adjacent metal atoms to form a confacial bioctahedron may occur as steps throughout this process.[17] This scheme, while not necessarily entirely accurate, provides a consistent explanation for the reactivity of $Mo_2O_4(S_2CNEt_2)_2$ toward acids and for the known structure of $Mo_2O_3(SPh)_2S_2CNEt_2)_2$[14b] and the presumed structure[16] of $Mo_2O_3(SCH_2CH_2O)(S_2CNEt_2)_2$. Interestingly, diprotic acids whose conjugate bases are powerful, inflexible chelating agents can remove the last bridging oxo ligand to yield mononuclear complexes.

Although the initial portion of this scheme would presumably apply to the reactions of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ with acids which were studied, one important aspect must be different. Since initial protonation can occur at either the bridging oxo or imido ligands, we must assume that the relative basicities of these ligands are in the same order as those of water and ammonia so that only the imido ligand is protonated. Further protonation of the amido ligand would be difficult because it would necessarily entail rupture of a Mo–N bond, a bond whose general stability has been demonstrated by the present studies. It is conceivable that other acids,[18] particularly diprotic chelating acids, could result in protonation of both the imido and oxo ligands. If this occurs, the bridging hydroxo ligand may well be susceptible to further protonation by analogy to the protonations of $Mo_2O_4(S_2CNEt_2)_2$.

Acknowledgment. Support from NSF Grant No. CHE 75-08188-A01 and a grant-in-aid from Indiana University is acknowledged.

Registry No. $MoO(S_2P(OEt)_2)_2$, 25395-91-9; $Mo_2O_3(NH)(S_2P(OEt)_2)_2$, 66741-00-2; $Mo_2O_3(NH_2)Cl(S_2P(OEt)_2)_2$, 73558-07-3; $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$, 73558-08-4; $Mo_2O_2(NPh)(S_2P(OEt)_2)_4$, 73558-09-5; NaN_3, 26628-22-8; phenyl azide, 622-37-7; HN_3, 7782-79-8; $Mo_2O_2(NH_2)(SCH_2CH_2O)_2(S_2P(OEt)_2)$, 73697-78-6.

(17) Although the reaction of $Mo_2O_4(S_2CNEt_2)_2$ with either $S_2CNEt_2^-$ or HS_2PR_2 in CH_2Cl_2 containing methyl alcohol results[16] in the formation of $Mo_2O_3L_4$ rather than a confacial bioctahedron, it may be that these chelating agents are incapable of occupying two bridging sites of a confacial bioctahedron.

(18) We have also shown that the reaction of HBr with $Mo_2O_3(NH)(S_2P(OEt)_2)_2$ gives $Mo_2O_3(NH_2)Br(S_2P(OEt)_2)_2$ with excellent analytical results. Similarly, the reaction of 2-mercaptoethanol with the imido complex leads to a compound which we formulate provisionally as $Mo_2O_2(NH_2)(S_2CH_2CH_2O)_2(S_2P(OEt)_2)$, again with excellent analytical results. The ^1H NMR spectrum in deuterated Me_2SO is complex but shows that the mercaptoethanolate ligands are not equivalent while resonances which can presumably be assigned to the bridging amido ligand occur at 8.30 and 8.65 ppm. If the formulation of this compound is correct, it represents the first example of a complex whose reaction with an acid leads to both the removal of a bridging oxo ligand as well as the protonation of the imido ligand. Reactions of the imido complex with acetic acid, thioacetic acid, 8-hydroxyquinoline, and *o*-aminothiophenol have also been observed. The death of Winston Edelblut, a tragic loss of a very promising young chemist, has prevented a thorough investigation of the products of these reactions.

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Asymmetric Transformation of α-Amino Acids Promoted by Optically Active Cobalt(III) Complexes

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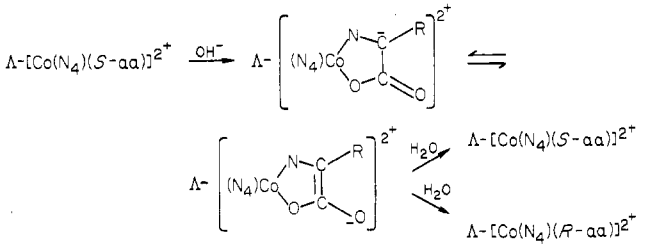
The hydroxide ion catalyzed epimerization of chelated α-amino acidates in Λ-β_2-[Co(N_4)(*S*- or *R*-aa)]$^{2+}$ ((N_4) = tetraamine ligand; aa = amino acidato) is an example of a "first-order asymmetric transformation" of α-amino acids promoted by chiral cobalt(III) complexes. Chiral derivatives of 2,3,2-tet (1,9-diamino-3,7-diazanonane) or triethylenetetramine were employed as quadridentate ligands. Epimerization of alaninate, valinate, and phenylalaninate moieties in Λ-β_2-[Co(N_4)(*S*- or *R*-aa)]$^{2+}$ were examined at pH 10–12 carbonate buffer, to give equilibrium mixtures of diastereomers (Λ-*R* and Λ-*S*). In the most discriminative case where (N_4) = *SS*-phyt and aa = α-alaninate the isomer ratio for Λ-*S*/Λ-*R* was 18/82. The energy difference between the Λ-*R* and Λ-*S* isomers is discussed in relation to the prediction of strain energy minimization calculations.

Introduction

It has been known that metal ions increase the reactivity of the α proton of chelated α-amino acids.[1] Sargeson and co-workers showed[2] that the α proton of chelated α-amino acidate moieties in dissymmetric complex ions undergoes OH^--catalyzed exchange in basic aqueous solution, to give a diastereomeric equilibrium mixture. They measured the equilibrium constants between the diastereomers Λ-[Co(en)$_2$(*R*-aa)]$^{2+}$ and Λ-[Co(en)$_2$(*S*-aa)]$^{2+}$ (aa represents the α-amino acidate coordinated as a bidentate ligand) and obtained the isomer ratio Λ-[Co(en)$_2$(*R*-val)]$^{2+}$/Λ-[Co(en)$_2$(*S*-val)]$^{2+}$ = 63/37 and Λ-[Co(en)$_2$(*R*-ala)]$^{2+}$/Λ-[Co(en)$_2$(*S*-ala)]$^{2+}$ = 50/50. Under the above conditions, the racemization of the chelated α-amino acidates occurred without change in the arrangement of three chelate rings around the cobalt(III) center (represented by Λ or Δ). The above reaction is applicable to the amino acidato complexes having the general formula [Co(N_4)(*R*- or *S*-aa)]$^{2+}$, where (N_4) indicates four amine nitrogen atoms of two diamines or a tetraamine.

Scheme I. Proposed Mechanism for the Epimerization of a Chelated α-Amino Acid in Basic Solution



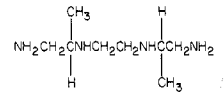
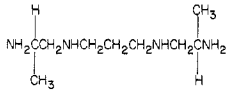
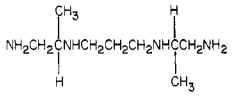
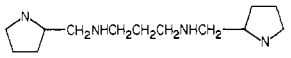
Scheme I shows the proposed mechanism for the OH^--promoted epimerization of an α-amino acid coordinated to a dissymmetric center in Λ-[Co(N_4)(*S*-aa)]$^{2+}$.[2] It can be expected that the ratio of two isomers (Λ-*R*/Λ-*S*) at equilibrium will be biased from 50/50, reflecting the free energy difference between the diastereomers. On this basis the epimerization in Λ-[Co(N_4)(*R*- or *S*-aa)]$^{2+}$ is considered as an example of

(1) (a) Sato, M.; Okawa, K.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 937. (b) Williams, D. H.; Busch, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 4644.

(2) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133.

0020-1669/80/1319-2010$01.00/0

Table I. Abbreviation and Structure of Ligands

structure	abbreviation
	3(*S*),8(*S*)-Me_2 trien
	2(*S*),10(*S*)-Me_2-2,3,2-tet
	3(*S*),9(*S*)-Me_2-2,3,2-tet
	*SS*-pyht

a "first-order asymmetric transformation"[3] of a racemic α-amino acid.

To gain insight into the influence of an α substituent of amino acid on the isomer ratio, we investigated alaninato, valinato, and phenylalaninato complexes. A few chiral derivatives of triethylenetetramine (trien) and 1,9-diamino-3,7-diazanonane (2,3,2-tet) were employed for (N_4). And Λ-β_2-$[Co(N_4)(aa)]^{2+}$ type complexes were prepared.[4] The structure and abbreviations for these tetraamines are summarized in Table I. The epimerizations of the amino acidato complexes were carried out in basic solutions. After equilibrium had been established, the isomer ratios were obtained by chromatographic separation of the diastereomers. The results are discussed in relation to the prediction of strain energy minimization calculations.

Experimental Section

All materials used were reagent grade. The ligands 3(*S*),8(*S*)-dimethyltriethylenetetramine (=3(*S*),8(*S*)-Me_2trien)[5] and 2(*S*),10(*S*)-4,8-diazaundecane-2,10-diamine (=2(*S*),10(*S*)-Me_2-2,3,2-tet)[6,7] were prepared by the method described previously. The ligand 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane (=*SS*-pyht) was prepared as reported by Jun and Liu[8] and isolated by distillation under reduced pressure (bp 134–148 °C (0.5 mmHg)). The ligand 2(*S*),8(*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (=3(*S*),9(*S*)-Me_2-2,3,2-tet) was prepared as follows.

2(*S*),8(*S*)-3,7-Diaza-2,8-dimethyl-1,9-dibromononane Dihydrobromide. Into a 300-mL four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser was placed L-alaninol[9] (45.4 g, 0.6 mol) which was heated to 130 °C with stirring. 1,3-Dichloropropane (30.3 g, 0.3 mol) was added dropwise at such a rate that the temperature was maintained between 130–40 °C. The mixture was stirred and heated at 130 °C for more than 3 h and then cooled to room temperature. To this mixture was added a solution of sodium (7.8 g) dissolved in methanol (140 mL) with stirring. After the solution stood overnight, the precipitated sodium chloride was removed by filtration and washed with 30 mL of methanol. The filtrate and washings were combined, and methanol and excess L-alaninol were removed by distillation under reduced pressure (20 mmHg and 3 mmHg, respectively). To a solution of the resulting pale yellow oil in water (70 mL) was added 48% hydrobromic acid (43 mL) in an ice bath. After removal of water under reduced pressure, phosphorus tribromide (29 mL) was added, and then the mixture in a round-bottomed flask equipped with a reflux condenser was heated on a boiling water bath with occasional shaking. Very viscous yellowish oil was formed. After being concentrated under reduced pressure and washed with three 100-mL portions of diethyl ether, the oily product was dissolved in 20 mL of water, and then the solution was concentrated to dryness with a rotary evaporator. The product, 3,9-diaza-2(*S*),8(*S*)-dimethyl-1,9-dibromononane, was used in the next step without further purification.

2(*S*),8(*S*)-2,8-Dimethyl-3,7-diazanonane-1,9-diamine (=3(*S*),9-(*S*)-Me_2-2,3,2-tet). 3,9-Diaza-2(*S*),8(*S*)-dimethyl-1,9-dibromononane (45 g) dissolved in a minimum amount of water was added to 28% ammonium hydroxide at ice-bath temperature. The solution was refluxed for 8 h, cooled to room temperature, and concentrated on a rotary evaporator to dryness. To the resulting yellow syrup was added solid sodium hydroxide until an oily layer separated. The oily layer was extracted with benzene, and the extract was dried over potassium hydroxide pellets. Benzene was removed at reduced pressure, and the residue was vacuum distilled as a pale yellow oil: bp 130–135 °C (3 mmHg); yield 7.0 g.

Preparation of *trans*-Dichlorocobalt(III) Complexes with Tetraamine. In general, *trans*-dichloro complexes have been prepared by an air-oxidation method.[7,8,10] In this work most of these complexes were prepared from (carbonato)(tetraamine)cobalt(III) complexes because of their higher yield, as compared with the air-oxidation methods.

trans-**$[CoCl_2$(3(*S*),8(*S*)-Me_2trien)$]ClO_4$ (1)** was prepared by an air-oxidation method (previously described[10]).

trans-**$[CoCl_2$(3(*S*),9(*S*)-Me_2-2,3,2-tet)$]ClO_4$ (3).** This was prepared from $[CoCO_3$(3(*S*),9(*S*)-Me_2-2,3,2-tet)$]^+$ as follows. To a mixture of 60% perchloric acid (10.7 g) and water (15 mL), cooled in an ice bath, was added 3(*S*),9(*S*)-Me_2-2,3,2-tet (4.0 g) dropwise with occasional stirring. This solution was added dropwise to a stirred slurry of sodium tris(carbonato)cobaltate(III) trihydrate (7.7 g)[11] in 50 mL of water. The mixture was heated on a water bath for 10 min. After the solution was cooled to room temperature, concentrated hydrochloric acid (10 mL) was added dropwise. After the evolution of carbon dioxide had ceased, 60% perchloric acid was added to the resultant deep red solution. Then the solution was evaporated on a water bath until the precipitation of green crystals was almost completed. The contents were cooled, and the crystals were filtered off, washed with ethanol and ether, and air-dried; yield 6.24 g (70%). Anal. Calcd for $[CoCl_2(C_9H_{24}N_4)]ClO_4$: C, 25.88; H, 5.79; N, 13.42. Found: C, 25.57; H, 5.67; N, 13.04.

trans-**$[CoCl_2$(2(*S*),10(*S*)-Me_2-2,3,2-tet)$]ClO_4$ (2)**[7] **and** *trans*-**$[CoCl_2$(*SS*-pyht)$]ClO_4$ (4)**[8] were prepared by the same procedure as above. Anal. Calcd for the 2(*S*),10(*S*)-Me_2-2,3,2-tet complex, $[CoCl_2(C_9H_{24}N_4)]ClO_4$: C, 25.88; H, 5.79; N, 13.42. Found: C, 25.89; H, 5.44; N, 13.13. Calcd for the *SS*-pyht complex, $[CoCl_2(C_{13}H_{28}N_4)]ClO_4$: C, 33.24; H, 6.01; N, 11.93. Found: C, 33.14; H, 5.95; N, 12.06.

Λ-β_2-$[Co$(3(*S*),8(*S*)-Me_2trien)(*R*- or *S*-ala)$]ZnCl_4 \cdot 1.5H_2O$ (5). Preparative Method I. To a solution of $LiOH \cdot H_2O$ (0.088 g) and (*R*)-alanine (or (*S*)-alanine) (0.178 g) in 5 mL of water was added **1** (0.80 g), and the solution was heated for 15 min on a water bath at 70 °C. A solution of $ZnCl_2$ (0.825 g) and LiCl (0.51 g) in a minimum amount of water was added. The solution was cooled overnight in a refrigerator: the yellow-orange crystals were collected, washed with ethanol and ether, and air-dried. The product was recrystallized from hot water; yield 0.58 g (55%) for (*R*)-alaninato complex ($\mathbf{5}_R$) and 0.15 g (16%) for (*S*)-alaninato ($\mathbf{5}_S$), respectively. Anal. Calcd for $[Co(C_8H_{22}N_4)(C_3H_6NO_2)]ZnCl_4 \cdot 1.5H_2O$: C, 23.78; H, 5.08; N, 12.61. Found: C, 23.64; H, 4.94; N, 12.72 for $\mathbf{5}_R$. Found: C, 23.68; H, 5.33; N, 12.74 for $\mathbf{5}_S$.

Λ-β_2-$[Co$(3(*S*),8(*S*)-Me_2trien)(*R*- or *S*-val)$](ClO_4)_2$ (6). Preparative Method II. (*R*)-Valine (or (*S*)-valine) (0.34 g) was dissolved in 30 mL of water, and **1** (0.80 g) was added, and the solution was heated for 30 min on a water bath at 70 °C, while the pH of this solution was maintained between 5.5 and 6.0 with 1 M NaOH. After the solution was made basic (pH 8) with 5 M NaOH, the solution was further heated on a water bath (70 °C) for 1.5 h with frequent checks to ensure the pH between 8.0 and 8.5. The resultant red solution was cooled to room temperature, diluted with water (200 mL),

(3) Turner, E. E.; Harris, M. M. *Q. Rev., Chem. Soc.* **1947**, *1*, 299.
(4) β_1 and β_2 refer to the two configurational isomers obtained using different or unsymmetrical donor ligands in the remaining octahedral sites. For amino acidate, β_2 refers to the isomer with O trans to the apical N of the tetraamine: Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1967**, *6*, 787; Buckingham, D. A.; Marzilli, L. G. *Ibid.* **1967**, *6*, 1042.
(5) Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 806.
(6) Harrington, P. C.; Linke, S.; Alexander, M. D. *Inorg. Chem.* **1973**, *12*, 168.
(7) Goto, M.; Makino, T.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1879.
(8) Jun, M.; Liu, C. F. *J. Coord. Chem.* **1975**, *5*, 1.
(9) Seki, H.; Koga, K.; Matsuo, H.; Ohki, S.; Matsuo, I.; Yamada, S. *Chem. Pharm. Bull.* **1965**, *13*, 995.
(10) Goto, M.; Okubo, A.; Sawai, T.; Yoshikawa, S. *Inorg. Chem.* **1970**, *9*, 1488.
(11) Bauer, H. F.; Drinkard, W. C. *Inorg. Synth.* **1900**, *8*, 202.

and poured on a column of SP-Sephadex C25 cation-exchange resin (4.0 × 40 cm) in the sodium form. The complexes were eluted with 0.1 M sodium perchlorate. The four bands were developed on the column. The eluant for each band was collected and identified by its electronic, circular dichroism, and ^{1}H NMR spectra. The first pink band (bottom) and the fourth brown band (top) moved at rates consistent with 1+ and 3+ ions, respectively, and the ^{1}H NMR spectra showed that the complexes for those bands do not contain valinate groups. The 1+ ion was assumed to be the carbonato complex, since by the addition of 12 N HCl to its evaporated residue, the trans dichloro complex was recovered. The two orange 2+ bands contained the valinate moiety. The minor second band and the major third band were assigned to the β_1- and β_2-valinato complexes, respectively. The third band was concentrated on a rotary evaporator below 50 °C until orange crystals began to precipitate. After the solution stood several hours at room temperature, the orange crystals were collected, washed with methanol and ether, and air-dried; yield 0.52 g (47%) for (*R*)-valinato complex (**6**$_R$) and 0.50 g (46%) for (*S*)-valinato (**6**$_S$). Anal. Calcd for $[Co(C_8H_{22}N_4)(C_5H_{10}NO_2)](ClO_4)_2$: C, 28.48; H, 5.88; N, 12.77. Found: C, 28.20; H, 5.57; N, 12.39 for **6**$_R$. Found: C, 28.44; H, 5.81; N, 12.42 for **6**$_S$.

Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*R*-ala)](ClO$_4$)$_2$·H$_2$O (7$_R$) was prepared from **2** (0.84 g) and (*R*)-alanine (0.28 g) by the above procedure. Orange-red crystals were obtained; yield 0.52 g (47%). Anal. Calcd for $[Co(C_9H_{24}N_4)(C_3H_6NO_2)](ClO_4)_2·H_2O$: C, 26.09; H, 5.84; N, 12.68. Found: C, 26.46; H, 5.75; N, 12.49.

Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*S*-ala)](ClO$_4$)$_2$·0.5H$_2$O (7$_S$) was prepared from **2** and (*S*)-alanine in the same manner as above; yield 0.48 g (44%). Anal. Calcd for $[Co(C_9H_{24}N_4)(C_3H_6NO_2)](ClO_4)_2·0.5H_2O$: C, 26.53; H, 5.75; N, 12.89. Found: C, 26.56; H, 5.92; N, 12.83.

Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*R*- or *S*-val)](ClO$_4$)$_2$ (8) was prepared from **2** (0.84 g) and (*R*)-valine (or (*S*-valine) (0.34 g) by the above procedure; yield 0.57 g (51%) for **8**$_R$ and 0.43 g (38%) for **8**$_S$. Anal. Calcd for $[Co(C_9H_{24}N_4)(C_5H_{10}NO_2)](ClO_4)_2$: C, 29.93; H, 6.09; N, 12.46. Found: C, 29.89; H, 6.35; N, 12.43 for **8**$_R$. Found: C, 29.78; H, 6.18; N, 12.26 for **8**$_S$.

Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*R*-phe)](ClO$_4$)$_2$·2H$_2$O (9$_R$) was prepared from **2** (0.84 g) and (*R*)-phenylalanine (0.40 g) by method II; yield 0.50 g (39%). A small amount of the compound was recrystallized from hot water for elemental analysis. Anal. Calcd for $[Co(C_9H_{24}N_4)(C_9H_{10}NO_2)](ClO_4)_2·2H_2O$: C, 33.45; H, 5.93; N, 10.84. Found: C, 33.50; H, 6.02; N, 10.66.

Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*S*-phe)](ClO$_4$)$_2$·H$_2$O (9$_S$) was prepared from **2** and (*S*)-phenylalanine in the same manner; yield 0.48 g (38%). It was recrystallized from hot water. Anal. Calcd for $[Co(C_9H_{24}N_4)(C_9H_{10}NO_2)](ClO_4)_2·H_2O$: C, 34.41; H, 5.77; N, 11.14. Found: C, 34.51; H, 5.79; N, 11.11.

Preparation of Λ-β_2-[Co(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)(aa)](ClO$_4$)$_2$·*n*H$_2$O. The preparation of alaninato, valinato, and phenylalaninato complexes was similar to those of the corresponding Λ-β_2-[Co(2-(*S*),10(*S*)-Me$_2$-2,3,2-tet)(aa)](ClO$_4$)$_2$ complexes by using **3** in place of **2**. Anal. Calcd for Λ-β_2-[Co(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)(*R*- or *S*-ala)](ClO$_4$)$_2$ (**10**), $[Co(C_9H_{24}N_4)(C_3H_6NO_2)](ClO_4)_2$: C, 26.98; H, 5.66; N, 13.11. Found: C, 26.75; H, 5.55; N, 12.83 for **10**$_R$. Found: C, 26.90; H, 5.21; N, 12.93 for **10**$_S$. Calcd for Λ-β_2-[Co(3(*S*),9-(*S*)-Me$_2$-2,3,2-tet)(*R*-val)](ClO$_4$)$_2$ (**11**$_R$), $[Co(C_9H_{24}N_4)(C_5H_{10}NO_2)](ClO_4)_2$: C, 29.93; H, 6.09; N, 12.46. Found: C, 30.19; H, 6.28; N, 12.50. Calcd for Λ-β_2-[Co(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)(*S*-val)](ClO$_4$)$_2$·H$_2$O (**11**$_S$), $[Co(C_9H_{24}N_4)(C_5H_{10}NO_2)](ClO_4)_2·H_2O$: C, 28.97; H, 6.25; N, 12.07. Found: C, 28.60; H, 6.24; N, 12.03. Calcd for Λ-β_2-[Co(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)(*R*-phe)]-(ClO$_4$)$_2$·2H$_2$O (**12**$_R$), $[Co(C_9H_{24}N_4)(C_9H_{10}NO_2)](ClO_4)_2·2H_2O$: C, 33.45; H, 5.93; N, 10.84. Found: C, 33.49; H, 5.89; N, 10.73. Calcd for Λ-β_2-[Co(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)(*S*-phe)](ClO$_4$)$_2$·1.5H$_2$O (**12**$_S$), $[Co(C_9H_{24}N_4)(C_9H_{10}NO_2)](ClO_4)_2·1.5H_2O$: C, 32.99; H, 6.00; N, 10.69. Found: C, 33.01; H, 6.11; N, 10.68.

Λ-β_2-[Co(SS-pyht)(*R*-ala)](ClO$_4$)$_2$·2H$_2$O (13$_R$) was prepared from **4** (1.84 g) and (*R*)-alanine (0.36 g) by method II. Three bands were distinguished on the column during the elution with 0.1 M $NaClO_4$. The second band, identified as the Λ-β_2 isomer (of which the crystal structure has been determined by X-ray diffraction method[12]), was collected and concentrated on a rotary evaporator until orange-red crystals precipitated. After filtration, the crystals were washed with methanol and then ether and air-dried. The product was recrystallized from hot water; yield 1.04 g (44%). Anal. Calcd for $[Co(C_{13}H_{28}N_4)(C_3H_6NO_2)](ClO_4)_2·2H_2O$: C, 30.86; H, 6.16; N, 11.26. Found: C, 31.39; H, 5.71; N, 11.25.

Λ-β_2-[Co(*SS*-pyht)(*S*-ala)](ClO$_4$)$_2$·2H$_2$O (13$_S$). Preparative Method III. A procedure analogous to that described above for the preparation of **13**$_R$ from **4** (0.92 g) was employed except that (*S*)-alanine (0.22 g) was substituted for (*R*)-alanine, and activated carbon (0.2 g) was added to the solution after the solution was adjusted to pH 8. The activated carbon was removed by filtration after the reaction was completed, and the filtrate was washed with a small amount of water. The filtrate and washings were combined, and the rest of the procedure was similar to method II; yield 0.38 g (30%). Anal. Calcd for $[Co(C_{13}H_{28}N_4)(C_3H_6NO_2)](ClO_4)_2·2H_2O$: C, 30.86; H, 6.16; N, 11.26. Found: C, 31.17; H, 6.17; N, 11.51.

Measurements. The pH was measured by using a Hitachi-Horiba F-7$_{DE}$ digital pH meter. Visible absorption spectra were measured with a Shimadzu UV-210 spectrophotometer. Circular dichroism curves were obtained with a JASCO-J20 recording spectropolarimeter. Proton magnetic resonance (^{1}H NMR) spectra (90 MHz) were obtained on a Hitachi R-40 spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard reference.

The perchlorate salts (about 50–60-mg samples) were suspended in 0.5 mL of D_2O and treated with twice the molar amount of tetraphenylarsonium chloride. The white precipitates were removed by filtration, and the filtrates were employed for ^{1}H NMR measurements.

Measurements of Isomer Ratios for Epimerization Reactions. Weighed samples (about 100 mg) of Λ-β_2-Co(*R*- or *S*-aa)(N$_4$)$^{2+}$ were dissolved in 100 mL of 0.02 M Na_2CO_3 buffer (pH 11.2), and the solution was warmed at 40 °C for 24 h. At this stage, the CD curve of the solution for the (*R*)-amino acidato complex and that for the (*S*)-amino acidato complex became identical within the experimental error. In the case of phenylalaninato complexes or alaninato complexes containing *SS*-pyht, the samples were dissolved in 100 mL of 0.02 M Na_2CO_3–0.02 M $NaHCO_3$ buffer (pH 10.1) because the samples were subject to base-catalyzed hydrolysis. Then the solution was warmed at 40 °C for 4 days (or at 25 °C for a month). Even in these conditions considerable decomposition occurred with phenylalaninato complexes and $[Co(SS\text{-ala})(ala)]^{2+}$ as shown below. The solution was poured on a SP-Sephadex C25 cation-exchange resin column (2.5 × 40 cm) in the sodium form. The complexes were eluted with 0.05 M NaH_2PO_4–0.05 M Na_2HPO_4. The eluants of the four bands were collected and identified by electronic absorption, CD, and ^{1}H NMR spectra. The first red-pink band (bottom of the column) and the fourth brown band (top) moved at rates consistent with 1+ and 3+ ions, respectively, which were assumed to be hydrolysis products. The other two orange (or orange-red) 2+ bands were Λ-β_2-$[Co(aa)(N_4)]^{2+}$ complexes. The second band was the (*S*)-amino acidato complex and the third band was the (*R*)-amino acidato complex in all cases. The concentrations of these two bands were spectrophotometrically determined by using the ϵ values of the first absorption band of each isomer listed in Table II. Then Λ-*S*/Λ-*R* ratios were calculated. However, some attempts to separate the diastereomers of Λ-β_2-[Co(3(*S*),8(*S*)-Me$_2$trien)(ala or val)]$^{2+}$ failed. Therefore, the isomer ratios were obtained by comparing their CD curves with those of the (*R*)- and (*S*)-amino acidato complexes. The best fitted curves derived from the (*R*)- and (*S*)-amino acidato complexes were calculated by least-squares method. The agreement between the observed and calculated curves was satisfactory.

The recoveries of the amino acidato complexes were about 95%, 80%, and 55% for alaninato, valinato, and phenylalaninato complexes, respectively. For $[Co(SS\text{-pyht})(ala)]^{2+}$, the recovery was about 40% at 40 °C and 55% at 25 °C. Isomer ratios were reproducible to better than ±1–2%.

Strain Energy Minimization Calculations. The strain energies of some complexes were calculated according to the method described by Buckingham and co-workers[13,14] except for the minimization

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Table II. Electronic and Circular Dichroism Spectral Data

no.	complex	abs max, nm (ϵ, M^{-1} cm^{-1})	CD max, nm ($\Delta\epsilon$, M^{-1} cm^{-1})
5_R	Λ-β_2-[Co(3(*S*),8(*S*)-Me_2trien)(*R*-ala)]$ZnCl_4 \cdot 1.5H_2O$	478 (164), 348 (160)	496 (1.38), 348 (−0.25)
5_S	Λ-β_2-[Co(3(*S*),8(*S*)-Me_2trien)(*S*-ala)]$ZnCl_4 \cdot 1.5H_2O$	478 (163), 347 (157)	502 (1.97), 439 (−0.14), 372 (0.08), 339 (−0.21)
6_R	Λ-β_2-[Co(3(*S*),8(*S*)-Me_2trien)(*R*-val)]$(ClO_4)_2$	478 (157), 348 (156)	486 (1.72), 344 (−0.25)
6_S	Λ-β_2-[Co(3(*S*),8(*S*)-Me_2trien)(*S*-val)]$(ClO_4)_2$	479 (158), 348 (154)	566 (−0.02), 496 (1.95), 441 (−0.32), 369 (0.06), 338 (−0.18)
7_R	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*R*-ala)]$(ClO_4)_2 \cdot H_2O$	496 (145), 352 (145)	527 (1.84), 470 (−0.28), 372 (0.11), 338 (0.14)
7_S	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*S*-ala)]$(ClO_4)_2 \cdot 0.5H_2O$	494 (137), 353 (138)	515 (1.70), 453 (−0.53), 354 (−0.12)
8_R	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*R*-val)]$(ClO_4)_2$	495 (134), 354 (138)	525 (1.81), 465 (−0.14), 372 (0.17), 337 (0.15)
8_S	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*S*-val)]$(ClO_4)_2$	497 (142), 355 (146)	516 (1.51), 456 (−0.60), 354 (−0.15)
9_R	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*R*-phe)]$(ClO_4)_2 \cdot 2H_2O$	497 (143), 353 (150)	525 (2.23), 466 (−0.37), 373 (0.18), 338 (0.22)
9_S	Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*S*-phe)]$(ClO_4)_2 \cdot H_2O$	497 (116), 353 (124)	515 (1.51), 455 (−0.58), 356 (−0.19)
10_R	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*R*-ala)]$(ClO_4)_2$	490 (139), 352 (139)	527 (1.63), 466 (−0.36), 380 (0.08), 337 (0.11)
10_S	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*S*-ala)]$(ClO_4)_2$	493 (144), 352 (145)	516 (1.77), 455 (−0.64), 356 (−0.22)
11_R	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*R*-val)]$(ClO_4)_2$	495 (133), 354 (137)	528 (1.72), 468 (−0.24), 378 (0.19), 340 (0.17)
11_S	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*S*-val)]$(ClO_4)_2 \cdot H_2O$	498 (150), 356 (151)	520 (1.53), 459 (−0.74), 358 (−0.24)
12_R	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*R*-phe)]$(ClO_4)_2 \cdot 2H_2O$	494 (139), 352 (147)	525 (1.49), 463 (−0.47), 370 (0.05), 332 (0.08)
12_S	Λ-β_2-[Co(3(*S*),9(*S*)-Me_2-2,3,2-tet)(*S*-phe)]$(ClO_4)_2 \cdot 1.5H_2O$	496 (143), 354 (151)	521 (1.49), 460 (−0.67), 359 (−0.19)
13_R	Λ-β_2-[Co(*SS*-pyht)(*R*-ala)]$(ClO_4)_2 \cdot 2H_2O$	511 (174), 362 (191)	542 (1.38), 459 (0.24), 344 (0.26)
13_S	Λ-β_2-[Co(*SS*-pyht)(*S*-ala)]$(ClO_4)_2 \cdot 2H_2O$	514 (181), 364 (207)	540 (1.62), 477 (−0.44), 348 (0.22)

technique. The total strain energy (U) is assumed to be expressed (eq 1) as a summation of terms representing bond length deformations,

$$U = \sum_{ij} U(r_{ij})_b + \sum_{ijk} U(\theta_{ijk}) + \sum_{ij} U(r_{ij})_{nb} + \sum_{ijkl} U(\phi_{ijkl}) + \sum_{ijkl} U(\Delta_l) \quad (1)$$

$(r_{ij})_b$, bond angle deformations, θ_{ijk}, nonbonded interatomic interactions, $(r_{ij})_{nb}$, torsional constraints, ϕ_{ijk}, and out-of-plane deformations, Δ_l. The potential functions and the force constants are the same as those used by Buckingham and co-workers.[14] Analytical first derivatives are calculated according to the potential functions. Minimization of the total strain energy was achieved by using a Broyden–Fletcher–Shanno variable metric method,[15] which is considered as a powerful method when the number of variables is large.[16] Minimization was terminated when the coordinate shift for each atom was less than 10^{-7} Å. Calculations were carried out on a HITAC 8700/8800 computer at the computer center of this university.

Trial coordinates for Λ-β_2-[Co(*SS*-pyht)(ala)]$^{2+}$ and Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(ala)]$^{2+}$ isomers were generated from the crystal structures of Λ-β_2-[Co(*SS*-pyht)(*R*-ala)]$^{2+}$ [12] and Δ-β_2-[Co(5(*R*)-Me-2,3,2-tet)$(NO_2)_2$]$^+$,[17] respectively, and hydrogen atoms were placed at calculated positions (regular tetrahedral geometry, d(N–H) = 1.03 Å, d(C–H) = 1.09 Å). The trial coordinates were orthogonalized, with a Cartesian coordinate system defined in the manner described by Buckingham et al.[13]

Results and Discussion

The β_2-[Co(aa)(N_4)]$^{2+}$ complexes were prepared by a modification of the method described by Brubaker and Schaefer.[18] The *trans*-$[CoCl_2(N_4)]^+$ complexes were treated with appropriate amino acid at pH about 5.5 for 30 min at 70 °C. This was followed by adjusting the pH to 8.0, and heating continued for an additional 1.5 h. Separation from the minor product, β_1 isomer, was achieved by cation-exchange chromatography. Orange-red crystals were obtained except for phenylalaninato complexes, for which pink powders formed.

The absolute configuration for the complexes was assigned as the Λ on the basis of their circular dichroism spectra. All of the 2,3,2-tet derivatives employed here showed stereoselectively the Λ-β configuration in the cis form.[5-7,19] Though *cis*-β-(3(*S*),8(*S*)-Me_2trien)Co^{III} complexes adopted both Δ and Λ configuration,[4,20] the [Co(aa)(3(*S*),8(*S*)-Me_2trien)]$^{2+}$ ions prepared from the *trans*-dichloro complex were found to take the Λ-β configuration. The electronic and circular dichroism spectra of Λ-β_2-[Co(aa)(N_4)]$^{2+}$ complexes are tabulated in Table II and those of Λ-β_2-[Co(aa)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$ (aa = ala, val, phe) and Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$ are shown in Figures 1 and 2. The complexes prepared in a manner similar to that described previously were expected to have the β_2 configuration.[18] These assignments were confirmed by the crystal structure determination of Λ-β_2-[Co(*R*-ala)(*SS*-pyht)]$^{2+}$.[12]

The ^1H NMR spectral data, obtained in D_2O, are listed in Table III. A pair of doublets at about 1.3–1.4 ppm was assigned to the *C*-methyl groups of tetraamine ligands. The ^1H NMR spectra of alaninato complexes (Figure 3) exhibit a doublet at 1.44–1.54 ppm and a quartet at 3.50–3.92 ppm arising from the *C*-methyl group and the *C*-H proton of the alaninate, respectively. The ^1H NMR spectra of valinato complexes (Figure 3) exhibit a pair of doublets at about

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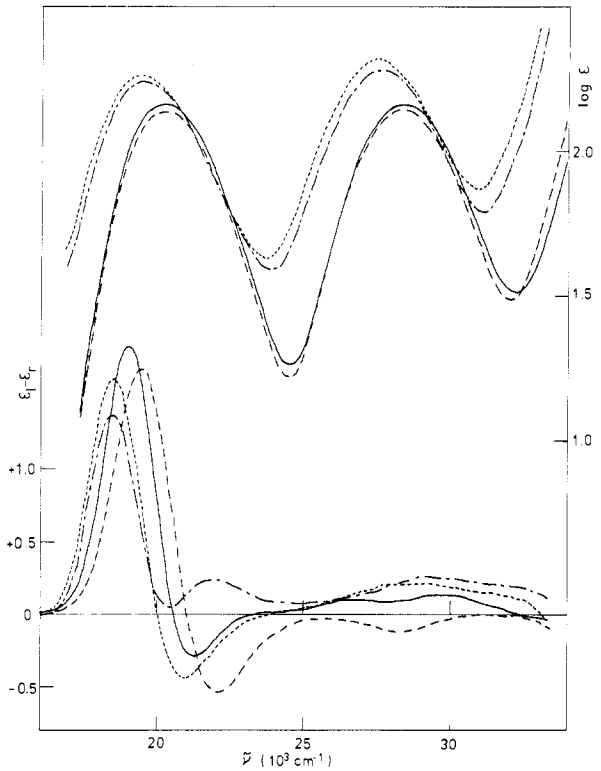

Figure 1. Electronic absorption and CD spectra of Λ-β_2-[Co(*R*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot H_2O$ (—), Λ-β_2-[Co(*S*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot 0.5H_2O$ (– – –), Λ-β_2-[Co(*R*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$ (– · –), and Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$ (– · · –).

Table III. Assignments of Proton Resonance Shifts[a]

no.	C-CH_3[b]	C-CH_3[c]	C-H[d]
5_R	1.38, 1.40	1.48	3.90[e]
5_S	1.37, 1.40	1.51	3.50[e]
6_R	1.35, 1.38	0.91, 1.12	3.73
6_S	1.34, 1.36	1.01, 1.13	[g]
7_R	1.33, 1.36	1.45	3.83[e]
7_S	1.31, 1.35	1.46	3.59[e]
8_R	1.33, 1.34	0.93, 1.11	3.73
8_S	1.32, 1.35	1.01, 1.11	3.33
9_R	1.16, 1.27	...	[g]
9_S	1.24, 1.33	...	[g]
10_R	1.35, 1.41	1.44	3.84[e]
10_S	1.34, 1.41	1.45	3.53[e]
11_R	1.36, 1.42	0.91, 1.10	3.77
11_S	1.35, 1.41	1.02, 1.13	3.24
12_R	1.31, 1.37	...	4.13[f]
12_S	1.28, 1.39	...	3.68[f]
13_R	...	1.50	3.92[e]
13_S	...	1.54	3.85[e]

[a] Ppm from DSS. Signals are doublets unless stated otherwise. [b] Methyl groups of tetraamine. [c] Methyl group(s) of amino acidate. [d] α proton of amino acidate. [e] Quartet. [f] Triplet. [g] Unobserved.

0.9–1.1 ppm due to the nonequivalent methyl groups in the isopropyl group of valinate.

In basic solution, the hydroxide ion catalyzed epimerization of the chelated α-amino acid occurs without change in the configuration about the Co(III) center and gives rise to a mixture of diastereomers after the equilibrium has been established (eq 2). Sargeson and co-workers[2] have performed

$$\Lambda\text{-}\beta_2\text{-}[Co(N_4)(R\text{-aa})]^{2+} \rightleftharpoons \Lambda\text{-}\beta_2\text{-}[Co(N_4)(S\text{-aa})]^{2+} \quad (2)$$

the epimerization in 0.01 M NaOH, while the carbonate buffer (pH 10–11) was used in the present study in order to minimize the decomposition of the complexes. The phenylalaninato

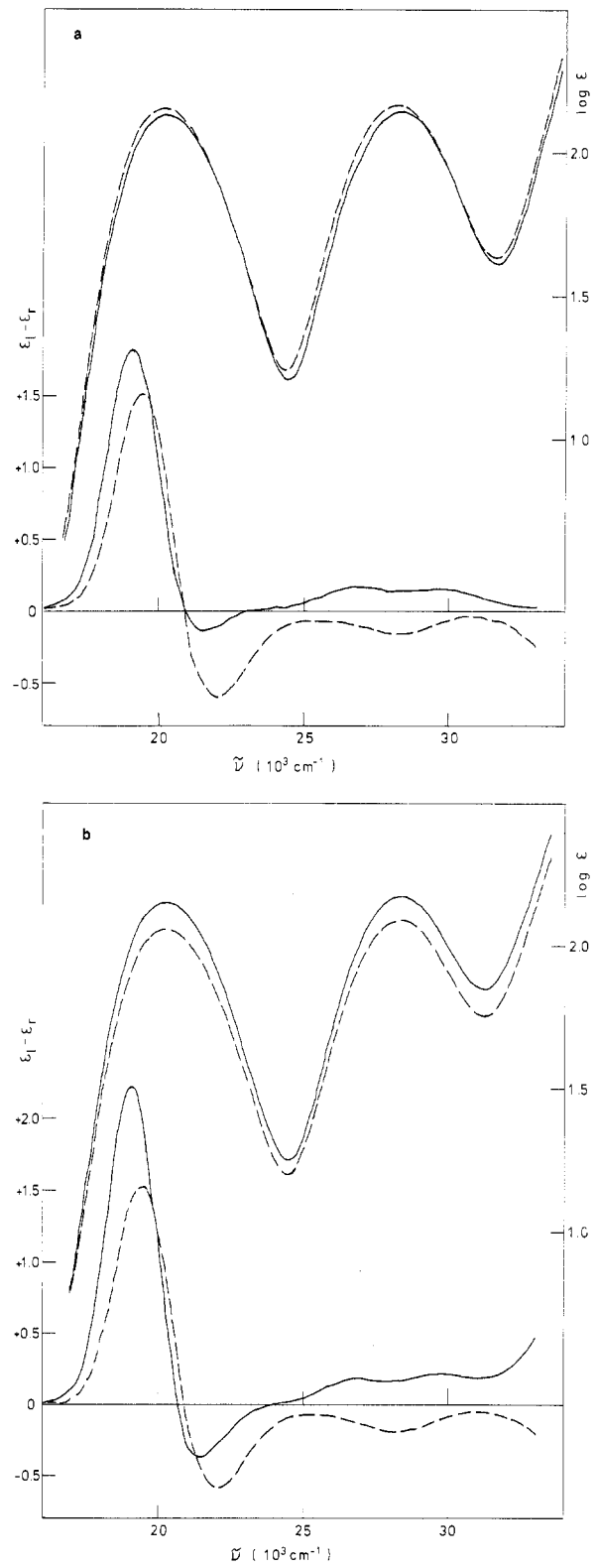

Figure 2. Electronic absorption and CD spectra of (a) Λ-β_2-[Co(*R*-val)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$ (—) and Λ-β_2[Co(*S*-val)(2-(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$ (– – –) and (b) Λ-β_2-[Co(*R*-phe)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot 2H_2O$ (—) and Λ-β_2-[Co-(*S*-phe)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot H_2O$ (– – –).

complexes and Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$ were relatively unstable, and considerable decomposition occurred even at pH 10.

The diastereomeric ratios (Λ-*S*/Λ-*R*) of the alaninato, valinato, and phenylalaninato complexes at equilibria were summarized in Table IV.

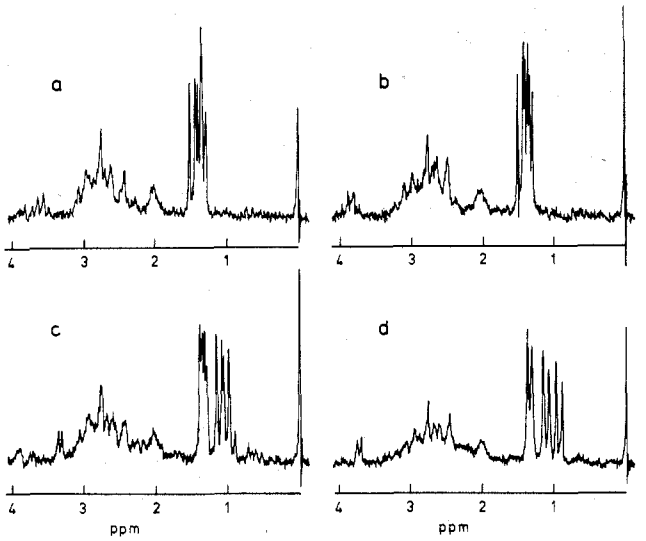

Figure 3. Proton magnetic spectra of (a) Λ-β_2-[Co(*S*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot 0.5H_2O$, (b) Λ-β_2-[Co(*R*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot H_2O$, (c) Λ-β_2-[Co(*S*-val)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$, and (d) Λ-β_2-[Co(*R*-val)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$.

Table IV. Isomeric Ratios (Λ-*S*/Λ-*R*) of $[Co(N_4)(aa)]^{2+}$ [a]

	Λ-*S*/Λ-*R*		
(N_4)	ala	val	phe
$(en)_2$	50/50[b]	37/63[b]	
3(*S*),8(*S*)-Me_2 trien	50/50[c]	34/66[c]	
2(*S*),10(*S*)-Me_2-2,3,2-tet	66/34	47/53[d]	61/39[e]
3(*S*),9(*S*)-Me_2-2,3,2-tet	61/39	30/70	64/36[e]
SS-pyht	18/82[e] (17/83[f])		

[a] At 40 °C and pH 11.2 unless stated otherwise. [b] Reference 2. [c] These ratios were calculated on the basis of their CD spectra (see text). [d] The corresponding value in ref 21 was erroneous. [e] At 40 °C and pH 10.1. [f] At 25 °C and pH 10.1.

It is remarkable that the predominant configuration of valinate is reversed in isomeric ratios to that of alaninate and phenylalaninate except for Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$. The alaninato and phenylalaninato complexes containing 2,3,2-tet derivatives showed a preference for the (*S*)-amino acidato isomer except for *SS*-pyht complex, while the (*R*)-valinato complex was the predominant isomer over the (*S*)-valinato one. Buckingham and co-workers suggested the possibility that the difference of solvation energies for the diastereomers may decide the isomeric stability. In our work the selectivities are completely reversed between the alaninato and valinato complexes containing 2,3,2-tet derivatives. Contrary to expectation the phenylalaninato complexes showed the same preference as the alaninato ones, though the bulkiness of the benzyl substituent is considered to be similar to that of isopropyl except for the difference of the β-carbon, secondary or tertiary. Thus, the trends in the isomeric ratio are complicated, and it seems to be difficult to explain the energy difference among the diastereomers on the basis of only the nonbonded interaction between amino acidate and tetraamine, which suggests the possibility of the effect of solvation.

With regard to the degree of the selectivity no significant improvement was found in the complexes with the ligands 3(*S*),8(*S*)-Me_2trien and 2(*S*),10(*S*)- and 3(*S*),9(*S*)-Me_2-2,3,2-tet for (N_4). For the stability difference between the diastereomers to be as large as possible, an N-substituted tetraamine at the terminal amino groups was employed. The

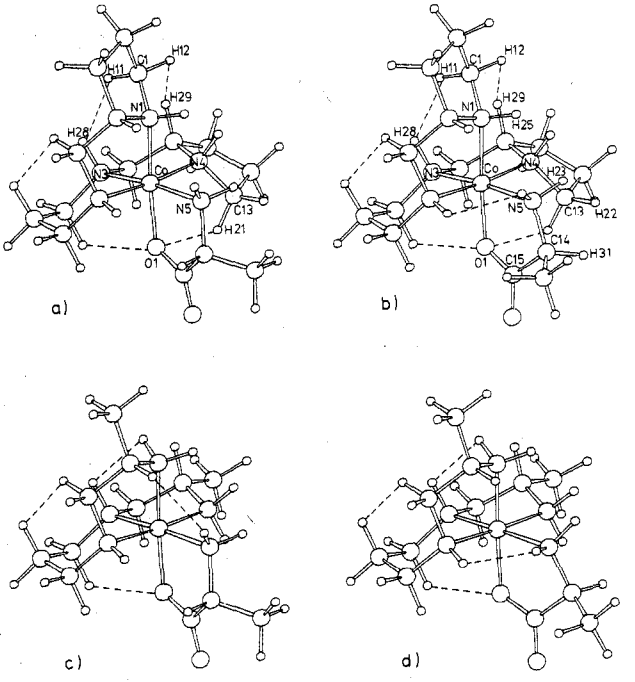

Figure 4. Minimized structures for (a) Λ-β_2-[Co(*R*-ala)(*SS*-pyht)]$^{2+}$, (b) Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$, (c) Λ-β_2-[Co(*R*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, and (d) Λ-β_2-[Co(*S*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$. Dotted lines show interatomic repulsions >0.3 kcal/mol, excluding those of 1,4 type.

Table V. Final Energy Terms (kcal/mol)

strain energy	*R*-ala	*S*-ala	SED
(i) For Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$			
bond length	1.39	1.40	0.01[a]
bond angle	13.90	13.72	−0.18
torsional	14.94	15.82	0.88
nonbonded	−4.26	−4.22	0.04
out-of-plane	0.00	0.00	0.00
total	25.97	26.72	0.75
(ii) For Λ-β_2-[Co(ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$			
bond length	0.80	0.81	−0.01[b]
bond angle	4.95	4.92	0.03
torsional	2.92	2.87	0.05
nonbonded	−4.08	−4.02	−0.06
out-of-plane	0.00	0.00	0.00
total	4.59	4.58	0.01

[a] Strain energy difference: (*S*-ala) − (*R*-ala). [b] Strain energy difference: (*R*-ala) − (*S*-ala).

(*SS*-pyht)Co^{III} complexes of (*R*)- and (*S*)-alaninate were prepared (*SS*-pyht = 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane). The *SS*-pyht was expected to give stereoselectivity in terms of both its own geometry and its effects on other ligands coordinated in the remaining two positions of the octahedron.[8] Though the recovery of amino acidato complexes was not satisfactory due to the considerable decomposition, the isomeric ratio in the equilibrated mixture showed the maximal value (Λ-*S*/Λ-*R* = 18/82, ΔG = −0.94 kcal/mol) as expected. This improvement of the chiral selectivity suggests that the pyrrolidine groups at the terminal amino groups of the *SS*-pyht causes more serious strain in the (*S*)-alaninato complex than in the (*R*)-alaninato complex.

The technique of strain energy minimization was applied to the Λ-β_2-[Co(*SS*-pyht)(*R*- and *S*-ala)]$^{2+}$ and Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*R*- and *S*-ala)]$^{2+}$ complexes. The final minimized structures for the diastereomeric isomers are shown in Figure 4, and the final energy terms are listed in Table V.[22]

(21) Yoshikawa, S.; Saburi, M.; Yamaguchi, M. *Pure Appl. Chem.* **1978**, *50*, 915.

The Λ-β_2-[Co(2(*S*),10(*S*)-Me_2-2,3,2-tet)(*R*- and *S*-ala)]$^{2+}$ complexes have less strained structures. The strain energies of the two isomers are about 4.6 kcal/mol and show only a slight difference. On the other hand, the *SS*-pyht complexes were found to have large strain energies owing to the pyrrolidine rings. Angle deformations and torsinal strains within the pyrrolidine rings are considerably large. Further, the H(11)···H(28) (2.01 Å, 1.1 kcal/mol), H(21)···O(1) (2.34 or 2.37 Å, 0.5 kcal/mol), and H(12)···H(29) (2.24 Å, 0.3 kcal/mol) interactions are derived from the methylene protons of the pyrrolidine rings. The significantly large repulsive contact between the methylene proton of the apical pyrrolidine ring and NH proton of N(3) atom (H(11)···H(28)) appears to cause a large angular distorsion: N(1)–Co–N(3), 98.6° (1.1 kcal/mol) in the *S*-ala complex and 98.5° (1.1 kcal/mol) in the *R*-ala complex. The Co–N(1)–C(1) and Co–N(4)–C(13) angles are expanded: *S*-ala complex, 124.1 (1.9) and 119.0° (0.8 kcal/mol), and *R*-ala complex, 123.9 (1.8) and 119.3° (0.9 kcal/mol), respectively. With respect to the bond length the Co–N(1) bonds are extended: 2.00 Å (0.36 kcal/mol) in both cations.

Final minimized strain energies indicate that the (*S*)-alaninato complex with *SS*-pyht is 0.75 kcal/mol less stable than the (*R*)-alaninato complex. Major contributions to the energy difference come from the torsional strain and angle deformations. Though the difference between the final nonbonded interaction terms is relatively small, initial calculations showed significantly large nonbonded interactions in *S*-ala complex: H(22)···H(31), between the C–H proton of alaninate and the methylene proton of the in-plane pyrrolidine ring, and H(23)···H(25), between the proton of the amino group of alaninate and that of the apical amino group of *SS*-pyht. Twisting about N(5)–C(14) reduces those close contacts, while the (*S*)-alaninate ring adopts a strained, near-planar, conformation: ϕ(N(5)–C(14)), ϕ(C(14)–C(15)), and ϕ(C(15)–O(1)) = 4.8 (1.5), 10.0 (0.4), and 10.5° (0.2 kcal/mol) respectively, in the *S*-ala complex; 23.9 (1.0), 20.7 (0.3), and 6.5° (0.1 kcal/mol), respectively, in the *R*-ala complex.

The strain energy minimization calculations are in good agreement with the relative stability and energy difference for the diastereomers of Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$. These results suggest that the destabilization of the Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$ ion was due mostly to intramolecular strain energy. However, it fails to predict the energy difference observed between the *R*-ala and *S*-ala complexes with 2(*S*),10(*S*)-Me_2-2,3,2-tet, though the difference was relatively small (Λ-*S*/Λ-*R* = 66/34, ΔG = −0.41 kcal/mol). In these calculations electrostatic or dipole interactions have been neglected. Hydrogen bonding and solvation energy are also not taken into consideration. It is possible that these effects play a significant role to make a difference between the diastereomers, though it is difficult to evaluate these terms.[16a,23]

From the viewpoint of asymmetric transformation, N-substitution of the tetraamine, as the pyrrolidine ring of *SS*-pyht, results in an improvement in the stereoselectivity described above. On the other hand, it accelerates some unfavorable side reactions. It seems rather hard to overcome these two conflicting demands for (N_4), selectivity and stability, but attempts directed at reducing the decomposition of complex are now in progress. With respect to amino acidate moieties, α-substituted amino acids appear to have a significant effect on the selectivity. In subsequent papers the results of epimerization of other amino acidato complexes will be reported.

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Registry No. **1**, 60872-59-5; **2**, 60801-67-4; **3**, 73396-02-8; **4**, 59202-14-1; $\mathbf{5}_R$, 73493-96-6; $\mathbf{5}_S$, 73453-08-4; $\mathbf{6}_R$, 73493-94-4; $\mathbf{6}_S$, 73453-06-2; $\mathbf{7}_R$, 68531-65-7; $\mathbf{7}_S$, 68567-19-1; $\mathbf{8}_R$, 73465-04-0; $\mathbf{8}_S$, 64387-64-0; $\mathbf{9}_R$, 73465-02-8; $\mathbf{9}_S$, 73396-00-6; $\mathbf{10}_R$, 73493-92-2; $\mathbf{10}_S$, 73453-04-0; $\mathbf{11}_R$, 73493-90-0; $\mathbf{11}_S$, 73453-02-8; $\mathbf{12}_R$, 73493-88-6; $\mathbf{12}_S$, 73453-00-6; $\mathbf{13}_R$, 64439-79-8; $\mathbf{13}_S$, 64387-62-8; 3(*S*),9(*S*)-Me_2-2,3,2-tet, 73384-41-5; 2(*S*),8(*S*)-3,7-diaza-2,8-dimethyl-1,9-dibromononane dihydrobromide, 73384-42-6; L-alaninol, 2749-11-3; 1,3-diaminopropane, 109-76-2; sodium tris(carbonato)cobaltate(III), 23311-39-9.

Supplementary Material Available: Final minimized Cartesian atomic coordinates and listings of internal coordinates with their individual strain energies (44 pages). Ordering information is given on any current masthead page.

(22) Supplementary material.

(23) (a) Weintraub, H. J. R.; Hopfinger, A. J. *J. Theor. Biol.* **1973**, *41*, 53. (b) Brunel, Y.; Faucher, H.; Gagnaire, D.; Rassat, A. *Tetrahedron* **1975**, *31*, 1075.

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Crystal Structure of $(+)_{589}$-β_2-((*R*)-Alaninato)(1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) Perchlorate Dihydrate

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The crystal structure of $(+)_{589}$-β_2-((*R*)-alaninato)(1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) perchlorate dihydrate, $(+)_{589}$-β_2-[Co(*R*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$, has been determined from three-dimensional X-ray data collected by the diffractometer method. The compound forms tetragonal crystals with a = 9.951 (3) Å, c = 52.537 (25) Å, and Z = 8, in space group $P4_12_12$. The structure has been solved by the heavy-atom method and refined by least-squares method with anisotropic temperature factors to give an R value of 0.056 for 1933 observed reflections. The absolute configuration of the complex cation is Λ; the configuration of the alaninato is β_2. The five-membered chelate rings of the tetraamine both have the δ-gauche conformation, and the six-membered chelate ring has a distorted chair conformation. The configuration at the asymmetric centers of the tetraamine are *R* for the inner nitrogen atoms and *S* for the terminal ones.

Introduction

In recent years, the crystal structures of several cobalt(III) complexes containing an α-amino acid and a tetraamine have been determined by X-ray analysis: for example, *cis*-α-, *cis*-β_1-, and *cis*-β_2-[Co(gly)(trien)]$^{2+}$ and Λ-β_2- and Δ-β_2-[Co(*S*-pro)(trien)]$^{2+}$.[1-3] In those studies the tetraamine was tri-

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