*O*), and (9) L-promp *trans*(*O*).

chelate ring is probably a reason for the stable existence of the meridionally coordinated form of the L-alamp, L-promp, and sarmp ligands. It may be worthwhile to note that the maximum intensities of the longer wavelength components of the first absorption bands for the *trans(O)* isomers are unusually large, and this fact is a reason for the apparently weak splitting of the first absorption bands of the *trans(O)* complexes.

Infrared Spectra. The IR spectra in the 1500—1800 cm^{-1} region are illustrated in Fig. 2. The *cis(O)* complexes with ida, L-alama, and L-proma show a strong band at 1630—1640 cm^{-1} and the *cis(O)* complexes with L-alamp, L-promp, and sarmp two strong bands at 1590—1610 cm^{-1} and 1630—1650 cm^{-1}, while the *trans(O)* complexes with L-alamp, L-promp, and sarmp show a strong band at 1585—1600 cm^{-1} with a shoulder at about 1635 cm^{-1}. The bands at 1620—1650 cm^{-1} region are assigned to the antisymmetric C=O stretching of the five-membered chelate ring.[7] The bands at 1585—1610 cm^{-1} region can be assigned to the corresponding carboxylate stretching of the six-membered chelate ring as in the case of [Co(aspartato)$_2$]$^{-}$[8] and [Co(ethylenediaminedisuccinato)]$^{-}$[9].

Stereospecific Formation of Isomers. Since the coordinated nitrogen atom of the *O*,*N*,*O*-tridentate complexes is asymmetric except for the ida complex, two isomers *R* and *S* with respect to the nitrogen atom are possible for each of the complexes. Experimentally, only one *cis(O)* isomer was obtained for [Co(L-proma)$(NH_3)_3$]$^+$, while each one of *cis(O)* and *trans(O)*

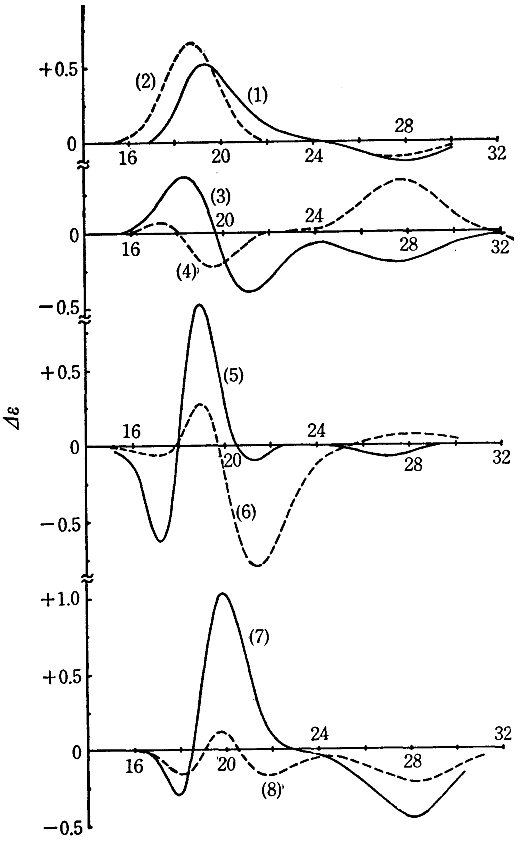

Fig. 3. CD curves of [Co(*O*,*N*,*O*-tridentato)$(NH_3)_3$]$^+$ complexes: (1) sarmp *cis*(*O*)-*R*, (2) L-promp *cis*(*O*)-*R*, (3) L-alamp *cis*(*O*)-*R*, (4) L-alamp *cis*(*O*)-*S*, (5) L-promp *trans*(*O*)-*R*, (6) L-alamp *trans*(*O*)-*R*, (7) L-proma *cis*(*O*)-*R*, and (8) L-alama *cis*(*O*)-*R*.

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7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, 1970, p. 232.

8) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*, **10**, 2187 (1971).

9) J. A. Neal and N. J. Rose, *ibid.*, **7**, 2405 (1968).

isomer for [Co(L-promp)$(NH_3)_3]^+$. It has been well established that the configuration of the nitrogen atom of L-prolinate-*N*-monocarboxylate is restricted to *R* by coordination.[1,2] Accordingly, the three complexes are resonably assigned to *R* configuration. As shown in Fig. 3 and Table 3, CD behavior of *cis(O)*-R-[Co(L-promp)$(NH_3)_3]^+$ is similar to that of *cis(O)*-R-[Co(sarmp)$(NH_3)_3]^+$, of which the absolute configuration has been determined by an X-ray study.[3]

One *trans(O)* and two *cis(O)* isomers were isolated for the [Co(L-alamp)$(NH_3)_3]^+$ complex. Of the two *cis(O)* isomers the latter eluent (isomer iii) was obtained in an extremely low yield. Molecular model constructions indicate that a repulsion between the methyl group of *N*-alaninate chelate ring and the ethylenic portion of the *N*-propionate ring exists so far as the nitrogen atom takes *S* configuration, while no repulsion arises for *R* configuration. This suggests that the isomer ii takes *R* configuration and the isomer iii *S* one, and the NMR data of the two *cis(O)* isomers lead us to the same conclusion. One methyl doublet appears at 1.57 and 1.56 ppm for the isomer ii and iii, respectively. According to a theory of C–O interchelate ring magnetic anisotropic deshielding,[11] the methyl protons in the *S* configuration should resonate up field from that of the *R* one. Accordingly, the isomer ii is assigned to *R* and the isomer iii to *S*. The stereospecific dominancy for *R* configuration of L-alamp is also substantiated for the *trans(O)* isomer, because the CD pattern of this isomer (—, +, and — longer wavelength side) isomer similar to that of *trans*-(*O*)-*R*-[Co(L-promp)$(NH_3)_3]^+$ in the first absorption band region (Fig. 3).

Contrary to the L-alamp complex, only one *cis(O)* isomer is obtained for the L-alama one. The NMR spectrum points out that the isomer obtained is not a mixture of *R* and *S* isomers. In a former work,[1] two isomers (*RR* and *RS*) of three possible ones (*RR*, *RS*, and *SS*) were obtained for *trans(N)*-[Co(L-alama)$_2]^-$ and the non-existence of *SS* isomer and the lower yield of *RS* isomer were explained from the repulsion between the *N*-alaninate methyl group and the protons of acetate of an *S* ligand. The same situation can be supposed for the present triammine complex, *cis(O)*-[Co(L-alama)$(NH_3)_3]^+$. It is thus concluded that the *cis(O)* L-alama isomer obtained takes *R* configuration.

CD and Absolute Configuration. The CD spectra are shown in Fig. 3 and Table 3. The diastereomeric pair of isomers of L-alamp *cis(O)* complex, *R*(N)–L(C) and *S*(N)–L(C), provides a tool to evaluate three vicinal CD contributions *R*(N), *S*(N), and L(C) by adoption of additivity rule[1,11,12]; *i.e.*, the curves (9) *R*(N), (10) *S*(N), and (11) L(C) in Fig. 4 were obtained.

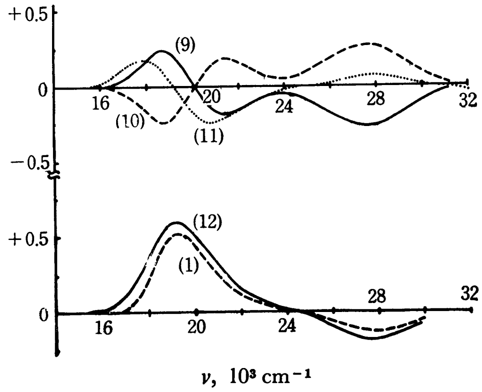

Fig. 4. Curve analyses of *cis*(*O*)-[Co(*O*,*N*,*O*-tridentato)-$(NH_3)_3]^+$ complexes: (9) *R* vicinal curve in L-alamp complex, 1/2×{(3)−(4)}, (10) *S* vicinal curve in L-alamp complex, 1/2×{(4)−(3)}, (11) L vicinal curve in L-alamp complex, 1/2×{(3)+(4)}, (12) *R* vicinal curve in L-promp complex, (2)—(11), compared with the observed R vicinal curve (1) of sarmp *cis*(*O*)-*R* complex.

Substraction of the curve (11) from the curve (2) in Fig. 3 produces a vicinal curve (12) for the *R*(N) contribution of L-promp *cis(O)* complex, and this coincides well with the observed CD curve (1) for the $(+)_{546}$-*cis(O)*-[Co(sarmp)$(NH_3)_3]^+$ complex, which has only one vicinal contribution of the asymmetric nitrogen center. This fact establishes the absolute configuration *R* of the sarmp $(+)_{546}$-*cis(O)* complex in accordance with the result from the X-ray study employing the Bijvoet method.[3] It is noteworthy that the *R*(N) vicinal curve (12) or (1) disagrees with the curve (9), but this may be acceptable since the former is for a tertiary amine nitrogen atom, while the latter for secondary amine nitrogen. Maricondi, Jordan, and Douglas[13,14] showed that a drastic change of the CD intensity of vicinal contribution occurred between the two kinds of coordinated nitrogen centers in some cobalt(III) complexes of edta and its derivatives.

In the first absorption band region, three CD components (—, +, and — from longer wavelength side) are observed for the L-promp *trans(O)-R* complex and this pattern corresponds well with that of the L-alamp *trans(O)-R* one, though there are some differences in intensities (Fig. 3 and Table 3). A similar correlation in CD components is also observed for the L-proma *cis(O)-R* and L-alama *cis(O)-R* complexes. In the last two pairs of complexes, it is not possible to evaluate the individual vicinal contributions of *R*(N) and L(C), because the sarmp *trans(O)* complex was not resolved (due to its lower yield) and the diastereomeric pair of *R*(N)–L(C) and *S*(N)–L(C) of L-alama complex was also not obtained.

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