

Studies on Cobalt(III) Complexes with (*R,S*)-8-Amino-2-methyl-3,6-diaza-octanoate Ion.

II. Determination of Absolute Configuration of Mixed Complexes with the (*S*)-Alaninate Ligand

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(Received November 3, 1986)

Abstract

Trans(O) and β -*mer*(N)*cis*(O) cobalt(III) complexes with (*R,S*)-8-amino-2-methyl-3,6-diazaoctanoate ion (abbreviated as (*R,S*)-amda and (*S*)-alaninate ion ((*S*)-ala) were prepared, subjected to cation exchange chromatography, and characterized by means of visible absorption, CD, and ¹H-NMR spectroscopy. The five optically active diastereoisomers chromatography, and their absolute configurations were assigned in the order of elution to $\Delta_R^S(3S,6R)$, $\Lambda_R^S(3R,6S)$, $\Delta_S^S(3S,6S)$, $\Delta_S^S(3S,6R)$ and $\Lambda_R^S(3R,6S)$ diastereoisomers. Here the subscripts *R* or *S* and superscript *S* designate the absolute configurations of the ligands (*R,S*)-amda and (*S*)-ala, respectively, and the configuration of the secondary amine nitrogen atom (sec-3N and sec-6N in the (*R,S*)-amda) is designated as (3*S*,6*R*) or (3*R*,6*S*). On the other hand, a sample of the β -*mer*(N)*cis*(O) form which was shown to be a mixture of diastereoisomers of ($\Delta_S^S(3S,6R) + \Lambda_R^S(3R,6S)$)-[Co((*S*)-ala)-((*R,S*)-amda)]ClO₄, could not so far be separated into components by ion-exchange chromatography.

Introduction

In the preceding paper, the authors reported on the syntheses and properties of mixed-amino acidato cobalt(III) complexes with (*R,S*)-8-amino-2-methyl-3,6-diazaoctanoate ion ((*R,S*)-amda) [1], which is a methyl-substitution product of 8-amino-3,6-diazaoctanoate ion (abbreviated as dtma or adao) [2–5]. The reaction of cobalt(III)–(*R,S*)-amda complexes with a bidentate amino acid such as glycine or (*S*)-alanine has been found to give many diastereoisomers owing to the situation of the methyl group or α -proton relative to the C–N bond adjacent to the N-substituted alaninate structure in the (*R,S*)-amda.

On the basis of the absorption spectra and ¹H NMR spectra (*cf.* Fig. 1), the racemic diastereoisomers of the complex [Co(gly)((*R,S*)-amda)]ClO₄ isolated by cation-exchange chromatography have been ascertained to be two sorts of *trans*(O) and one sort of β -*mer*(N)*cis*(O) form, whereas, those of the complex [Co(α -ala)((*R,S*)-amda)]ClO₄ to be five sorts of *trans*(O) and two sorts of *cis*(O) forms. It occurred to the present authors that the determination of the absolute configuration of the *trans*(O) isomers in the [Co(α -ala)((*R,S*)-amda)]⁺ might be rendered possible by introducing (*S*)-alanine in place of α -alanine in the preparation of the complexes.

The present paper thus deals with the isolation and the absolute configuration of the [Co((*S*)-ala)-((*R,S*)-amda)]⁺ complex as performed by using cation-exchange column chromatography, and electronic absorption, CD and ¹H NMR spectroscopy.

Experimental

Preparation

trans(O)-[Co((*S*)-ala)((*R,S*)-amda)]ClO₄

The ligand (*R,S*)-amda and the complex *trans*(O)-[Co((*S*)-ala)((*R,S*)-amda)]ClO₄ were prepared in 0.2 molar scale by a method similar to that given in the preceding paper [1], using the complex Na₃[Co(CO₃)₃]·3H₂O [6, 7] as a starting material. Yield: 27 g (*ca.* 31%).

In order to separate the diastereoisomers, 2.0 g of the product obtained was dissolved in water and chromatographed on cation-exchange resin (Dowex 50WX8, Na⁺ form, 100–200 mesh, ϕ : 36 × 770 mm column). By eluting with a 0.08 M aqueous solution of sodium chloride, the adsorbed layer on the resin was separated into five red bands. Each eluant was

TABLE I. Analytical Data and Yield of the Complexes

Label	Complex	C (%)		H (%)		N (%)		Yield (%)
		Found	Calc.	Found	Calc.	Found	Calc.	
E-1	[Co(<i>S</i>)-ala)((<i>R</i>)-amda)]ClO ₄ ·0.5H ₂ O	28.38	27.95	5.94	5.39	13.14	13.04	5
E-2	[Co(<i>S</i>)-ala)((<i>S</i>)-amda)]ClO ₄ ·0.5H ₂ O	28.08	27.95	5.22	5.39	13.25	13.04	7
E-3	[Co(<i>S</i>)-ala)((<i>S</i>)-amda)]Cl·H ₂ O	32.28	32.05	6.32	6.46	15.04	14.96	2
E-4	[Co(<i>S</i>)-ala)((<i>S</i>)-amda)]ClO ₄ ·1.5H ₂ O	27.13	26.83	5.05	5.63	12.04	12.51	7
E-5	[Co(<i>S</i>)-ala)((<i>R</i>)-amda)]ClO ₄ ·1.5H ₂ O	26.84	26.83	5.70	5.63	12.31	12.51	7
	<i>β</i> -mer(<i>N</i>)- <i>cis</i> (<i>O</i>)- [Co(<i>S</i>)-ala)((<i>R,S</i>)-amda)]ClO ₄ ·0.5H ₂ O	27.96	27.95	5.20	5.39	12.44	13.04	35

TABLE II. Absolute Configurations of the Isomeric Compounds of Mixed Complexes [Co(B)(A)]⁺ Separated by Ion-exchange Chromatography

Label	Ligand A = (<i>R,S</i>)-amda, Ligand B =		
	(<i>S</i>)-ala	(<i>R,S</i>)-ala ^a	gly ^a
E-1	$\Delta_R^S(3S,6R)$	$\Delta_R^S(3S,6R) + \Lambda_S^R(3R,6S)$	$\Delta_R(3S,6R) + \Lambda_S(3R,6S)$
E-2	$\Lambda_S^S(3R,6S)$	$\Delta_R^R(3S,6R) + \Lambda_S^S(3R,6S)$	
E-3	$\Delta_S^S(3S,6S)$	$\Delta_S^S(3S,6S) + \Lambda_R^R(3R,6R)$	$\Delta_S(3S,6R) + \Lambda_R(3R,6S)$
E-4	$\Delta_S^S(3S,6R)$	$\Delta_S^S(3S,6R) + \Lambda_R^R(3R,6S)$	
E-5	$\Lambda_R^S(3R,6S)$	$\Delta_S^R(3S,6R) + \Lambda_R^S(3R,6S)$	$\Delta_S(3S,6R) + \Lambda_R(3R,6S)$
<i>β</i> -mer(<i>N</i>)- <i>cis</i> (<i>O</i>)	$\Delta_S^S(3S,6R)$	$\Delta_S^S(3S,6R) + \Lambda_R^R(3R,6S)$	
	$\Lambda_R^S(3R,6S)$	$\Delta_S^R(3S,6R) + \Lambda_R^S(3R,6S)$	$\Delta_S(3S,6R) + \Lambda_R(3R,6S)$

^aRef. 1.

concentrated at the temperature below 35 °C under reduced pressure. The isomers were obtained as the perchlorate salts by addition of sodium perchlorate to the concentrate, except the third-eluted isomer which was obtained as the chloride salt from the concentrate after removal of sodium chloride. The five isomers thus isolated were found to be optically active complexes in accordance with expectation, as mentioned in the next section. These isomers were labelled as E-1, E-2, E-3, E-4 and E-5 in their eluting order. The analytical data and yields of the isomers obtained are listed in Table I together with *β*-mer(*N*)-*cis*(*O*)-[Co(*S*)-ala)((*R,S*)-amda)]ClO₄.

β-mer(*N*)-*cis*(*O*)-[Co(*S*)-ala)((*R,S*)-amda)]ClO₄

To ca. 50 ml of an aqueous solution containing [CoCl₂((*R,S*)-amda)]·0.5H₂O (12.5 g, 0.04 mol) [1], sodium hydroxide (1.6 g, 0.04 mol), (*S*)-alanine (3.6 g, 0.04 mol) and sodium perchlorate (4.9 g, 0.04 mol) were added in this order. The mixture was then heated and stirred in a water bath at 60–65 °C for 2 h. The red crystals were obtained when the solution was allowed to stand overnight in a refrigerator. The product obtained was recrystallized from water. Yield: 6.0 g (35%).

Attempts to isolate the desired diastereoisomers of the complex of the *β*-mer(*N*)-*cis*(*O*) form by means of cation-exchange chromatography were unsuccessful.

Measurements

The electronic absorption spectra of the complexes were measured in an aqueous solution with a Hitachi 124 spectrophotometer. ¹H NMR spectra were obtained on JEOL, JNM-MH 100 spectrometer at 100 MHz, using deuterium oxide as solvent, and the chemical shifts were measured relative to sodium 2,2-di-methyl-2-silapentane-5-sulfonate (DSS). The CD spectra were measured with a JASCO J-40A spectropolarimeter by Dr. Takashi Takakuwa at his applied laboratory of Japan Spectroscopic Co., Ltd.

Results and Discussion

Diastereoisomers

Table II shows the symbols of the absolute configuration of a series of *trans*(*O*)- and *β*-mer(*N*)-*cis*(*O*)-[Co(*S*)-ala)((*R,S*)-amda)]⁺ complexes obtained, in comparison with those of the [Co(*R,S*)-ala)((*R,S*)-

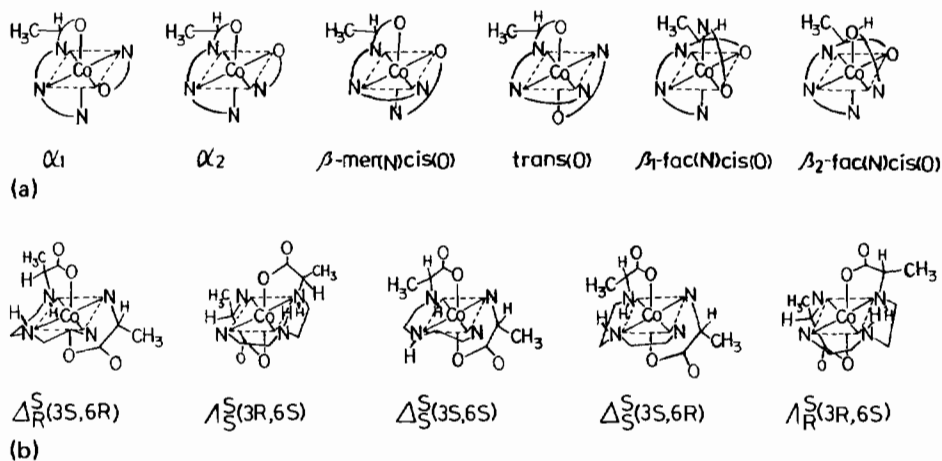


Fig. 1. (a) The possible geometric isomers of $[\text{Co}(\text{N}-\text{O})((R,S)\text{-amda})]^+$ complex; (b) the absolute configurations of $\text{trans}(\text{O})$ - $[\text{Co}(\text{S})\text{-ala}((R,S)\text{-amda})]^+$ isomers.

$\text{amda}]^+$ and $[\text{Co}(\text{gly})((R,S)\text{-amda})]^+$ complexes. Figure 1a shows possible configurations of the cobalt(III) complexes containing the tetradentate- $(R,S)\text{-amda}$ and a bidentate ligand such as glycinate or α -alaninate ion and Fig. 1b, the absolute configurations of the $\text{trans}(\text{O})$ isomers. The β -mer(N)-cis(O) complex was obtained as a mixture of the diastereoisomers of the steric conformation $\Delta_S^S(3S,6R)$ and $\Lambda_S^S(3R,6S)$ and could not be separated into components even by column chromatography.

In the previous paper we pointed out that in the $\text{trans}(\text{O})$ complexes, the elution-order of the diastereoisomers is mainly determined by the fashion of the orientation of the methyl group of the $(R,S)\text{-amda}$ ligand and then by that of orientation of the methyl group of the α -alaninate [1]. Thus, in the $\text{trans}(\text{O})$ - $[\text{Co}(\text{gly})((R,S)\text{-amda})]^+$ complex, the isomer first eluted by chromatography does not have a methyl group located over the C-N bond adjacent to the N-substituted alaninate ring of the $(R,S)\text{-amda}$, and the one eluted second has the methyl group located over the C-N bond. Similarly, in the $\text{trans}(\text{O})$ - $[\text{Co}((R,S)\text{-ala})((R,S)\text{-amda})]^+$ complex, the isomers in the first two eluting bands (E-1, E-2) do not have the methyl group located over the C-N bond, and those of the remaining three bands (E-3-E-5) have the methyl group located over the C-N bond. On the other hand, the factor of dominating elution-order between the two isomers E-1 and E-2 in the first group and between E-3 or E-4 and E-5 in the second group of the $\text{trans}(\text{O})$ - $[\text{Co}((R,S)\text{-ala})((R,S)\text{-amda})]^+$ isomers is the fashion of the orientation of the methyl group of the α -alaninate.

Detailed examination of the molecular models shows that the steric configuration of the $\text{trans}(\text{O})$ - $\Delta_S^S(3S,6R)$ form (E-1) is bulky due to spreading of the methyl group of α -alaninate, compared with the $\text{trans}(\text{O})$ - $\Lambda_S^S(3R,6S)$ form (E-2). Similarly, the $\text{trans}(\text{O})$ - $\Delta_S^S(3S,6S)$ (E-3) and $\Delta_S^S(3S,6R)$ (E-4)

forms have bulky configurations due to the outside orientation of the methyl group of the α -alaninate in octahedron.

The difficulty of separating β -mer(N)-cis(O)- $\Delta_S^S(3S,6R)$ and $\Lambda_S^S(3R,6S)$ by column chromatography may be explained in terms of the small difference in steric compression between the α proton of the alaninate and the α proton or amine protons of $(R,S)\text{-amda}$ in these two isomers (cf. Fig. 5 below). The absolute configuration of the $\text{trans}(\text{O})$ isomers obtained was assigned on the basis of the CD and ^1H NMR spectroscopic data as will be described below.

Electronic Absorption and CD Spectra

The electronic absorption and CD spectra of the isomers from E-1 to E-5 are given in Fig. 2. The data of the absorption and CD bands of the isomers obtained are summarized in Table III. As these isomers (E-1-E-5) show remarkable splitting in their first absorption bands, they can be assigned

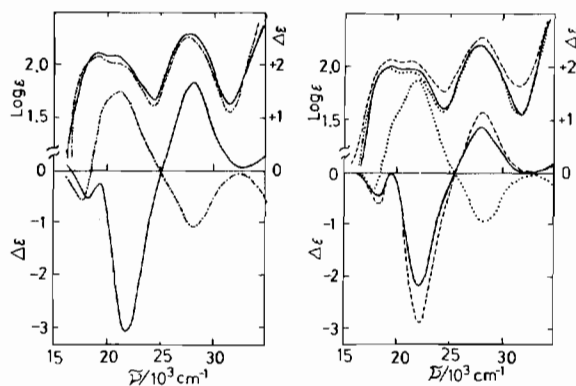


Fig. 2. Absorption and CD spectra of the isomers of $\text{trans}(\text{O})$ - $[\text{Co}((S)\text{-ala})((R,S)\text{-amda})]^+$ complex. (a): E-1, —; E-2, - - -; (b): E-3, ·····; E-4, —; E-5, ·····.

TABLE III. Absorption and CD data of $[\text{Co}((S)\text{-ala})((R,S)\text{-amda})]^+$ Complexes

	I band				CD		II band			
	Absorption				CD		Absorption		CD	
	Ia		Ib		ν max	$\Delta\epsilon^b$	ν max	log ϵ	ν max	$\Delta\epsilon$
	ν max ^a	log ϵ	ν max	log ϵ						
E-1	19.11	2.11	20.20	2.08	18.18	-0.55	27.74	2.30	28.01	+1.68
					21.79	-3.09				
E-2	18.95	2.07	21.45	2.00	17.61	-0.57	27.82	2.26	28.17	-1.07
					21.14	+1.50				
E-3	19.16	2.06	21.41	2.05	18.18	-0.48	27.93	2.27	28.01	+0.84
					22.12	-2.16				
E-4	19.15	2.17	21.35	2.14	18.18	-0.49	27.82	2.35	28.01	+0.86
					22.08	-2.20				
E-5	19.05	2.02	21.45	1.98	17.64	-0.32	27.78	2.22	28.25	-0.93
						+1.76				
β -mer(N)cis(O) form			20.00	2.29	18.94	+0.03	27.69	2.19	29.41	-0.16
					21.10	-0.16				

^aWave numbers are given in 10^3 cm^{-1} . ^b $\Delta\epsilon$ values are given in $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.

to all the *trans*(O) forms; such a spectroscopic behavior is typical of a *trans*(O) isomer in $\text{Co(III)}\text{-N}_4\text{O}_2^+$ form complexes [8–10]. Of the five *trans*(O) isomers, E-3 shows an especially marked splitting as well as that of the racemic diastereoisomer *trans*(O)- $[\text{Co}((R,S)\text{-ala})((R,S)\text{-amda})]\text{ClO}_4$ described previously [1]. Such a phenomena may be considered to result from a specific configuration of the two aza groups ($-\text{NH}-$); it seems reasonable to adopt the absolute configuration (3*S*,6*S*) of the secondary aza groups in E-3. On the other hand, the complex derived from $[\text{CoCl}_2((R,S)\text{-amda})] \cdot 0.5\text{H}_2\text{O}$ and (*S*)-alanine has no shoulder absorption in the first absorption band and its absorption spectrum is quite similar to that of β -mer(N)cis(O)- $[\text{Co}((R,S)\text{-ala})((R,S)\text{-amda})]\text{ClO}_4$.

The absolute configuration of the cobalt(III) complexes with a symmetrical tetradentate ligand such as ethylenediaminediacetate (EDDA) [11] has been assigned on the basis of the sign of major CD band in the first absorption band region and the absolute configuration of *trans*(O)- $[\text{Co}(\text{en})(\text{EDDA})]^+$ complex has been established by Schoenberg *et al.*, using the preparation and ^1H NMR study of *trans*(O)- $[\text{Co}(\text{en})(\text{LL-EDDP})]^+$ complex where LL-EDDP (ethylenediamine-*N,N'*-di- α -propionate) [12] is a dimethylsubstitution product of EDDA. If this same rule is applied to the present complexes, the isomers E-1, E-3 and E-4, which give the positive sign of the maximal component of the CD band in the first absorption band region, can be assigned to *trans*(O)- $\Delta_R^S(3S,6R)$, *trans*(O)- $\Delta_S^S(3S,6S)$ and *trans*(O)- $\Delta_S^S(3S,6R)$, respectively, while the isomers E-2 and E-5, which have the negative sign of the maximal component of the CD band in the same region, can be assigned to *trans*(O)- $\Lambda_S^S(3R,6S)$ and *trans*(O)- $\Lambda_R^S(3R,6S)$, respectively.

The difference of the intensities ($\Delta\epsilon$) of (–) major bands between E-3 and E-4 may be due to one of the absolute configurations of the corresponding sixth aza group of (*S*)-amda coordinated, as described above. Namely, the sixth unsymmetrical aza nitrogen (sec-N(6*S*)) of (*S*)-amda in E-3 seems to give an additive vicinal effect and the one of (*S*)-amda in E-4 not to give the additive effect.

^1H NMR spectra

The ^1H NMR spectra of the *trans*(O) isomers (E-1–E-5) and the β -mer(N)cis(O) one are given in Fig. 3, in comparison with that of the *trans*(O)- $[\text{Co}(\text{gly})((R,S)\text{-amda})]^+$ isomer [1]. In the ^1H NMR spectra of these isomers, triplet or quartet peaks in the high magnetic field region between 1 and 2 ppm

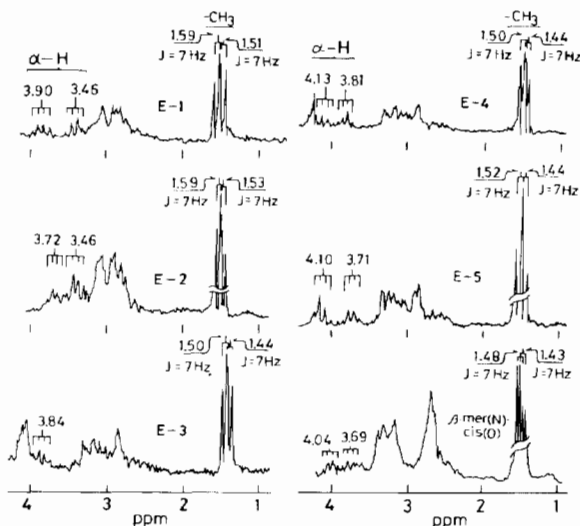


Fig. 3. ^1H NMR spectra of the isomers of *trans*(O)- and β -mer(N)cis(O)- $[\text{Co}((S)\text{-ala})((R,S)\text{-amda})]^+$ complex.

can be assigned to the mixed-resonance of the methyl protons of the coordinated (*R,S*)-amda and (*S*)-ala. On the other hand, the double quartet peaks due to the α -proton of (*R,S*)-amda and (*S*)-ala are observable at a relatively high magnetic field (3.5–4.5 ppm). It is well known that the different chemical shifts of the α -proton or the methyl protons of the ethylenediamine-*N,N'*-di-*L*-propionate (LL-EDDP) in the $[\text{Co}(\text{en})(\text{LL-EDDP})]^+$ complex can be explained in terms of the magnetic anisotropy of the C–N bond [12, 13]. Namely, the signals due to the α -proton or the methyl protons located over the C–N bond adjacent to the N-substituted alaninate ring in the coordinated (*R,S*)-amda shift to a higher magnetic field than ones not located over the C–N bond. In previous work, we have reported that the chemical shift value of 1.59–1.60 ppm in the $[\text{Co}((R,S)\text{-ala})((R,S)\text{-amda})]^+$ isomers can be assigned to the methyl protons located over the C–N bond of the (*R,S*)-amda and that one of 1.43–1.46 ppm in the isomers assigned to the methyl protons not located over the C–N bond on the basis of the consideration of the data of *trans*(O)-[Co(gly)((*R,S*)-amda)]-ClO₄. The chemical shift value of 1.50–1.53 ppm in the $[\text{Co}((S)\text{-ala})((R,S)\text{-amda})]^+$ complexes can be assigned to the methyl protons of (*S*)-alaninate coordinated because of little shifting due to the absence of magnetic anisotropy caused by the C–N bond. Dabrowiak and Cooke succeeded in determining the absolute configuration of a series of bis-(amino acid)cobalt(III) complexes containing optically active amino acids using ¹H NMR steric compression of the isomers [14–16]; the proton involved in the steric compression resonates at a lower magnetic field than when the compression is absent. As can be seen from Fig. 2, the α -proton of the bidentate (*S*)-ala in E-1 (3.90 ppm) resonates at a lower magnetic field than that in E-2 (3.72 ppm). Similarly, in E-3, E-4 and E-5, the α -protons of (*S*)-ala in these isomers evidently shift the resonance position to a slightly higher field in the elution order of the isomers: E-3, 3.84 ppm; E-4, 3.81 ppm; E-5, 3.71 ppm. In considering the absolute configuration of E-1, the configuration $\Delta_R^S(3S,6R)$ places the α -proton of (*S*)-ala in the neighbourhood of a third aza-proton of (*R,S*)-amda at some distance while in the configuration $\Lambda_S^S(3R,6S)$ of E-2, this α -proton locates between two 8-amino protons of (*R,S*)-amda, as schematically shown in Fig. 4. The former isomer should then exhibit slightly higher steric compression than that of the latter. In the methyl protons on coordinated (*S*)-alaninate, the shift is not so great because of its near-equatorial position [14]. Using similar reasoning, it is possible to assign the absolute configuration and ring conformation of obtained *trans*(O) isomers. In this way the *trans*(O) isomers E-1 and E-2 can be considered to have $\Delta_R^S(3S,6R)$ -(λ,λ,λ) and $\Lambda_S^S(3R,6S)$ (δ,λ,δ) while the *trans*(O)

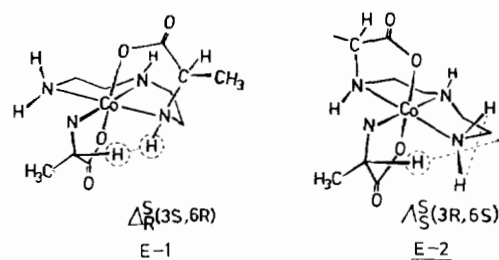


Fig. 4. The diastereoisomers of *trans*(O)-[Co((*S*)-ala)((*R,S*)-amda)]⁺ complex (E-1 and E-2). The H atoms in broken line circles are those in E-1 involved in compressions. The H atom in E-2 is involved in no steric compression. The bond lengths to these atoms have been exaggerated to emphasize the interactions involved in compression.

isomers E-3, E-4 and E-5 are considered to have $\Delta_S^S(3S,6S)$ (δ,λ,δ), $\Delta_S^S(3S,6R)$ (λ,δ,δ) and $\Lambda_R^S(3R,6S)$ (δ,λ,δ), respectively. Here the symbols such as δ or λ in the second bracket represent the ring conformations of the (*S*)-alaninate ring, centre en ring and end en ring on (*R,S*)-amda in this order. The α -proton of the bidentate (*S*)-alaninate in E-3 resonates at a slightly lower field than that of the bidentate (*S*)-alaninate in E-4 because the steric compression in the configuration of *trans*(O)- $\Delta_S^S(3S,6S)$ (δ,λ,δ) of the former should be slightly higher than that in the latter. The ring conformation of the bidentate (*S*)-alaninate in the five *trans*(O) diastereoisomers obtained can thus be considered to have a δ form.

As shown in Fig. 3, the methyl protons of (*R,S*)-amda in the complex $\beta\text{-mer}(\text{N})\text{cis}(\text{O})\text{-}[\text{Co}((S)\text{-ala})((R,S)\text{-amda})]\text{ClO}_4$ resonate at 1.43 ppm, this shows that the methyl group is placed over the C–N bond adjacent to the N-substituted alaninate ring in the coordinated (*R,S*)-amda. On the other hand, the shift value of 3.69 ppm assigned to the α -proton of the (*R,S*)-amda shows that this α -proton is not located over the C–N bond of the (*R,S*)-amda. Since the α -proton of (*S*)-ala in this isomer resonates at 4.04 ppm in the low field, this proton is considered to be placed in the environment under a fairly high steric compression.

In considering the $\beta\text{-mer}(\text{N})\text{cis}(\text{O})$ complex, both of the $\Delta_S^S(3S,6R)$ and $\Lambda_R^S(3R,6S)$ isomers can satisfy the results of the ¹H NMR study described above. Namely, the former configuration places the α -proton of (*S*)-ala near to the α -proton of the (*S*)-alaninate ring on the (*S*)-amda at some distance and in the latter this proton is near one of the two 8-amino protons of the (*R*)-amda, as shown schematically in Fig. 5. Both of them should consequently exhibit a steric compression. Since it is difficult to distinguish clearly among the corresponding signals based on each α -proton from the ¹H NMR spectra (Fig. 3), these $\beta\text{-mer}(\text{N})\text{cis}(\text{O})$ isomers seems to produce little difference in the steric compression.

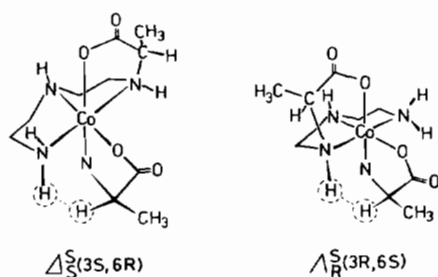


Fig. 5. The diastereoisomers of β -mer(N)cis(O)-[Co(*S*)-ala]-((*R,S*)amda)⁺ complex. The H atoms in broken line circles are those involved in compression. The bond lengths to these atoms have been exaggerated to emphasize the interactions involved in compression.

As seen in Table III, the β -mer(N)cis(O) complex obtained does not exhibit CD intensities except for that due to (*S*)-alaninate, the product obtained is therefore considered to be an equivalent mixture of the $\Delta_S^S(3S,6R)$ and $\Lambda_R^S(3R,6S)$ diastereoisomers.

Acknowledgements

The authors wish to express their thanks to Professor Ryokichi Tsuchiya of Kanazawa Women's Junior College for encouragement and the many helpful suggestions, and to Professor Masayasu Mori of

Osaka City University for much helpful advice in preparing this paper.

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