Cobalt(III) Complexes with Tripodlike Quadridentate Ligands. II.[1] Preparations, Absorption Spectra and Circular Dichroism of (Amino carboxylato or 1,2-diamine)[*N*,*N*-bis(2-aminoethyl)-glycinato]cobalt(III) Complexes

Keiji Akamatsu,* Takashi Komorita, and Yoichi Shimura
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
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Four glycinato, six L-alaninato, and three (*R*)-propylenediamine cobalt(III) complexes of a tripodlike quadridentate ligand, *N*,*N*-bis(2-aminoethyl)glycinate have been prepared. The geometrical configurations are assigned on the basis of their absorption and circular dichroism spectra, ^{1}H-NMR spectra, the elution behavior in ion-exchanger column chromatography, and the optical resolution of chiral isomers. The absolute configurations of the chiral complexes are tentatively assigned and the characteristics of the tripodlike ligand are discussed.

A tripodlike quadridentate ligand *i*-dtma[2] can take two different configurations in six-coordinate metal complexes (Fig. 1). The left configuration with a plane of symmetry and the right one without it are called *s*-type (symmetrical) and *u*-type (unsymmetrical), respectively. An *s*-type configuration is achiral, while a *u*-type chiral. A complex with a tripodlike ligand of *s*-type configuration can also become chiral when unsymmetrical (such as *meso*-2,4-pentanediamine or *meso*-2,3-butanediamine) or asymmetric (such as L-alaninate or (*R*)-propylenediamine) bidentate ligands occupy the remaining two coordination sites. Only *s*-type configuration is possible for some typical tripodlike ligands, ata^{3-} and tren. It was pointed out in the previous paper[1] concerning the ata and tren cobalt(III) complexes with chiral bidentate (L-amino carboxylate or 1,2-diamine) that the CD spectra in the first and second d-d absorption band region for these complexes were considerably different in pattern and/or intensity from those for the corresponding bis- or tris(bidentate) or tetrakis(unidentate) complexes with the same L-amino carboxylate or 1,2-diamine. The differences were attributed to a new source of optical activity, which was called the "quasi-enantiomeric" effect, because this mainly determined the CD patterns in the first and second d-d band region: the CD patterns in the region are helpful in determining the coordination modes of the residual bidentate ligands, especially, those of L-amino carboxylates.

A further problem arises on the complexes of *u*-type structure which are chiral regardless of the residual ligands. Absolute configurations of cobalt(III) complexes with multidentate ligands have generally been correlated with that of a simple tris(bidentate) complex, for example, $[Co(en)_3]^{3+}$, by use of the ring-pairing-method.[3] Meanwhile, the method cannot be applied to *u*-type isomers of the complexes with tripodlike ligands such as aeida and *i*-dtma, because these isomers lack the ring-pairing chirality. Furthermore, the available data are too limited to derive any empirical rule, though Koine *et al.* have reported some L- or D-alada[4] and *β*-alada[5] complexes with amino carboxylate.

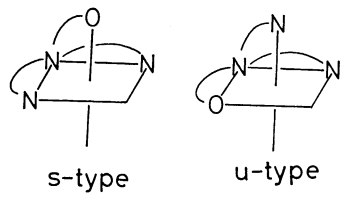

Fig. 1. Two different coordination modes of *i*-dtma ligand.

In the present paper the isomers of *i*-dtma cobalt(III) complexes with amino carboxylate or 1,2-diamine are reported.

Experimental

Preparations. *(1)* *[Co(gly)(i-dtma)]*$^+$: Two grams of *fac(N)*-[CoCl(*i*-dtma)(H_2O)]Cl·H_2O[6] was dissolved in 10 cm^3 of water, and to this violet solution was added a solution of glycine (1 g) neutralized with an equimolar amount of NaOH. The mixture was mechanically stirred at 70 °C for 2 h. The resulting red solution was poured onto a cation-exchanger column (SP-Sephadex C-25, Na^+ form) and the adsorbed complex was eluted with a 0.2 M NaCl aqueous solution (1 M=1 mol dm^{-3}). Two bands appeared; a red-orange and a purple one in this order. The second band contained mainly $[Co(i\text{-dtma})(H_2O)_2]^{2+}$. To the first eluate which had been evaporated to a small volume below 40 °C on a rotary evaporator was added a small amount of methanol to precipitate NaCl, which was filtered off with suction, as much sodium chloride as possible was removed by repetition of the procedure.

The resulting red-orange solution was then loaded on a strongly acidic cation exchanger column (Dowex 50w-x8, 2.6×40 cm, 200—400 mesh, Na^+ form) and eluted with a NaH_2PO_4–Na_2HPO_4 buffer of pH 6.8 ($NaH_2PO_4\cdot 2H_2O$, 25 g and $Na_2HPO_4\cdot 12H_2O$, 14 g per 1 dm^3 of solution). The adsorbed band had split into four well-resolved bands, which were eluted out in the following order; yellow-orange, orange, purple, and red-orange one. These are called G-1, G-2, G-3, and G-4, respectively. Each of the four fractions was treated with 44 g of $CaCl_2\cdot 2H_2O$ and 14 g of NaOH for every 1 dm^3 of eluate to convert the phosphate salts into the corresponding chloride salts. After removal of $Ca_3(PO_4)_2$ by filtration, the filtrate was evaporated to a small volume and to this was added methanol to precipitate NaCl, which was then filtered off. The procedure was repeated to remove as much sodium chloride as possible. Sodium perchlorate was added to the concentrated solution almost free from NaCl and the solution was kept standing in a refrigerator. After a few days, deposited crystals were collected with suction and recrystallized from warm water,

washed with methanol and ether and dried in air. Found for G-1: C, 23.17; H, 4.85; N, 13.64%. Calcd for [Co(gly)(*i*-dtma)]$ClO_4 \cdot H_2O$: C, 23.39; H, 4.92; N, 13.65%. Found for G-2: C, 24.24; H, 4.65; N, 14.18%. Calcd for [Co(gly)(*i*-dtma)]ClO_4: C, 24.47; H, 4.63; N, 14.27%. Found for G-3: C, 24.36; H, 4.61; N, 14.29%. Calcd for [Co(gly)(*i*-dtma)]ClO_4: C, 24.47; H, 4.63; N, 14.27%. Found for G-4: C, 24.33; H, 4.72; N, 14.20%. Calcd for [Co(gly)(*i*-dtma)]ClO_4: C, 24.47; H, 4.62; N, 14.27%.

(2) Optical Resolution of G-2: The orange isomer (G-2) of [Co(gly)(*i*-dtma)]ClO_4 (0.72 g; 1.8×10^{-3} mol) was dissolved in 10 cm^3 of warm water and converted into the chloride with a Dowex anion-exchanger column (1-x8, 100—200 mesh, Cl^- form). To the eluate was added $(+)_{589}$-Na[$Co(NO_2)_3$(edma)](vide post) (0.31 g; 0.91×10^{-3} mol) with stirring at 40 °C, and the mixture was kept standing overnight in a refrigerator. The pale orange powder deposited was filtered and washed with a small amount of water. The less-soluble diastereomer was recrystallized from warm water, washed with water, and then with methanol and ether and dried in air. Found: C, 22.56; H, 4.78; N, 19.82%. Calcd for [Co(gly)(*i*-dtma)][$Co(NO_2)_3$(edma)]·$1.5H_2O$: C, 22.72; H, 4.78; N, 19.88%.

A solution of the diastereomer in warm water was poured onto a Sephadex column (C-25, Na^+ form) and after being washed with water the adsorbed band was eluted with an aqueous $NaClO_4$ solution. The eluate was evaporated almost to dryness and a small amount of methanol was added to the residue. The $(-)_{589}$-perchlorate salt deposited was recrystallized from water. Found: C, 24.27; H, 4.60; N, 13.99%. Calcd for $(-)_{589}$-[Co(gly)(*i*-dtma)]ClO_4: C, 24.47; H. 4.63; N, 14.27%. $[M]_{589} = -520°$.

(3) [Co(L-ala)(i-dtma)]$^+$: A solution containing the desired products was prepared by the same method as that for the glycinato analogs using L-alanine instead of glycine. The red-orange solution (free from bivalent complex cations) was loaded on a Dowex cation-exchanger column (50w-x8, 200—400 mesh, Na^+ form). When eluted with the NaH_2PO_4–Na_2HPO_4 buffer described in (1), the adsorbed band separated into six, which are named A-1, A-2-a, A-2-b, A-3-a, A-3-b, and A-4 in the elution order. The eluted phosphate salts were converted into the corresponding chloride in the following way: each of the six fractions was diluted with triple volumes of water and then passed through a Dowex cation-exchanger column (50w-x8, 200—400 mesh, Na^+ form). The band on the column was washed with water and eluted with an aqueous NaCl solution. After removal of NaCl by the method previously mentioned, the desired complexes were obtained as perchlorate salts by adding $NaClO_4$ to the concentrated solution and recrystallized from warm water. The crystallization of A-3-a was not carried out because of the low yield and the high solubility in water of the isomer. Found for A-1: C, 26.05; H, 5.13; N, 13.76%. Calcd for [Co(L-ala)(*i*-dtma)]ClO_4·$0.5H_2O$: C, 26,00; H, 5.10; N, 13.48%. Found for A-2-a: C. 26.78; H, 5.04; N, 13.94%. Calcd for [Co(L-ala)(*i*-dtma)]ClO_4: C, 26.58; H, 4.93; N, 13.78%. Found for A-2-b: C, 26.82; H, 5.00; N, 13.95%. Calcd for [Co(L-ala)(*i*-dtma)]ClO_4: C, 26.58; H, 4.93; N, 13.78%. Found for A-3-b: C, 25.03; H, 5.33; N, 12.95%. Calcd for [Co(L-ala)(*i*-dtma)]ClO_4·$1.5H_2O$: C, 24.92; H, 5.36; N, 12.92%. Found for A-4: C, 26.05; H, 5.18; N, 13.30%. Calcd for [Co(L-ala)(*i*-dtma)]ClO_4·$0.5H_2O$: C, 26.00; H, 5.10; N, 13.48%.

(4) [Co(i-dtma)((R)-pn)]$^{2+}$: One gram of *fac(N)*-[CoCl(*i*-dtma)(H_2O)]Cl·H_2O[6] was suspended in 60 cm^3 of DMF (*N*,*N*-dimethylformamide). (*R*)-Propylenediamine (0.5 g) was added dropwise to this blue suspension with stirring and the mechanical stirring was continued for 2 h at 60 °C in a water bath. The orange powder formed was filtered, washed with methanol and ether and air-dried. A solution of this powder in 15 cm^3 of water was poured onto a cation-exchanger column (SP-Sephadex C-25, 2.6 cm × 50 cm, Na^+ form). When the adsorbed band was eluted with a NaH_2PO_4–Na_2HPO_4 buffer solution ($NaH_2PO_4 \cdot 2H_2O$, 12.5 g and $Na_2HPO_4 \cdot 12H_2O$, 7 g per 1 dm^3 of solution), it split into two orange bands. These are called P-1 and P-2 in the elution order, respectively. Each fraction was diluted with the same volume of water, passed through a Sephadex column (SP-Sephadex C-25) and then the column was washed with water to remove phosphate salts. The P-2 band concentrated on the column was eluted with an aqueous $NaClO_4$ solution. The eluate was evaporated almost to dryness below 40 °C on a rotary evaporator and to this residue was added ethanol to precipitate the perchlorate salt of P-2, which was filtered off, washed with methanol and dried in air. Found for P-2; C, 21.48; H, 5.04; N, 13.94%. Calcd for [Co(*i*-dtma)((*R*)-pn)]$(ClO_4)_2 \cdot 0.5H_2O \cdot 0.53NaClO_4$: C, 21.52; H, 5.03; N, 13.95%.

Although P-1 did not split completely, both ends of the band revealed nearly enantiomeric CD spectra. Two isomers, P-1-a and -b, were separated from the P-1 band by means of fractional crystallizations; the P-1 band was treated in the same way as that for P-2, described above, using NaCl instead of $NaClO_4$ as the eluting agent. The eluate was evaporated amost to dryness and to the residue was added methanol to remove NaCl. The deposited P-1-a including NaCl was filtered and recrystallized from warm water. The filtrate containing P-1-b was then evaporated to dryness and from the residue P-1-b was extracted into methanol. The chloride salt of P-1-a was converted into the chloride perchlorate by adding $NaClO_4$ to the solution and that of P-1-b into the perchlorate by use of a column chromatographic method similar to that in (2). Found for P-1-a: C, 24.97; H, 5.62; N, 16.40%. Calcd for [Co(*i*-dtma)((*R*)-pn)]Cl(ClO_4): C, 25.24; H, 5.66; N, 16.36%. Found for P-1-b: C, 21.88; H, 4.98; N, 14.04%. Calcd for [Co(*i*-dtma)((*R*)-pn)]$(ClO_4)_2 \cdot 0.25H_2O$: C, 21.76; H, 4.98; N, 14.10%.

(5) [Co(i-dtma)(en)]$^{2+}$: This complex was prepared with a method similar to that for the corresponding (*R*)-pn complex. Two isomers (E-1 and E-2 in the elution order) were isolated as perchlorates. Found for E-1: C, 20.05; H, 4.60; N, 14.91%. Calcd for [Co(*i*-dtma)(en)]$(ClO_4)_2$: C, 20.09; H, 4.65; N, 14.65%. Found for E-2: C, 19.82; H, 4.73; N, 14.45%. Calcd for [Co(*i*-dtma)(en)]$(ClO_4)_2 \cdot 0.5H_2O$: C, 19.72; H, 4.77; N, 14.38%.

(6) Optical Resolution of E-1: An aqueous solution of E-1, [Co(*i*-dtma)(en)]$(ClO_4)_2$ (1.3 g; 2.7×10^{-3} mol) was passed through an anion-exchanger column (Dowex 1-x8, 50—100 mesh, Cl^- form). To the eluate concentrated to 20 cm^3 on a rotary evaporator was added silver antimony tartrate (2.1 g; 2.8×10^{-3} mol) with stirring at 60 °C. After 10 min the precipitated silver chloride was filtered off and the filtrate was cooled in an ice bath with scratching the beaker to induce crystallization. The orange crystals deposited were collected by filtration, recrystallized from warm water, washed with a small amount of water, with methanol and ether and dried in air. Found: C, 22.62; H, 3.59; N, 8.29%. Calcd for [Co(*i*-dtma)(en)][Sb_2(tart)$_2$]·$2H_2O$: C, 22.58; H, 3.56; N, 8.23%.

The less-soluble diastereomer was converted into $(-)_{589}$-perchlorate salt by use of the same method as that in (2). Found: C, 20.22; H, 4.63; N, 14.73%. Calcd for $(-)_{589}$-

$[Co(i\text{-dtma})(en)](ClO_4)_2$: C, 20.09; H, 4.65; N, 14.65%. $[M]_{589}=-850°$.

(7) Preparation and Optical Resolution of $[Co(NO_2)_3(edma)]^-$: The racemate, $Na[Co(NO_2)_3(edma)]\cdot 3H_2O$, was isolated in the course of the preparation for $Na[Co(NO_2)_2(aeida)]\cdot 2H_2O$[7] by a usual column chromatographic method. Found: C, 12.34; H, 3.79; N, 18.01%. Calcd for $[Na(NO_2)_3(edma)]\cdot 3H_2O$: C, 12.28; H, 3.87; N, 17.91%.

The optical resolution was carried out as follows: one and four tenths gram of $Na[Co(NO_2)_3(edma)]\cdot 3H_2O$ (3.6×10^{-3} mol) was dissolved in 50 cm^3 of water at 50 °C, and to this solution was added $(-)_{589}$-$[Co(ox)(en)_2]Cl\cdot H_2O$ (0.6 g; 2.3×10^{-3} mol). Mechanical stirring was continued for 10 min after orange crystals began to deposite. While the reaction mixture was still warm, crystals of the diastereomer were collected on a glass filter, recrystallized from warm water, washed with a small amount of water and then with methanol and ether and dried in air. Found: C, 19.59; H, 4.74; N, 20.50%. Calcd for $[Co(NO_2)_3(edma)][Co(ox)(en)]\cdot 2H_2O$: C, 19.45; H, 4.74; N, 20.42%.

The less-soluble diastereomer was converted into the $(+)_{589}$-sodium salt by passing through a cation-exchanger column (Na^+ form) and evaporating the eluate on a rotary evaporator. Found: C, 14.39; H, 2.89; N, 20.58%. Calcd for $(+)_{589}$-$Na[Co(NO_2)_3(edma)]$: C, 14.25; H, 2.70; N, 20.78%. $[M]_{589}=+475°$.

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu UV-200 spectrophotometer in aqueous solutions. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter and the ^{1}H-NMR spectra were obtained in deuterium oxide (D_2O) on a Varian XL-100-15 spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal standard.

Results and Discussion

Four isomers are possible for a [Co(am)(*i*-dtma)]-type complex (Fig. 2). As both ends are indistinguishable in free ethylenediamine, only two isomers, *s*-α (or *s*-β) and *u*-α (or *u*-β), are possible for the complex containing en instead of gly$^-$. The upper two (*s*-type) have a plane of symmetry in the absence of a substituent group on the chelate ring, while the lower two (*u*-type) have none of the plane of symmetry even for the glycinato and ethylenediamine complexes and are optically resolvable. Accordingly, the en complex has one achiral isomer and a pair of enantiomers, the glycinato complex two achiral ones and two pairs of enantiomers, and the L-alaninato and (*R*)-pn complexes six chiral ones.

Amino Carboxylato Complexes with i-*dtma*: Several attempts were made under different conditions to prepare the glycinato and L-alaninato complexes; temperature and time in the substitution reaction were varied and activated charcoal was added or not. As for the reaction temperature and time, the condition described in the experimental section is suitable to prepare all the four and six isomers for the glycinato and L-alaninato complexes, respectively. Though, in the presence of activated charcoal, the complete substitution took place at low temperature in short time and none of the bivalent complex cation $[Co(i\text{-dtma})(H_2O)_2]^{2+}$ was detected, only two isomers (G-1 and G-2) of the four for the glycinato and only three (A-1, A-2-a, and-b)

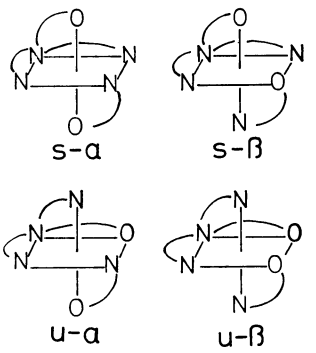

Fig. 2. Four geometrical isomers of [Co(am)(*i*-dtma)]-type complex (am=amino carboxylate).

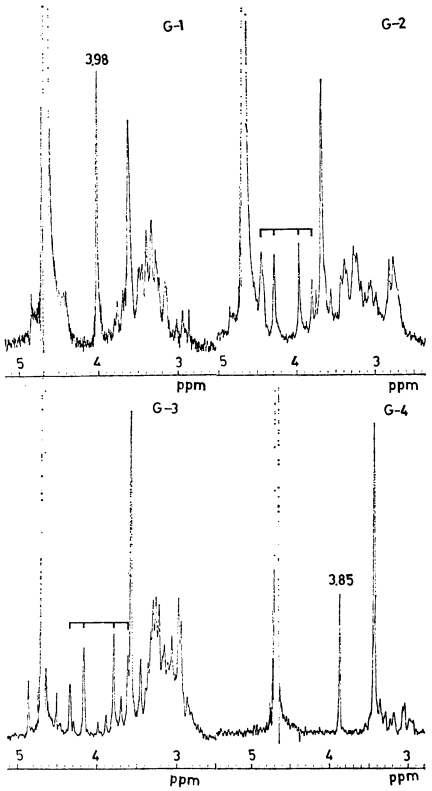

Fig. 3. ^{1}H-NMR spectra of isomers of [Co(gly)(*i*-dtma)]$^+$.

of the six for the L-alaninato complex were formed.

All isomers of the glycinato and L-alaninato complexes were ultimately isolated as crystals except for one isomer of the L-alaninato complex, A-3-a. Isomers, G-1, G-2, G-3, and G-4 were found from their absorption spectra to correspond to A-1, A-2, A-3, and A-4, respectively. A-2 and A-3 were separated into the respective pairs of the diastereomers on an ion-exchanger column. These facts indicate that G-1, G-4, A-1, and A-4 have either structure *s*-α or *s*-β and G-2, G-3, A-2, and A-3 either *u*-α or *u*-β. The two isomers, *s*-α and *s*-β are also distinguishable from *u*-α and *u*-β by means of ^{1}H-NMR spectra.

Figures 3 and 4 show the ^{1}H-NMR spectra of the gly and the en isomers. The isomers, G-1, G-4, and E-2, show a singlet due to the methylene protons of the acetate group in *i*-dtma (3.98 ppm for G-1; 3.85

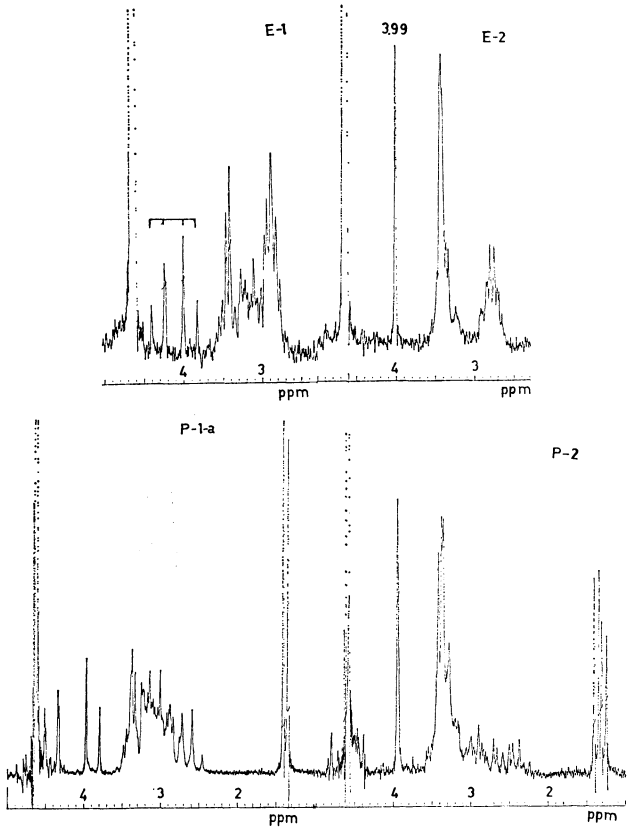

Fig. 4. ^{1}H-NMR spectra of isomers of [Co(en)(*i*-dtma)]$^{2+}$ and [Co((*R*)-pn)(*i*-dtma)]$^{2+}$.

ppm for G-4; and 3.99 ppm for E-2), while the other isomers and AB quartet due to the relevant protons with the coupling constants of 17—19 Hz (4.45, 4.28, 3.97, and 3.79 ppm for G-2; 4.31, 4.13, 3.76, and 3.57 ppm for G-3; and 4.40, 4.22, 3.99, and 3.82 ppm for E-1). The gly complex has another acetate group, not the constituent of *i*-dtma but that of glycine. The methylene protons should also show a singlet for G-1 and G-4 and an AB quartet for G-2 and G-3, and can be assigned to the signals at 3.4—3.6 ppm, though it is difficult to distinguish them from the signals of the ethylene protons of *i*-dtma.

With regard to the complexes of CoN_4O_2 chromophore, the splitting of the first spin-allowed d-d absorption band is larger for a *trans*(*O*) isomer than for a *cis*(*O*). G-1 and A-1 which show the splitting (Figs. 5 and 6) are assigned to (structure) *s*-α, and therefore, G-4 and A-4 to *s*-β. It is difficult to distinguish G-2 and A-2 from G-3 and A-3 by means of their absorption and ^{1}H-NMR spectra. G-2 and G-3 have only one kind of chirality, which is due to chiral arrangement of the tripodlike *i*-dtma ligand. On the other hand, A-2 and A-3 have two kinds of chiralities, one being the same as in G-2 and G-3 and the other a vicinal chirality of the L-alaninate ligand. In the previous paper of this series,[1] it has been shown that the vicinal chirality is such [Co(am)(tripod)]-type complexes consists of two factors, one being asymmetric carbon of the am$^-$ ligand, the other quasi-enantiomeric chirality due to the geometrical configurations. The observed CD pattern is mainly

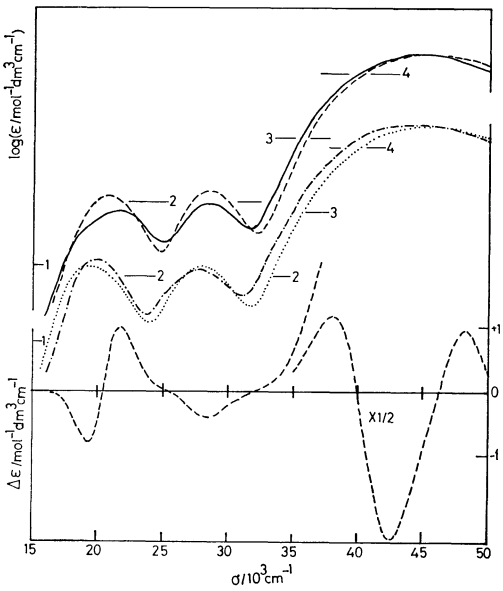

Fig. 5. Absorption and CD curves of four isomers of [Co(gly)(*i*-dtma)]$^+$: G-1 (——), G-2 (----), G-3 (·····), and G-4 (—·—).

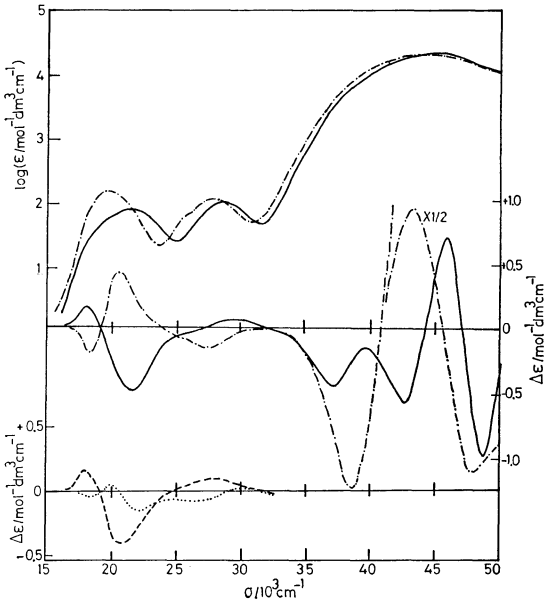

Fig. 6. Absorption and CD curves of A-1 (——) and A-4 (—·—) isomers of [Co(L-ala)(*i*-dtma)]$^+$. Calculated CD curves for asymmetric carbon (·····) and quasi-enantiomeric (----) effects are also shown.

determined by the quasi-enantiomeric effect. The CD contribution of the quasi-enantiomeric effect of [Co(L-ala)(tripod)]-type complexes in the first d-d transition band region is (+) and (—) from the longer wavelength for *s*-α isomers, and (—) and (+) for *s*-β ones, the pattern being almost unaffected by the geometry of chromophores. On the assumption that contributions from the chiral arrangement of *i*-dtma and from the vicinal effect are additive, calculated vicinal CD curves of 1/2{CD[A-2-a]+CD[A-2-b]} and 1/2{CD[A-3-a]+CD[A-3-b]} are shown together with the original CD of the isomers in Figs. 7 and 8. The calculated vicinal curves show the patterns (+) and (—)

Table 1. Absorption data of [Co(A-B)(*i*-dtma)]-type complexes (A-B=gly, L-ala, en, and (*R*)-pn)
Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.

Complex	d-d Transition band		Ultraviolet band
	1st	2nd	
(G-1)-[Co(gly)(*i*-dtma)]$^+$	18.5 sh(1.5) 21.51 (1.85)	28.45 (1.97)	45.25 (4.31)
(G-2)-[Co(gly)(*i*-dtma)]$^+$	20.77 (2.08)	28.45 (2.16)	45.66 (4.29)
(G-3)-[Co(gly)(*i*-dtma)]$^+$	19.27 (2.13)	26 sh (1.9) 27.89 (2.13)	45.05 (4.31)
(G-4)-[Co(gly)(*i*-dtma)]$^+$	19.80 (2.24)	25.5 sh(1.8) 27.70 (2.08)	44.54 (4.34)
(A-1)-[Co(L-ala)(*i*-dtma)]$^+$	18.5 sh(1.5) 21.46 (1.89)	28.53 (2.00)	44.84 (4.34)
(A-2-a)-[Co(L-ala)(*i*-dtma)]$^+$	20.83 (2.10)	28.49 (2.17)	45.66 (4.31)
(A-2-b)[Co(L-ala)(*i*-dtma)]$^+$	20.88 (2.12)	28.49 (2.17)	45.35 (4.33)
(A-3-b)-[Co(L-ala)(*i*-dtma)]$^+$	19.19 (2.12)	26 sh 27.93 (2.12)	44.94 (4.30)
(A-4)-[Co(L-ala)(*i*-dtma)]$^+$	19.84 (2.18)	25.5 sh(1.8) 27.86 (2.05)	44.35 (4.31)
(E-1)-[Co(*i*-dtma)(en)]$^{2+}$	20.53 (2.08)	28.94 (2.12)	45.15 (4.29)
(E-2)-[Co(*i*-dtma)(en)]$^{2+}$	20.83 (2.00)	28.99 (2.05)	44.84 (4.32)
(P-1-a)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	20.58 (2.07)	28.94 (2.11)	45.15 (4.27)
(P-1-b)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	20.58 (2.08)	28.88 (2.10)	45.25 (4.25)
(P-2)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	20.88 (1.99)	28.94 (2.05)	44.69 (4.32)
$(+)_{589}$-[$Co(NO_2)_3$(edma)]$^-$	22.22 (2.50)		30.08 (3.93) 39.60 (4.45) 49.02 (4.33)

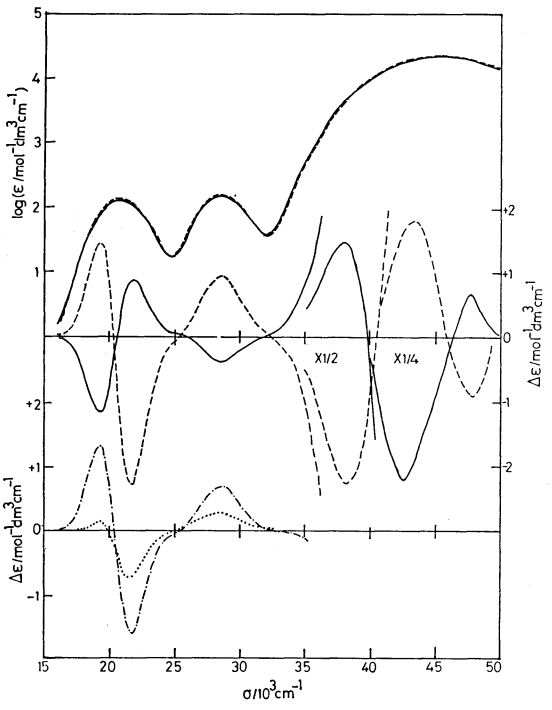

Fig. 7. Absorption and CD curves of A-2-a (——) and A-2-b (----) isomers of [Co(L-ala)(*i*-dtma)]$^+$. Two calculated CD curves of the vicinal (……) and arrangement (—·—) effects are also shown.

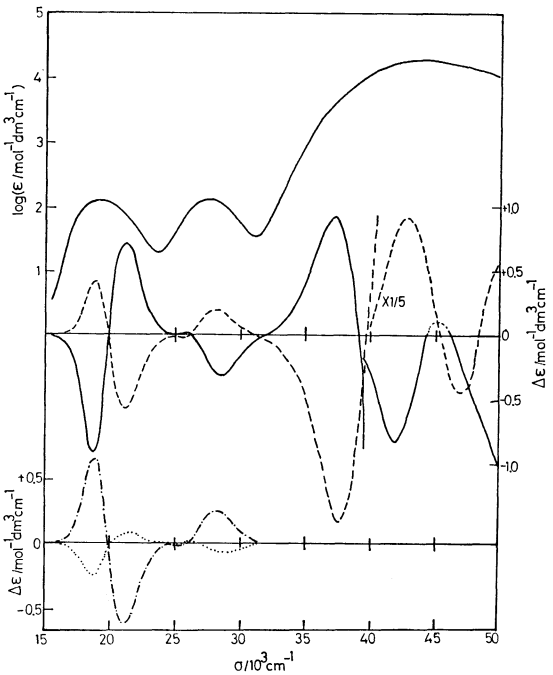

Fig. 8. Absorption and CD curves of A-3-a (----) and A-3-b (——) isomers of [Co(L-ala)(*i*-dtma)]$^+$. Two calculated CD curves of the vicinal (……) and arrangement (—·—) effects are also shown.

for A-2, and (−) and (+) for A-3, respectively, in the first d-d absorption band region. These results lead one to the assignment that A-2 (and G-2) has structure *u*-α and A-3 (and G-3) *u*-β. Therefore, all the four and six isomers obtained for the glycinato and L-alaninato complexes, respectively, are assigned to have the following geometrical structures: G-1 and A-1 are *s*-α, G-2 and A-2 (a and b) are *u*-α, G-3 and A-3 (a and b) are *u*-β, and G-4 and A-4 are *s*-β. Without activated charcoal, the substitution reaction of [CoCl(*i*-dtma)(H_2O)]$^+$ with an amino carboxylate

TABLE 2. CD DATA OF [Co(A-B)(*i*-dtma)]-TYPE COMPLEXES (A-B=gly, L-ala, en, AND (*R*)-pn)
Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in $10^3\,cm^{-1}$ and $mol^{-1}\,dm^3\,cm^{-1}$, respectively.

Complex	d-d Transition band		Ultraviolet band
	1 st	2 nd	
$(-)_{589}$-(G-2)-[Co(gly)(*i*-dtma)]$^+$	19.31 (−0.787) 21.74 (+1.00)	28.41 (−0.395)	38.02 (+2.30) 42.55 (−4.60) 48.08 (+1.88)
(A-1)-[Co(L-ala)(*i*-dtma)]$^+$	18.12 (+0.158) 21.57 (−0.489)	29.28 (+0.062)	36.90 (−0.448) 42.55 (−0.581) 45.66 (+0.715)
(A-2-a)-[Co(L-ala)(*i*-dtma)]$^+$	19.38 (−1.20) 21.88 (+0.867)	28.57 (−0.401)	38.02 (+2.90) 42.55 (−9.02) 47.62 (+2.64)
(A-2-b)-[Co(L-ala)(*i*-dtma)]$^+$	19.38 (+1.44) 21.74 (−2.32)	28.65 (+0.917)	38.17 (−4.60) 43.29 (+7.12) 47.85 (−3.80)
(A-3-a)-[Co(L-ala)(*i*-dtma)]$^+$ [a]	18.89 (+0.415) 21.10 (−0.577)	25.64 (−0.017) 28.09 (+0.189)	37.59 (−1.47) 43.01 (+4.53) 47.06 (−2.28)
(A-3-b)-[Co(L-ala)(*i*-dtma)]$^+$	18.83 (−0.906) 21.16 (+0.701)	25.84 (+0.016) 28.53 (−0.315)	37.31 (+0.913) 41.84 (−4.18)
(A-4)-[Co(L-ala)(*i*-dtma)]$^+$	18.45 (−0.205) 20.55 (+0.422)	25.2 (−0.083) 27.59 (−0.163)	38.48 (−1.24) 43.29 (+1.88) 47.6 (−2.2)
$(-)_{589}$-(E-1)-[Co(*i*-dtma)(en)]$^{2+}$	19.53 (−1.16) 22.17 (+0.72)	26 sh 29.15 (−0.310)	37.74 (+2.22) 43.96 (−6.43)
(P-1-a)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	19.65 (+1.14) 22.22 (−0.587)	26.46 (−0.096) 29.15 (+0.216)	37.12 (−1.79) 44.24 (+9.74)
(P-1-b)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	19.49 (−1.20) 22.10 (+0.905)	29.03 (−0.456)	38.76 (+3.11) 44.05 (−1.43)
(P-2)-[Co(*i*-dtma)((*R*)-pn)]$^{2+}$	19.98 (−0.173) 22.27 (+0.300)	26.88 (−0.073) 29.24 (−0.053)	43.48 (+4.17)
$(+)_{589}$-[Co$(NO_2)_3$(edma)]$^-$	20.64 (+1.095) 23.42 (−0.822)		26 sh 29.76 (+1.49) 36.90 (−6.03) 42.55 (+19.4)

a) The $\Delta\varepsilon$ values were determined on assumption that the absorption spectrum of A-3-a is identical with that of A-3-b.

gave a mixture of the four isomers, whose formation ratios decreased in the following order; *u*-α, *u*-β, *s*-α, and *s*-β. Activated charcoal caused the formation of only *s*-α and *u*-α isomers, for which the nitrogen donor atom of the amino carboxylate is located at the trans position of the tertiary amine of *i*-dtma, with a preponderant yield of *u*-α.

The absorption spectra of the amino carboxylato complexes studied in the present work are rather distinct from those of usual tris-bidentate complexes with the same CoN_4O_2 chromophore. The color of G-1, *trans*(*O*), is yellow-orange, while that of *trans*(*O*)-[Co(gly)$_2$(en)]$^+$ is red. This can be explained by the fact that the intensity ratio of the split components of the first d-d absorption band is reversed between the two complexes: $18.5\times10^3\,cm^{-1}$ (sh, log ε=1.5) and 21.5 (1.85) for G-1 and 18.9 (1.94) and 22 (sh, 1.6) for *trans*(*O*)-[Co(gly)$_2$(en)]$^+$ [8]. As for the other three *cis*(*O*) isomers, the absorption maxima due to d-d transitions are generally at lower energies than those of C_1- and C_2-*cis*(*O*)-[Co(gly)$_2$(en)]$^+$ with the order of increasing energies; G-3 (*u*-β), G-4 (*s*-β), and G-2 (*u*-α) (Fig. 5). G-4 and A-4 show a trend of splitting in the second d-d transition band region (see also Table 1).

A-1 and A-4 are mutually quasi-enantiomeric isomers[1] and the CD spectra are approximately enantiomeric in the d-d transition band region but similar in the charge-transfer transition region (Fig. 6 and Table 2). On the basis of the same assumption as for the ata and tren complexes that the "quasi-enantiomeric" contribution, CD[*trans*]=−CD[*cis*], and the "asymmetric carbon" contribution, CD[S], are additive, the individual CD curves calculated from the observed CD curves of A-1 and A-4 are shown in Fig. 6. The CD[*trans*](=1/2{CD[A-1]−CD[A-4]}) curve showed a pattern similar to those of the corresponding ata and tren complexes:[1] two (+ and −) components in the first and one (+) component in the second d-d transition band region, respectively, while the pattern of CD[S] contribution for the *i*-dtma complex, 1/2{CD[A-1]+CD[A-4]} also resembled that of the vicinal CD for *trans*(*O*)-[Co(L-ala)$_2$-(en)]$^+$ [8] in the first d-d transition band region.

Isomers A-2-a and -b as well as A-3-a and -b are a pair of the diastereomers, which reveal approximately enantiomeric CD spectra over the whole range of wave numbers (Figs. 7 and 8). These CD curves consist of two contributions from the vicinal effect of the L-alaninate ligand and from the chiral arrange-

ment of *i*-dtma ligand. The contributions were separated into two, those of the chiral arrangement of the *i*-dtma; 1/2{CD[A-2-b]−CD[A-2-a]} for A-2 and 1/2{CD[A-3-a]−CD[A-3-b]} for A-3 and those of the vicinal; 1/2{CD[A-2-b]+CD[A-2-a]} for A-2 and 1/2-{CD[a-3-a]+CD[A-3-b]} for A-3, respectively, which are also shown in Figs. 7 and 8. The patterns of the former contributions are similar to that of $(+)_{589}$-(G-2)-[Co(gly)(*i*-dtma)]$^+$ which shows three (−, + and −) components in the d-d transition band region. Those of the latter contributions in the d-d transition band region are approximately enantiomeric, which means that A-2 and A-3 have the quasi-enantiomeric configurations in regard to the L-alaninate ligand. Both contributions of A-2 in the d-d transition band region are twice larger than those of A-3. For both A-2 and A-3 the CD contributions of chiral arrangement of *i*-dtma are larger than those of the vicinal; that is, the patterns of the observed CD for these *u*-type complexes are mainly determined by the chiral arrangement of the *i*-dtma ligand.

1,2-Diamine Complex with i-dtma: On preparing the 1,2-diamine complexes, the substitution reaction in an aqueous solution on a steam bath with activated charcoal[6] yielded a brown product (probably, organic compound) and a tris-bidentate complex besides the desired complex. However, none of the brown product and a rather small amount of the tris-diamine complex were formed when DMF was used as solvent. The main product was isomer E-1 or P-1, irrespective of the solvent, DMF or water.

Both the possible two isomers (E-1 and -2) were isolated for the en complex and the chiral isomer (E-1) was optically resolved. Six chiral isomers, four of which are two pairs of diastereomers, are possible for the (*R*)-pn complex but only three (P-1-a and -b and P-2) were isolated. It is found from their absorption spectra that P-1 and P-2 are analogous to E-1 and E-2, respectively. On the basis of the ^{1}H-NMR spectra (Fig. 4) E-1 is assigned to *u*-type, and E-2 to *s*-type. The optical resolution of E-1 confirms this assignment. The ^{1}H-NMR spectrum of P-2 (*s*-type) shows two doublets (1.40 and 1.34; 1.30 and 1.24 ppm) due to the methyl protons of the (*R*)-pn, while that of P-1-a one methyl doublet (1.38 and 1.32 ppm) and an AB quartet (4.53, 4.34, 3.97, and 3.79 ppm) due to the acetate methylene protons of *i*-dtma (Fig. 4). It is concluded from these results that P-2 is a mixture of the two *s*-type isomers, *s*-α and *s*-β, and that P-1-a comprises only one isomer of structure *u*-α or *u*-β.

The (*i*-dtma)(1,2-diamine) complexes have a CoN_5O chromophore. Figures 9, 10, and 11 show the electronic absorption and CD spectra of the en and (*R*)-pn complexes. The isomers of *u*-type, E-1 and P-1, have the absorption maxima at the energies slightly higher than *s*-type, E-2 and P-2 (Table 1). This suggests that the *i*-dtma ligand has different average ligand-field strengths in the different configurations; the strength of the *i*-dtma coordinating to the central metal facially with the three nitrogen atoms of *u*-type is smaller than that of the same ligand with *meridional*-(*N*)-coordination of *s*-type. The same argument seems

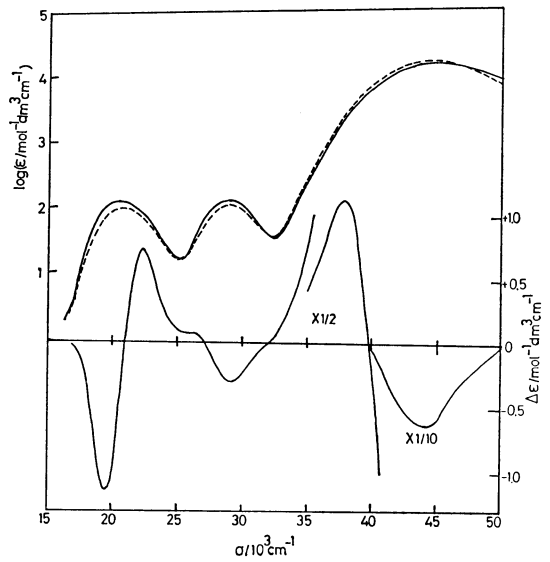

Fig. 9. Absorption and CD curves of E-1 (——) and E-2 (----) isomers of [Co(*i*-dtma)(en)]$^{2+}$.

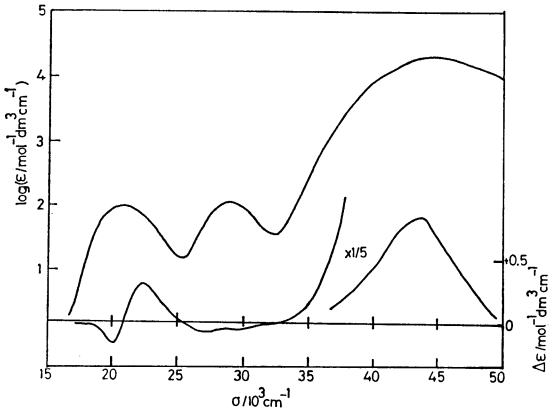

Fig. 10. Absorption and CD curves of P-2 isomer of [Co(*i*-dtma)((*R*)-pn)]$^{2+}$.

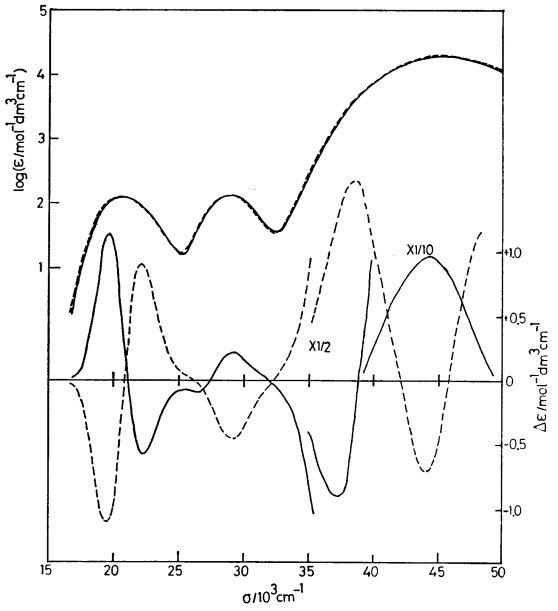

Fig. 11. Absorption and CD curves of P-1-a (——) and P-1-b (----) isomers of [Co(*i*-dtma)((*R*)-pn)]$^{2+}$.

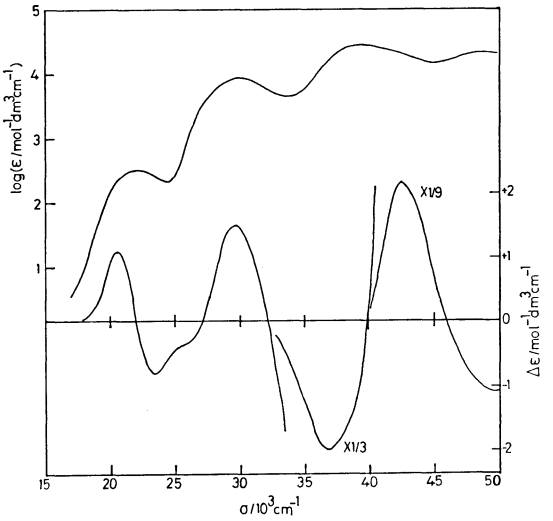

Fig. 12. Absorption and CD curves of $(+)_{589}$-isomer of $[Co(NO_2)_3(edma)]^-$.

to hold for the other complexes, [Co(*i*-dtma)(A-A)] (A-A=CO_3^{2-} [9], ox^{2-}, and $acac^-$[6]). For the *i*-dtma complexes, the molar extinction coefficients of the *u*-type *fac*(*N*) isomers are generally larger than those of the *s*-type *mer*(*N*) isomers.

[*Co*(NO_2)$_3$(*edma*)]$^-$: Two geometrical isomers, *mer*-(NO_2) and *fac*(NO_2), are possible for the edma complex. Though both isomers should be optically resolvable, the sources of their optical activities may be quite different from each other; for *mer*(NO_2) isomer the contribution from the asymmetric nitrogen atom in edma, while for *fac*(NO_2) isomer two contributions from the asymmetric nitrogen and from the chiral arrangement of the edma ligand. It has been known that the active *mer*-$[Co(dien)_2]^{3+}$ (dien=diethylenetriamine) completely racemizes within 5 min in an aqueous solution at pH 10, though it is stable in an acidic solution at 20 °C.[10] Figure 12 shows the absorption and CD spectra of $(+)_{589}$-$[Co(NO_2)_3$-(edma)]$^-$. The fact that the CD spectrum was little affected in a LiOH solution (pH 10) at room temperature for 12 h indicates that the obtained isomer is *fac*(NO_2).

Absolute Configurations: The ring-pairing method cannot be applied to the absolute configurations of the *u*-type complexes. The absolute configurations for the isomers are tentatively predicted as follows. Isomers, A-2-a and A-3-b, should have the same absolute configurations as $(-)_{589}$-(G-2)-[Co(gly)(*i*-dtma)]$^+$ (Fig. 7) in regard to *i*-dtma. The isomers of the L-alaninato complex were separated on an ion-exchanger column by eluting with a NaH_2PO_4–Na_2HPO_4 buffer. Figure 13 shows four absolute configurations of the diastereomers, where **N** signifies an amino group which can associate with phosphate species. The upper two isomers have three **N**'s in facial arrangement while the lower two have three **N**'s in meridional arrangement. The facial arrangement of the three amino group is preferable to the meridional arrangement for the association.[11] The formation of such an ion pair will decrease the average positive charge on the cationic

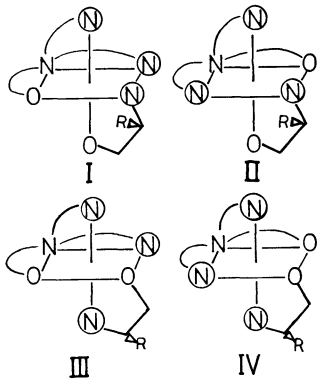

Fig. 13. Absolute configurations of four diastereomers of [Co(L-ala)(*i*-dtma)]$^+$ with u-type structure, where R=CH_3.

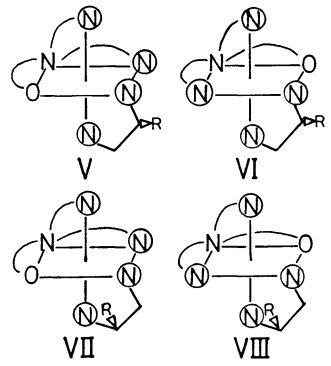

Fig. 14. Absolute configurations of four diastereomers of [Co(*i*-dtma)((*R*)-pn)]$^{2+}$ with *u*-type structure, where R=CH_3.

species and facilitate the elution of the complex. Hence it is predicted that *fac*(**N**) isomers, (I and II), should be eluted faster than *mer*(**N**), (III and IV). The *fac*(**N**) and the *mer*(**N**) isomers correspond to the structure *u*-α and *u*-β, respectively. In *fac*(**N**) isomers, isomer I should be eluted faster than II, because the methyl substituent of II will make the ion pair less stable than that of I. As for *mer*(**N**) isomers which may form an ion pair with phosphate anions not so firmly as the *fac*(**N**) isomers, the phosphate will yet prefer isomer IV to III, the former having a methyl substituent directed far from the plane of three **N**'s. Thus, the A-2-a, -b, A-3-a, and -b isomers are assigned to I, II, IV, and III, respectively, and the absolute configuration of $(-)_{589}$-[Co-(gly)(*i*-dtma)]$^+$ (G-2) to I.

From the CD spectra the P-1-b should have the same absolute configuration of *i*-dtma as that of $(-)_{589}$-$[Co(i\text{-dtma})(en)]^{2+}$ (Fig. 9) and also those of A-2-a, A-3-b, and $(-)_{589}$-(G-2)-[Co(gly)(*i*-dtma)]$^+$ (Figs. 4, 6, and 7), because the CD contribution from the *u*-type configurational effect of *i*-dtma is expected to be larger than that from the so-called "vicinal" effect of (*R*)-pn and to show the same pattern as that of L-alaninato complex in the first and second d-d transition band region. Thus the absolute configurations of P-1-a and -b may be assigned to (VI or VII) and (V or VIII), respectively.

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2) Abbreviations of ligands: acac$^-$=acetylacetonate, aeida^{2-}=*N*-(2-aminoethyl)iminodiacetate, L-ala$^-$=L-alaninate, *β*-alada^{3-}=*N*,*N*-bis(carboxylatomethyl)-*β*-alaninate, ata^{3-}=nitrilotriacetate, *i*-dtma$^-$=*N*,*N*-bis(2-aminoethyl)glycinate, edma$^-$=ethylenediamine-*N*-acetate, gly$^-$=glycinate, ox^{2-}=oxalate, (*R*)-pn=(*R*)-propylenediamine, tren=tris(2-aminoethyl)amine.

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