Studies on Cobalt(III) Complexes with dl-8-amino-2-methyl-3,6-diazaoctanoate Ion.
I. Preparation and Properties of (Amino acidato)(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(III) Complexes

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Abstract

Some new cobalt(III) complexes with dl-8-amino-2-methyl-3,6-diazaoctanoate ion (abbreviated as dl-amda) and glycinate or dl-alaninate ion were prepared and the geometrical isomers of the respective complexes were separated by cation exchange chromatography. The three isomers of (glycinato)-(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(III) perchlorate isolated were assigned in the order of elution to (Δ_R(3S,6R) + Λ_S(3R,6S)) – *trans*(O), (Δ_S(3S,6R) + Λ_R(3R,6S)) – *trans*(O) and (Δ_S(3S, 6R) + Λ_R(3R,6S))-*β-mer*(N)*cis*(O) type on the basis of their elemental analyses, visible absorption spectra and ^{1}H NMR spectra, where the subscripts R and S designate the absolute configuration of the dl-amda, and the configuration of the secondary amine nitrogen atom (sec-3N and sec-6N in the dl-amda) such as (3S,6R) or (3R,6S) is described by the R or S rule proposed by Cahn, Ingold and Prelog [1]. In the case of the mixed complex of dl-alanine and dl-amda, [Co(dl-ala)(dl-amda)]ClO_4, the isomers obtained were assigned in the order of elution as: (Δ^S_R(3S,6R) + Λ^R_S(3R,6S))-*trans*(O), (Δ^R_R(3S,6R) + Λ^S_S(3R,6S))-*trans*(O), (Δ^S_S(3S,6S) + Λ^R_R(3R, 6R))-*trans*(O), (Δ^S_S(3S,6R) + (Λ^R_R(3R,6S))-*trans*-(O), (Δ^R_S(3S,6R) + Λ^S_R(3R,6S))-*trans*(O), α or *β-fac*(N)*cis*(O) and *β-mer*(N)*cis*(O) isomers. Here the superscripts R and S designate the absolute configuration of the dl-alanine.

Introduction

The (amino acidato)cobalt(III) complexes with linear quadridentate ligand 8-amino-3,6-diazaoctanoate ion ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2COO^-$, abbreviated as dtma or adao) having an N-substituted glycinate structure were first investigated by Schneider and Collman [2]. Subsequently, several reports were made on mixed (amino acidato) cobalt-(III) complexes with adao [3–6].

In the present study, dl-8-amino-2-methyl-3,6-diazaoctanoate ion ($NH_2CH_2CH_2NHCH_2CH_2$-$NHCH(CH_3)COO^-$, abbreviated as dl-amda), was used as a racemic, linear-quadridentate ligand. This is a methyl-substitution product of dtma. Consideration of molecular models of octahedral complexes of this ligand suggests that such insertion of a methyl group should give considerable steric effects on the molecules and various interesting physical and spectral properties are expected. The present paper deals with the preparation and structure of the racemic diastereoisomers of new complexes of [Co-(gly)(dl-amda)]ClO_4 and [Co(dl-ala)(dl-amda)]ClO_4 on the basis of the results of the cation exchange-chromatography, the electronic absorption spectra, and ^{1}H NMR spectra.

Experimental

Preparation

dl-8-Amino-2-methyl-3,6-diazaoctanoic acid

This quadridentate ligand, dl-Hamda, was prepared by applying the method for the preparation of Hadao described by Schneider and Collman [2] with a slight modification. Sodium bicarbonate (37.0 g, 0.44 mol) was added to a solution containing 2-chloropropionic acid (47.7 g, 0.44 mol) in 40 ml of water. After the generation of carbon dioxide ceased, diethylenetriamine (41.3 g, 0.40 mol) and then 25 ml of an aqueous solution containing sodium hydroxide (17.6 g, 0.44 mol) were added to the solution. The mixed solution was then stirred for 30 min.

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The exothermic reaction proceeded for *ca.* 20 min. Since the chelating agent (dl-Hamda) desired could not be isolated as crystals, the reaction mixture was used directly for the preparation of the following complexes.

Dinitro(dl-8-amino-2-methyl-3,6-diazaoctanoato)-cobalt(III), [Co(NO_2)$_2$(dl-amda)]

To *ca.* 100 ml of an aqueous solution containing cobalt(II) chloride hexahydrate (95.2 g, 0.40 mol), the dl-amda solution prepared in (1) was added slowly and the pH of the mixture was brought to 5–6 with acetic acid. Sodium nitrite (59.4 g, 0.86 mol) was then added to the solution. The resulting dark brown solution was oxidized by air bubbling for 5 h, and the dinitro complex was separated out as a yellow precipitate. The crude crystals were washed with an aqueous solution containing a small amount of acetic acid, water–ethanol and ether, and then dried in air. Yield: 75 g (57.6%). The complex is sparingly soluble in hot water, and is insoluble in ethanol and ether.

Dichloro(dl-8-amino-2-methyl-3,6-diazaoctanoato)-cobalt(III) hemihydrate, [$CoCl_2$(dl-amda)]·0.5H_2O

The crude dichloro complex was obtained by suspending the above dinitro complex in concentrated hydrochloric acid and warming on a water bath at 80–90 °C until the liberation of nitrogen dioxide ceased, and then evaporating the solution to dryness on a water bath. The pure crystals of dichloro complexes were obtained by recrystallization from hot concentrated hydrochloric acid.

Anal. Found: C, 26.65; H, 5.15; N, 13.42%. Calcd. for [$CoCl_2$(dl-amda)]·0.5H_2O: C, 26.85; H, 5.47; N, 13.42%.

β-mer(N)cis(O)-glycinato(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(III) perchlorate, β-mer(N)-cis(O)-[Co(gly)(dl-amda)]ClO_4

A solution containing sodium hydroxide (2.8 g, 0.07 mol) and glycine (5.3 g, 0.07 mol) in 50 ml of water was added to a solution of [$CoCl_2$(dl-amda)]·0.5H_2O (20 g, 0.07 mol) and sodium perchlorate monohydrate (9.8 g, 0.07 mol) in 60 ml of water. The mixture was then heated and stirred in a water bath at about 50 °C for 2 h. The solution thus obtained was concentrated to about 50 ml by heating at *ca.* 50 °C under reduced pressure. Red crystals were obtained when the solution was allowed to stand in a refrigerator overnight. The isomer obtained was labelled as A-3. Yield: 5.2 g (19.7%).

Anal. Found: C, 26.51; H, 4.97; N, 13.91%. Calcd. for [Co(gly)(dl-amda)]ClO_4: C, 26.58; H, 4.97; N, 13.78%.

trans(O)-glycinato(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(III) perchlorate, trans(O)-[Co(gly)(dl-amda)]ClO_4

After adjusting the pH of *ca.* 30 ml of dl-8-amino-2-methyl-3,6-diazaoctanoate solution (0.05 mol) at 5–6 with 6 N HCl, 18.1 g (0.05 mol) of Na-[$Co(CO_3)_3$]·3H_2O [7, 8] was slowly added to the solution. After the evolution of carbon dioxide ceased, 3.8 g (0.05 mol) of glycine and 6.1 g (0.05 mol) of sodium perchlorate monohydrate were added to the solution and the mixture was warmed in a water bath at *ca.* 50 °C for 3 h. The solution was cooled to room temperature, when the reddish-violet complex deposited out. The product obtained was recrystallized from water. Yield: 2.0 g (25.0%).

In order to separate the isomer, 3.5 g of the product obtained was dissolved in water and was chromatographed on cation-exchange resin (Dowex 50W–X8, Na^+ form, 100–200 mesh, ϕ 36 × 800 mm column). By eluting with 0.08 M aqueous solution of sodium chloride, the adsorbed layer on the resin was separated into red bands, and the two sorts of isomer were obtained as perchlorates by the addition of $NaClO_4$ to the eluates and the concentration of the solution. The isomers obtained were labelled as A-1 and A-2 in their eluting order. Yield: A-1; 1.00 g (28.6%), A-2; 0.34 g (9.7%). Recovery: 38.3%.

Anal. A-1: Found: C, 26.08; H, 4.97; N, 13.67%. Calcd. for [Co(gly)(dl-amda)]ClO_4·0.5H_2O: C, 26.00; H, 5.09; N, 13.48%. A-2: Found: C, 26.04; H, 5.10; H, 13.77%. Calcd. for [Co(gly)(dl-amda)]-ClO_4·0.5H_2O: C, 26.00; H, 5.09; N, 13.48%.

β-mer(N)cis(O)-dl-alaninato(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(III) perchlorate, β-mer(N)cis(O)-[Co(dl-ala)(dl-amda)]ClO_4

This complex was prepared by the same procedure as for β-mer(N)*cis*(O)-[Co(gly)(dl-amda)]$^+$ complex, using dl-alanine instead of glycine in 0.04 molar scale. Yield: 4.0 g (23.8%).

Anal. Found: C, 28.18; H, 5.41; N, 13.09%. Calcd. for [Co(dl-ala)(dl-amda)]ClO_4·0.5H_2O: C, 27.95; H, 5.39; N, 13.04%.

Column chromatography of the complex [Co(dl-ala)(dl-amda)]$^+$: A solution containing sodium hydroxide (1.6 g, 0.04 mol) and dl-alanine (3.6 g, 0.04 mol) in 20 ml of water was added to the solution of [$CoCl_2$(dl-amda)]·0.5H_2O (12.5 g, 0.04 mol) in 50 ml of water, and then the mixture was heated in a water bath at 60–65 °C for 2 h. In order to separate the isomers the reaction mixture was chromatographed on cation-exchange resin (Dowex 50W–X8, Na^+ form, 100–200 mesh). In this case, the cation-exchange resin (*ca.* 120 ml) was added into the reaction mixture of the complex. The resin which adsorbed the complexes was then filtered, washed with distilled water, suspended in water,

TABLE I. Analytical Data and Label of the Complexes.

Label	Complex	C %		H %		N %		Yield (g)
		Found	Calcd.	Found	Calcd.	Found	Calcd.	
B-1	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4$	28.72	28.55	5.32	5.27	12.98	13.32	0.10
B-2	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot H_2O$	27.49	27.38	5.48	5.51	12.75	12.77	0.10
B-3	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot H_2O$	27.53	27.38	5.62	5.51	12.74	12.77	0.07
B-4	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot 0.5H_2O$	28.02	27.95	5.36	5.39	12.73	13.04	0.07
B-5	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4$	28.31	28.55	5.16	5.27	13.23	13.32	0.07
B-6	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot H_2O$	27.48	27.38	5.31	5.51	13.23	12.77	0.10
B-7	Unanalyzed							
B-8	$[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot H_2O$	26.87	27.38	5.26	5.51	13.30	12.77	1.50

and poured very slowly onto an Na^+ form resin previously packed in a column (ϕ 45 X 480 mm). After distilled water was passed through the column overnight, the adsorbed layer on the resin was separated into eight red bands by elution with 0.08 M sodium chloride.

Each eluted solution was concentrated at 35–40 °C under reduced pressure. The isomers were obtained as the perchlorate salts by addition of sodium perchlorate to the concentrate, except for the seventh elution band. The seven isomers obtained were labelled as B-1, B-2, B-3, B-4, B-5, B-6, B-7 (uncrystallized) and B-8 in their eluting order. It was concluded that isomers from B-1 to B-5 were *trans*-(O), and B-6 and B-8 were *cis*(O) form, as mentioned in next section. The analytical data and yields of the isomers are listed in Table I.

trans(O)-dl-alaninato(dl-8-amino-2-methyl-3,6-diazaoctanoato)cobalt(II) perchlorate, trans(O)-[Co(dl-ala)(dl-amda)]$ClO_4 \cdot 0.5H_2O$

This complex was prepared by the same procedure as that for the complex of *trans*(O)-[Co(gly)(dl-amda)]$^+$, using dl-alanine instead of glycine in 0.04 molar scale. The red product obtained was recrystallized from water. Yield: 3.0 g (18.0%).

Anal. Found: C, 27.98; H, 5.42; N, 13.02%. Calcd. for $[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4 \cdot 0.5H_2O$, C, 27.95; H, 5.39; N, 13.04%.

Measurements

The electronic absorption spectra of complexes were measured in an aqueous solution with a Hitachi 124 spectrophotometer. ^1H NMR spectra were recorded with a JNM-MH-100 NMR spectrometer

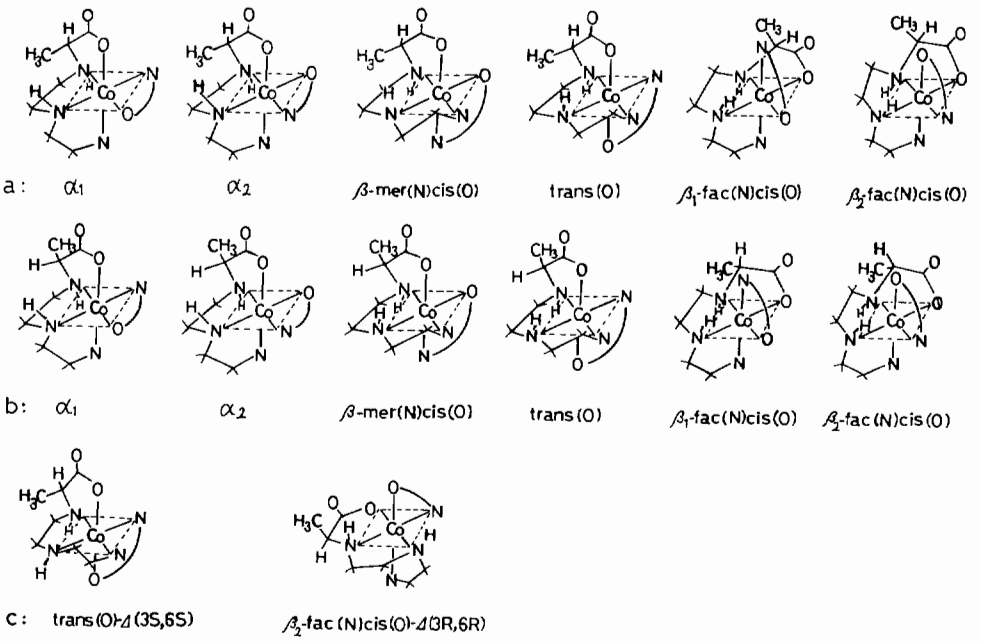

Fig. 1. The possible geometric isomers of $[Co(N-O)(dl\text{-}amda)]^+$ complex.

and the chemical shifts were measured with DSS as an internal reference in deuterium oxide.

Results and Discussion

Possible Isomers, Preparation, and Electronic Spectra

In the complexes containing dl-amda and a bidentate such as glycine or dl-alanine, six geometrical isomers are conceivable, as shown in Fig. 1a. After Schneider and Collman [2], the complexes will be designated as *α-fac*(N), *β-mer*(N), *β-fac*(N). Two diastereoisomers are possible in each geometrical configuration 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 dl-amda (Fig. 1b). If optically-active isomers including (3S,6R) or (3R,6S) chiral isomers (Fig. 1c) based on the two secondary amine nitrogens in the *β-mer*(N) and *β-fac*(N) type are taken into account, the number of the isomers increase further. It can be seen in Fig. 1a that the methyl group of each isomer is spatially located above the C–N bond axis of the dl-amda, while the α-proton of the N-substituted alaninate structure in each isomer (as shown in Fig. 1b) is located above the C–N bond axis.

However, not all of the possible isomers could be isolated. The syntheses of the complexes were initiated with the preparation of isomeric mixtures through both of the following routes.

Route 1: $[CoCl_2(dl\text{-amda})]$ → (1) gly^-, (2) $NaClO_4$ → $[Co(gly)(dl\text{-amda})]ClO_4$; (1) $dl\text{-ala}^-$, (2) $NaClO_4$ → $[Co(dl\text{-ala})(dl\text{-amda})]ClO_4$

Route 2: $Na_3[Co(CO_3)_3]\cdot 3H_2O$ + dl-amda → (1) gly^-, (2) $NaClO_4$ → $[Co(gly)(dl\text{-amda})]ClO_4$; (1) $dl\text{-ala}^-$, (2) $NaClO_4$ → $[Co(dl\text{-ala})(dl\text{-amda})]ClO_4$

For the preparation of both $[Co(gly)(dl\text{-amda})]ClO_4$ (A-3) and $[Co(dl\text{-ala})(dl\text{-amda})]ClO_4$ (B-8), route 1 gave precipitates which are thought to have the *β-mer*(N)*cis*(O) configuration, because of the resemblance of their absorption spectral data to that of *β-mer*(N)*cis*(O)-$[Co(gly)(dtma)]ClO_4$ [2], shown in Table II. Route 2, on the other hand, gave diastereoisomers (A-1 and A-2) of *trans*(O) configuration which were separated from each other by means of ion-exchange chromatography. Labels A-1 and A-2 will be given in their eluting order to the isomers isolated by the cation exchange chromatography of the $[Co(gly)(dl\text{-amda})]^+$ complex obtained by means of route 2, and label A-3 given to that obtained via route 1 since this isomer was shown to be bound to the ion–exchange resin more tightly than A-1 and A-2 contained in the mixture prepared through route 2.

TABLE II. Absorption Data of the Complexes.

Label	$\nu/10^3$ cm^{-1} (Log ε)		
	Band Ia	Band Ib	Band II
A-1	18.8(2.05)	21.5(1.98)	27.7(2.24)
A-2	19.0(2.01)	21.5(1.95)	27.9(2.21)
A-3	20.1(2.25)		27.8(2.17)
B-1	19.0(2.05)	20.8(2.01)	27.9(2.23)
B-2	18.9(2.05)	21.0(1.99)	27.7(2.24)
B-3	19.3(2.06)	21.6(2.05)	27.8(2.28)
B-4	19.2(2.02)	21.3(1.98)	27.9(2.20)
B-5	19.2(1.98)	21.5(1.94)	27.9(2.18)
B-6	20.5(2.23)		28.1(2.20)
B-8	19.8(2.32)		27.7(2.21)
†	19.96(2.24)		27.77(2.16)

† *β-mer*(N)*cis*(O)-$[Co(gly)(dtma)]ClO_4$ [2]

Reaction mixtures of the $[Co(dl\text{-ala})(dl\text{-amda})]^+$ complex obtained via route 1 were chromatographed on cation-exchange resin and eluted into eight fractions which labelled B-1, B-2....B-8 in the order of elution. Table I shows that preparation of the $[Co(dl\text{-ala})(dl\text{-amda})]^+$ complex by means of route 1 leads largely to the *β-mer*(N)*cis*(O) complex (B-8) compared with others from B-1 to B-6.

Electronic Spectra

The electronic absorption spectra of the isomers A-1, A-2 and A-3 are shown in Fig. 2 along with those of the isomers from B-1 to B-8, except for B-7, given in Fig. 3. The isomers A-1 and A-2 in Fig. 2 and those from B-1 to B-5 in Fig. 3 have shoulder

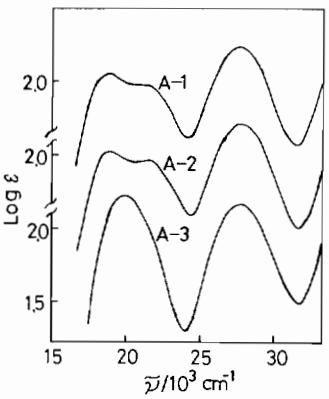

Fig. 2. Absorption spectra of the isomers of *trans*(O)- and *β-mer*(N)*cis*(O)-$[Co(gly)(dl\text{-amda})]^+$: A-1 (*trans*(O)), A-2(*trans*(O)) and A-3(*β-mer*(N)*cis*(O)).

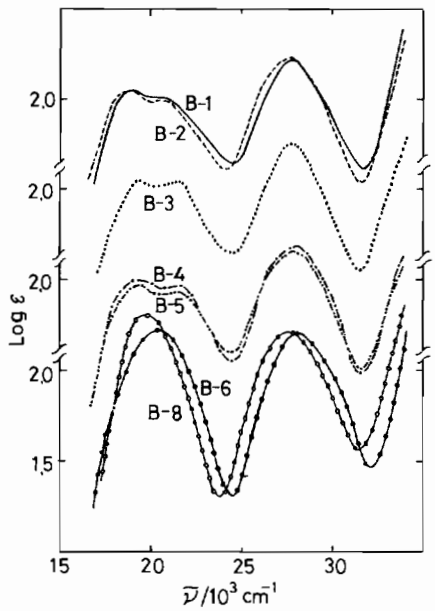

Fig. 3. Absorption spectra of the isomers of *trans*(O)- and *cis*-(O)-[Co(dl-ala)(dl-amda)]$^+$. B-1: ———, B-2: -------, B-3: ·····, B-4: —·—·—, B-5: —··—··—, B-6: —●—●—, B-8: —○—○—.

absorption in the first absorption bands, which is typical of *trans*(O) isomers in Co–N_4O_2 form complexes [9–11]. The isomers A-3, B-6 and B-8, on the other hand, have no shoulder absorption in the first absorption band, and are considered to assume the *cis*(O) form [9–11]. Of the *trans*(O) complexes in Fig. 2 and Fig. 3, A-1, B-1 and B-2 show a peak accompanied by a flat shoulder in the first absorption band, while in the spectra of A-2, B-3, B-4 and B-5 it is possible to observe two split peaks in the same region, where B-3 shows an especially marked splitting. In the *trans*(O)-[Co(gly)(dl-amda)]$^+$ complexes four racemic diastereoisomers, (Δ_R(3S,6R) + Λ_S(3R,6S)), (Δ_S(3S,6R) + Λ_R(3R,6S)), (Δ_R(3S,6S) + Λ_S(3R,6R)) and (Δ_S(3S,6S) + Λ_R(3R,6R)), are possible if the position of methyl group of dl-amda and the configuration of the two secondary amine nitrogens are taken into account.

In the *trans*(O)-[Co(dl-ala)(dl-amda)]$^+$ complexes, on the other hand, there are eight possible racemic diastereoisomers: (Δ^S_R(3S,6R) + Λ^R_S(3R,6S)), (Δ^R_R-(3S,6R) + Λ^S_S(3R,6S)), (Δ^S_S(3S,6R) + Λ^R_R(3R,6S)), (Δ^R_S(3S,6R) + Λ^S_R(3R,6S)), (Δ^S_R(3S,6S) + Λ^R_S-(3R,6R)), (Δ^R_R(3S,6S) + Λ^S_S(3R,6R)), (Δ^S_S(3S,6S) + (Λ^R_R(3R,6R)) and (Δ^R_S(3S,6S) + Λ^S_R(3R,6R)). The five kinds of the *trans*(O) isomers were all obtained in the present work. The assignment of the configuration of the *trans*(O) isomers obtained is thought to be very difficult on the basis of electronic absorption spectra only. The agreement of the absorption spectrum of the fraction of B-8 with that of the *β-mer*(N)*cis*(O)-[Co(dl-ala)(dl-amda)]ClO_4 obtained through route 1 proved the identity of these preparations. The B-6 may be assigned to either of the following: α_1-*fac*(N)*cis*(O), α_2-*fac*(N)*cis*(O), β_1-*fac*(N)*cis*(O) and β_2-*fac*(N)*cis*(O) configuration shown in Fig. 1.

^{1}H NMR Spectra

The ^{1}H NMR spectra of A-1, A-2, A-3 and trans-(O)-[Co(gly)(dtma)]ClO_4 are shown in Fig. 4. Complexes, A-1, A-2 and A-3 have a methyl group substituted for Ha or Hb of dtma in [Co(gly)(dtma)]$^+$ complex. In the ^{1}H NMR spectra of A-1, A-2 and A-3, the doublet peaks in the high-field region between 1 and 2 ppm in Fig. 4 can be assigned to the resonance of the methyl protons. On the other hand, the quartet peaks based on the unsubstituted α-proton are observed at relatively higher magnetic fields in A-1. These phenomena related to the dif-

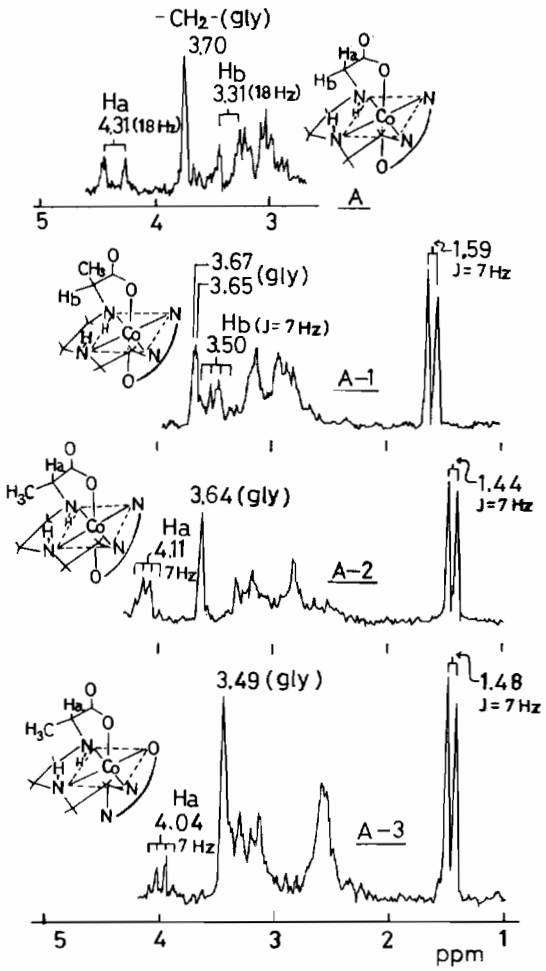

Fig. 4. ^{1}H NMR spectra of *trans*(O)-[Co(gly)(dtma)]ClO_4 (A) and the isomers (A-1, A-2 and A-3) of [Co(gly)(dl-amda)]ClO_4.

ferent chemical shifts of the α-proton or methyl protons may be explained by the magnetic anisotropy of the C–N bond [12, 13]. The signals based on the α-proton (Hb) or methyl protons located above the C–N bond axis adjacent to the N-substituted alaninate ring in the di-amda coordinated should shift to higher magnetic fields than those not located above the C–N bond axis. These considerations suggest that the configurations of A-1, A-2 and A-3 may be assigned to those shown in Fig. 4. The assignment of the *β-mer*(N)*cis*(O) structure to A-3 has already been discussed in the previous section on electronic spectra.

The singlet peaks at 3.65 ppm (A-1), 3.64 ppm (A-2), 3.49 ppm (A-3) and 3.70 ppm (*β-mer*(N)-*cis*(O)-[Co(gly)(dtma)]ClO_4 may be assigned to the methylene protons of the glycinate ligand. Thus such a methylene signal of A-3 is seen to appear at somewhat higher magnetic fields than that of A-2, in contrast to the very similar chemical shifts of methyl protons of both A-2 and A-3. These different chemical shifts of the methylene protons may be due to the difference of the steric configuration between *cis*(O) and *trans*(O) complexes [3]. On the basis of these ^1H NMR data it seems possible to regard A-1, A-2 and A-3 as racemic isomers, (Δ_R(3S,6R) + Λ_S(3R,6S)), (Δ_S(3S,6R) + Λ_R(3R,6S)) and *β-mer*-(N)*cis*(O)-(Δ_S(3S,6R) + Λ_R(3R,6S)), respectively. The methyl groups in the complexes, A-1, A-2 and A-3 are thought to be directed toward an equatorial plane for the N-substituted alaninate ring of the dl-amda. Figure 5 shows the triplet or quartet peaks due to the methyl groups of dl-amda and dl-ala in the complexes of $[Co(dl\text{-}ala)(dl\text{-}amda)]^+$.

The coordination mode of the dl-amda in B-1 and B-2 of the *trans*(O) form is thought to be the same as A-1 described above because of the similarity of the chemical shifts (1.60 and 1.59 ppm) to that of A-1 (1.59 ppm). Similarly, the configuration of B-4 and B-5 having chemical shifts of 1.43 and 1.46 ppm may be thought to be the same as that of A-2 (1.44 ppm). The double signals having the chemical shift values of 1.49–1.53 ppm may be assigned to the methyl protons of the coordinated dl-alaninate. Accordingly, the chemical shift values of 1.43 and 1.49 ppm may be assigned to the methyl protons of dl-amda and dl-ala, respectively. On the other hand, the resonance signals of the methyl groups in the B-3 shift to a considerably higher magnetic field compared with those in B-4 and B-5. Complex B-3 also shows a fairly large splitting of a band in the absorption spectra, as described in the above section. No complex possessing spectroscopic behaviors similar to those of B-3 has been obtained in the $[Co(gly)(dl\text{-}amda)]^+$ series. Accordingly, B-3 is thought to have the secondary amine nitrogen atom, taking the different absolute configuration which is not possessed by the other *trans*(O) complexes.

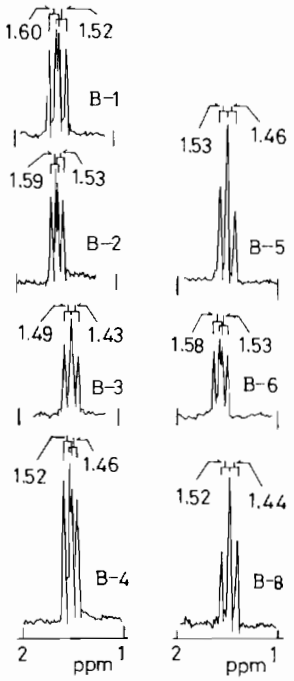

Fig. 5. ^1H NMR spectra of *trans*(O) and *cis*(O) isomers of $[Co(dl\text{-}ala)(dl\text{-}amda)]ClO_4$.

The configuration of B-3 is thus considered to be the *trans*(O)-(Δ_S^S(3S,6S) + Λ_R^R(3R,6R)) form.

It is possible to assign the conformation of dl-amda in the isomeric molecules by supposing that a methyl proton not located above the C–N bond axis resonates at a lower magnetic field. In this way B-1 and B-2 are considered to have the *trans*-(O)-(Δ_R^S(3S,6R) + Λ_S^R(3R,6S)) and *trans*-(O)-(Δ_R^R(3S,6R) + Λ_S^S(3R,6S)) configurations while B-4 and B-5 are considered to have the *trans*(O)-(Δ_S^S(3S,6R) + Λ_R^R(3R,6S)) and *trans*-(O)-(Δ_S^R-(3S,6R) + Λ_R^S(3R,6S)) configurations, respectively. The values of the chemical shift in B-6 and B-8 are respectively 1.58 and 1.44 ppm, which may be assigned to the methyl protons of the dl-amda in the complexes. The methyl group in the former seems to be located above the C–N bond axis, and that in the latter to be out of the influence of the C–N bond. It has already been described in the above section that the configuration of B-8 is thought to assume the *β-mer*(N)*cis*(O) form, like A-3 on the basis of the absorption spectra. Although it is difficult to determine the steric configuration of B-6, it may be apparent that the methyl group of the dl-amda in the complex is not located above the C–N bond axis judging from the value of the chemical shift, 1.58 ppm. Accordingly, in the *cis*-(O) complexes of B-6 and B-8, the configuration of the former seems to be either α-(or *β-*)*fac*(N)*cis*(O)-(Δ_R^S(3S,6R) + Λ_S^R(3R,6S)) or α-(or *β-*)*fac*(N)*cis*-(O) – (Δ_R^R(3S,6R) + Λ_S^S(3R,6S)), and that of the

latter to be either *β-mer*(N)*cis*(O)-(Δ^{S}_{S}(3S,6R) + Λ^{R}_{R}(3R,6S)) or *β-mer*(N)*cis*(O)-(Δ^{R}_{S}(3S,6R) + Λ^{S}_{R}-(3R,6S)) form.

The Order of Elution of the Isomers in Cation-exchange Chromatography

The order of elution of the two *trans*(O) isomers of $[Co(gly)(dl\text{-}amda)]^{+}$ seems to be dominated by whether or not the methyl group of the dl-amda in the complex ion is located above the C–N bond axis, and in the $[Co(dl\text{-}ala)(dl\text{-}amda)]^{+}$, by the orientation of the methyl groups of the dl-ala and dl-amda coordinated as well. The rate of elution of B-1 and B-2 which have a methyl group not located above the C–N bond is faster than the rate of elution of B-3, B-4 and B-5, which all have a methyl group located directly above the C–N bond axis. This is consistent with the result of the column chromatography of A-1 and A-2. On the other hand, the factor which causes different elutions between B-1 and B-2 (or B-4 and B-5) seems to be the coordination mode of the bidentate dl-alaninate ion in the complexes. Among the three *trans*(O) isomers having the methyl group located directly above the C–N bond, B-3, B-4 and B-5, B-3 has the highest rate of elution, probably due to the configuration of racemic (Δ^{S}_{S}(3S,6S) + Λ^{R}_{R}(3R,6R)) which has two secondary amine protons parallel to each other.

The absolute configuration for five *trans*(O) isomers in the $[Co(dl\text{-}ala)(dl\text{-}amda)]^{+}$ complex may be clarified by introducing (R)-alanine or (S)-alanine in the place of dl-alanine in the preparation of the complexes and by column chromatography.

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