hydrogenation and hydroformylation.

The intercalation of metal clusters containing P–P$^+$ in hectorite is governed mainly by the accessibility of Na$^+$ exchange ions on the basal surfaces. Since the swelling of the clay by organic solvents is limited, the size of the metal cluster complex exceeds the initial gallery height of the clay and the rate of intercalation is low. However, if the clay is swollen and largely delaminated by dispersion in water, then the Na$^+$ ions on the basal surfaces are readily accessible for exchange and ordered intercalation compounds are formed upon face to face flocculation of the silicate layers in the presence of the cluster cations.

$H_2Os_3(CO)_9(P–P^+)$–hectorite, the first reported example of an intercalated metal cluster catalyst, is active for the isomerization of 1-hexene in solvents that swell the clay interlayers (e.g., acetone and methanol), as well as in solvents that are nonswelling (e.g., toluene). The activity in nonswelling solvents is attributed to a pillaring effect which leads to a large gallery height (~16 Å) and allows for the interlayer penetration of the substrate. The longevity of the intercalated catalyst parallels that of the homogeneous catalyst, further indicating that the metal cluster complex retains solution-like properties in the intercalated state.

Acknowledgment. The partial support of this research by the National Science Foundation through Grant CHE-8306583 is gratefully acknowledged.

Registry No. $(P–P^+)(BF_4)$, 71243-21-5; $[Ru_3(CO)_9(P–P^+)_3][BF_4]_3$, 97920-21-3; $[Os_3(CO)_{11}(P–P^+)][BF_4]$, 97920-23-5; $[Ir_4(CO)_9(P–P^+)_3][BF_4]_3$, 97950-39-5; $[H_4Ru_4(CO)_8(P–P^+)_4][BF_4]$, 97920-25-7; $[H_2Os_3(CO)_{10}(P–P^+)][BF_4]$, 97920-27-9; $[H_2Os_3(CO)_9(P–P^+)][BF_4]$, 97920-29-1; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{11}(CH_3CN)$, 65702-94-5; $Ir_4(CO)_{12}$, 18827-81-1; $H_4Ru_4(CO)_{12}$, 34438-91-0; $H_2Os_3(CO)_{10}$, 41766-80-7; $[HOs_3(CO)_9(CH{=}CH_2)(P–P^+)]^+$, 97950-40-8; acetylene, 74-86-2; hectorite, 12173-47-6.

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Importance of an Axially Orientated *C*-Methyl Group in the Stereospecific Formation of the Λ-β-(Oxalato)((4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine)cobalt(III) Ion

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cis-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$ (5*S*-Me-2,3,2-tet = (*S*)-4-methyl-3,7-diaza-1,9-nonanediamine) has been newly synthesized. Two stereoisomers, Λ-β- and Δ-β-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$, have been obtained and characterized by elementary analyses and by ^{1}H and ^{13}C NMR, absorption, and circular dichroism spectroscopies. The distribution of these isomers at thermodynamic equilibrium has been examined in order to elucidate roles of the two *C*-methyl groups in the stereospecific formation of Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ (5*R*,7*R*-Me$_2$-2,3,2-tet = (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine). Factors of the stereospecific formation of Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ are discussed in relation to the predictions of the strain energy minimization calculations. The results suggest that the existence of the equatorially orientated *C*-methyl group of the tetraamine is not the essential factor, but the axially orientated *C*-methyl group plays an important role in the occurrence of the stereospecificity.

Introduction

As a source of asymmetry in asymmetric syntheses, the utility of chiral transition-metal complexes has been of current interest. We have previously developed a cyclic system for asymmetric syntheses of α-amino acids[1] using a chiral cobalt(III) complex containing an optical active tetraamine, 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet.[2] In the system, the stereospecific feature of 5*R*,7*R*-Me$_2$-2,3,2-tet[3] which binds to the cobalt(III) center only in the Λ-cis-β form[4] has been applied fundamentally in order to provide two chiral coordination sites. A close investigation of the factors related to the appearance of this remarkable stereospecificity should provide important information in designing ligands suitable for metal-assisted asymmetric syntheses. However, no study has discussed the factors of the appearance of this stereospecificity. Therefore, this work is aimed at clarifying the origin of this stereospecificity of the tetraamine.

Our other X-ray studies of the *cis* cobalt(III) complexes containing 5*R*,7*R*-Me$_2$-2,3,2-tet or 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet have shown that the central six-membered chelate ring of the tetraamine ligand adopts the chair conformation with one methyl group axial and the other equatorial.[1,5,6] Formation of the two diastereoisomers, Λ-β or Δ-β, is determined by which of the two terminal five-membered chelate rings links to the apical position (Figure 1). It is a striking feature that the Λ-β isomer is stereospecifically obtained although the skeleton of the six-membered chelate ring takes the achiral chair conformation. It seems that the axially orientated *C*-methyl group on the six-membered chelate ring plays an important role in the appearance of the remarkable stereospecificity of the tetraamine. In this investigation, in order to elucidate the role of the axially orientated *C*-methyl group of the tetraamine, we have newly prepared *cis*-[Co(ox)(5*S*-Me-2,3,2-tet[7,8])]$^+$, which is expected to have the structure that may result from removing the axially orientated *C*-methyl group from *cis*-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$, and have examined its stereochemistry.

In addition, in order to evaluate factors of the appearance of the remarkable stereospecificity in more detail, we have performed strain energy minimization calculations for four related complex ions: Λ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Δ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$, and Δ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$.

Experimental Section

Measurements. Absorption spectra were obtained on a Shimadzu UV-210 double-beam spectrophotometer. Circular dichroism spectra were obtained on a JASCO J-500A spectropolarimeter. These measurements were made on aqueous solutions at concentrations near 2×10^{-3} M.

^{1}H NMR spectra were obtained on a JEOL GX-400 instrument (400 MHz) with sodium 3-(trimethylsilyl)propanesulfonate as an internal reference in D_2O.

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(1) Ajioka, M.; Yano, S.; Matsuda, K.; Yoshikawa, S. *J. Am. Chem. Soc.* **1981**, *103*, 2459.

(2) The fully systematic name is (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane.

(3) The fully systematic name is (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine.

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(6) Yashiro, M.; Ajioka, M.; Yano, S.; Toriumi, K.; Ito, T.; Yoshikawa, S., submitted for publication.

(7) The fully systematic name is (*S*)-4-methyl-3,7-diaza-1,9-nonanediamine.

(8) In order to compare with the 5*R*,7*R*-Me$_2$-2,3,2-tet system clearly, in place of the *S* form, upon which we actually experimented, its enantiomer (*R* form) was employed to discuss.

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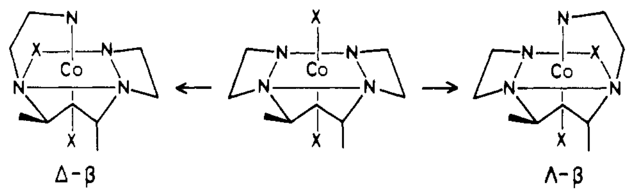

Figure 1. Two isomers of the cis-β cobalt(III) complex containing $5R,7R$-Me_2-2,3,2-tet, which may be derived from the trans isomer.

Optical rotations were obtained on a JASCO DIP-4 polarimeter. Elemental analyses were performed by the Shonan Bunseki Center Co., Ltd.

Preparations. Λ-β-[Co(ox)($5R,7R$-Me_2-2,3,2-tet)]ClO_4 was prepared by the method of Mizukami.[4]

Racemic 1,3-butanediamine was prepared by the method of Strack and Schwaneberg.[9] It was optically resolved by the reported procedure[10] with (+)-tartrate ions. The less soluble form (S)-1,3-butanediamine bis((+)-hydrogen tartrate) was obtained ($[\alpha]^{25}_D$ +19.4°). Free (S)-1,3-butanediamine gave α^{25}_D +0.909° (neat, l = 1 cm).

N-(*tert*-Butoxycarbonyl)glycine (*N*-*t*-Boc-gly) was purchased from Nakarai Chemicals, Co., Ltd. Other reagents were reagent grade and were used without further purification.

5*S*-Me-2,3,2-tet. A 17.5-g (0.10-mol) amount of *N*-*t*-Boc-gly and 10.1 g (0.10 mol) of triethylamine were dissolved in 300 mL of chloroform in a 1-L three-necked round-bottomed flask, and the mixture was cooled below −10 °C in an ice–salt bath. With vigorous stirring, 10.9 mL (0.10 mol) of ethyl chloroformate was added dropwise. Ten minutes later, 3.53 g (0.04 mol) of (S)-1,3-butanediamine was added dropwise, and the mixture was allowed to stand overnight. The reaction mixture was washed twice with 150 mL of water and dried over anhydrous sodium sulfate. After the solvent had been removed on a rotary evaporator, 4 N hydrogen chloride methanolic solution was added and the mixture was heated to 40–50 °C until the residue dissolved completely. The solvent was removed and dried in vacuo over P_2O_5.

The resulting solid (10 g) was ground well and placed in a 500-mL four-necked round-bottomed flask fitted with a mechanical stirrer, a condenser, and a drying tube. A 150-mL portion of absolute THF was added. Then 11 g of lithium aluminum hydride was carefully added with stirring. After the addition had been completed, the mixture was heated under reflux for 80 h. The reaction mixture was cooled and carefully quenched by the dropwise addition of 20 mL of water. The mixture was refluxed for 40 min and filtered. The white precipitate was washed three times with THF under reflux and filtered off. The filtrate and the washings were combined, and the solvent was removed.

The product was then collected by vacuum distillation: bp 105 °C (3 mmHg); yield 3.9 g.

Λ-β- and Δ-β-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO_4. A 3.7-g (7.5-mmol) sample of potassium tris(oxalato)cobaltate(III)[11] was dissolved in 100 mL of water. To this solution were added 1.5 g (8.3 mmol) of 5*S*-Me-2,3,2-tet and a small amount of activated charcoal, and the mixture was stirred for 3 h at 50 °C. Then the reaction mixture was filtered, and the filtrate was adsorbed onto an SP-Sephadex C-25 column (o.d. = 4.5 cm, h = 70 cm). After being washed with 1 L of water, the complex was eluted with 0.01 N $NaClO_4$ solution. Fractions of the singly charged band were collected and concentrated to dryness. The ^1H NMR spectrum indicated that it was the mixture of two isomers. Then, the mixture was adsorbed onto a Dowex 50W-X2 (Na^+ form) column (o.d. = 4.5 cm, h = 70 cm). By elution with 0.2 N $NaClO_4$ solution, they were separated into two bands. Red needlelike crystals were obtained from the first fraction off the column (Λ-β form), and red powder was obtained from the second fraction (Δ-β form). Anal. Calcd for $C_{10}H_{22}N_4O_8ClCo$: C, 28.55; H, 5.27; N, 13.32; Cl, 8.43. Found, Λ-β form: C, 28.69; H, 5.26; N, 13.64; Cl, 8.26. Found, Δ-β form: C, 28.64; H, 5.21; N, 13.19; Cl, 8.24. (*Caution*! Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities).

Equilibrium Study. Thermodynamic equilibrium of *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO_4 was attained by using the technique for the equilibrium of [Co(ox)(R-pn)$_2$]ClO_4,[12] where R-pn is (R)-propylenediamine.

A 10-mg sample of each isomer, Λ-β or Δ-β form, was dissolved in 10 mL of water, and the mixture was boiled for 1 h under oxygen-free nitrogen in the presence of activated charcoal. Three drops of 0.3% $K_2C_2O_4$ aqueous solution and 3 drops of 0.3% $Co^{II}Cl_2$ aqueous solution were added, and the mixture was boiled for a further 0.5 h. After the mixture had been cooled, 3 drops of 0.3% 5*S*-Me-2,3,2-tet aqueous solution were added. The resultant mixture was stirred with a magnetic stirrer under N_2 at room temperature and then filtered, and the absorption and circular dichroism spectra were obtained. The reaction was continued until the CD spectrum of the reactant from each isomer coincided with that of the other, which was satisfied after 72 h.

The equilibrium ratio between the two isomers (Λ-β/Δ-β) was calculated from the concentrations of the Λ-β isomer ($C_{\Lambda\text{-}\beta}$) and of the Δ-β isomer ($C_{\Delta\text{-}\beta}$), which are estimated according to the equations

$$\epsilon_{eq} = C_{\Lambda\text{-}\beta}\epsilon_{\Lambda\text{-}\beta} + C_{\Delta\text{-}\beta}\epsilon_{\Delta\text{-}\beta} \qquad (1)$$

$$\Delta\epsilon_{eq} = C_{\Lambda\text{-}\beta}\Delta\epsilon_{\Lambda\text{-}\beta} + C_{\Delta\text{-}\beta}\Delta\epsilon_{\Delta\text{-}\beta} \qquad (2)$$

where ϵ_{eq}, $\epsilon_{\Lambda\text{-}\beta}$, and $\epsilon_{\Delta\text{-}\beta}$ are the absorbances at 500 nm of the equilibrium mixture, of the authentic Λ-β isomer, and of the authentic Δ-β isomer, while $\Delta\epsilon_{eq}$, $\Delta\epsilon_{\Lambda\text{-}\beta}$, and $\Delta\epsilon_{\Delta\text{-}\beta}$ are the CD strengths at 590 and/or 478 nm of the equilibrium mixture, of the authentic Λ-β isomer, and of the authentic Δ-β isomer, respectively.

The equilibrium mixture was adsorbed onto an SP-Sephadex C-25 column. After being washed with water, the complex was eluted with 0.01 N NaCl solution. All the singly charged bands were collected and evaporated to dryness. After the residue had been completely dried in vacuo, ^1H NMR spectrum was obtained in D_2O.

Equilibrium of Λ-β-[Co(ox)($5R,7R$-Me_2-2,3,2-tet)]ClO_4 was also attempted by using the same technique as described above.

Strain Energy Minimization Calculations. The strain energies of some complex ions were calculated by using the program CONFAN2[13] on a HITAC M280/200H computer at the computer center of this university.

The energy functions defined by Buckingham et al.[14] were employed. The total strain energy U is assumed to be expressed as

$$U = \sum_{ij} U(r_{ij})_b + \sum_{ijk} U(\theta_{ijk}) + \sum_{ij} U(r_{ij})_{nb} + \sum_{ijkl} U(\phi_{ijkl}) + \sum_{ijkl} U(\Delta_l) \qquad (3)$$

a summation of terms representing bond length deformations, $(r_{ij})_b$, bond angle deformations, θ_{ijk}, nonbonded interatomic interactions, $(r_{ij})_{nb}$, torsional constraints, ϕ_{ijkl}, and out-of-plane deformations, Δ_l. The force constants were taken from ref 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] Minimization was terminated when the coordinate shift for each atom was less than 0.005 Å.

Trial coordinates for Λ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Δ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Λ-β-[Co(ox)($5R,7R$-Me_2-2,3,2-tet)]$^+$, and Δ-β-[Co(ox)($5R,7R$-Me_2-2,3,2-tet)]$^+$ complex ions were generated from the crystal structure of Λ-β-[Co(ox)($5R,7R$-Me_2-2,3,2-tet)]ClO_4[5] or from the strain energy minimized structure of the Λ-β-[Co(S-ala)($2S,10S$-Me_2-2,3,2-tet)]$^+$ ion.[13] Hydrogen atoms and methyl groups were placed at calculated positions (regular tetrahedral geometry, d(C–H) = 1.09 Å, d(C–C) = 1.50 Å, angle = 109.28°). The trial coordinates were orthogonalized with a Cartesian coordinate system defined in the manner described by Buckingham et al.[14]

The perspective views of the minimized structures were drawn by using the program ORTEP2.

Results

Characterization of the Two Isomers of *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO_4. The *cis*-(oxalato)cobalt(III) complex containing 5*S*-Me-2,3,2-tet, *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO_4, was prepared from the reaction of potassium tris(oxalato)cobaltate(III) and the tetraamine in the presence of activated charcoal. Two singly charged isomers were obtained which were successfully separated by column chromatography (Dowex 50W-X2 cation exchange resin). Each isomer crystallized as a red perchlorate salt. ^1H and ^{13}C NMR spectra indicate that each isomer is stereochemically pure in solution. The ^1H NMR spectrum of each isomer shows one sharp doublet due to a C-methyl group (at δ 1.34 for the first isomer eluted from the column and at δ 1.35 for the second isomer). The ^{13}C NMR spectrum of each isomer shows ten signals, including two signals at about δ 170 due to the oxalato moiety.

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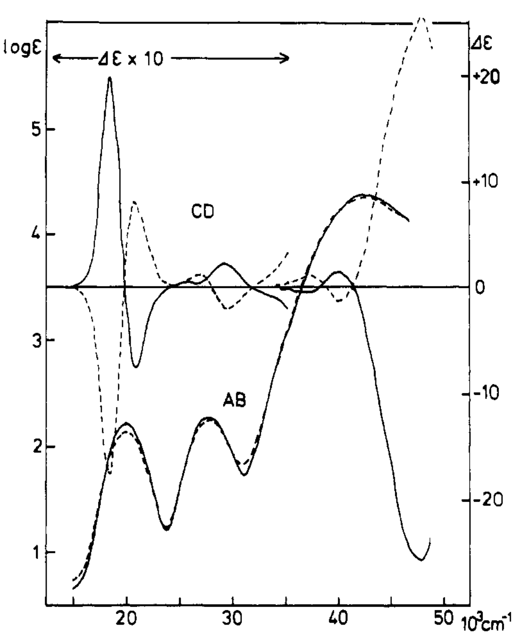

Figure 2. Absorption (AB) and circular dichroism (CD) spectra of the two isomers of *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$: (i) Λ-β isomer (—); (ii) Δ-β isomer (---).

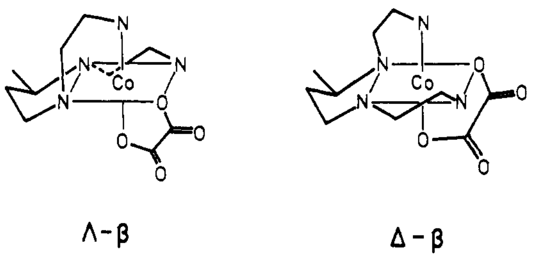

Figure 3. Two isomers of *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$.[8]

Their absorption (AB) and circular dichroism (CD) spectra are shown in Figure 2. The positions of the absorption maxima and the line shapes of the AB spectra for the two isomers are very similar to those for *cis*-Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$.[3] These observations are typical for the type of the *cis*-N_4O_2-cobalt(III) system.

The geometries of the two obtained isomers have been characterized with the aid of the examination of the molecular model. It is generally accepted that a methyl substituent prefers the equatorial to the axial orientation and that a six-membered chelate ring prefers the chair to the skew-boat conformation in an octahedral cobalt(III) system. From these considerations, only two isomers are regarded to be energetically stable in the *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$ system, i.e. the Λ-β and the Δ-β geometries, which are drawn in Figure 3.[8] Therefore, the two obtained isomers should correspond to these two geometries. The CD spectra of the two isomers indicate that they are approximately mirror images of each other. The first isomer eluted from the column shows positive and negative Cotton effects from lower to higher energy in the first absorption region, while the second isomer shows negative and positive Cotton effects from lower energy in the same region. From the empirical rule on the CD signs in this region, the first isomer can be assigned to the Λ-β geometry and the second isomer to the Δ-β geometry, respectively. The binding mode of the tetraamine in the Λ-β isomer had been observed in the X-ray crystallographically established structure of *cis*-Δ-β-[Co(NO$_2$)$_2$(5*R*-Me-2,3,2-tet)]Br.[16]

The production ratio between these two isomers was determined from the AB and CD strengths, and the value was Λ-β/Δ-β = 50/50 (±3).

Table I. Final Energy Terms (kcal/mol)

strain energy	Λ-β	Δ-β	SED[a]
(i) *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$			
bond length	0.72	0.62	0.10
bond angle	6.75	6.61	0.14
torsional	1.64	1.72	-0.08
nonbonded	-3.47	-3.84	0.37
out of plane	0.00	0.00	0.00
total	5.64	5.11	0.53
(ii) *cis*-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$			
bond length	1.00	1.06	-0.06
bond angle	8.50	10.59	-2.09
torsional	2.17	1.80	0.37
nonbonded	-2.98	-2.47	-0.52
out of plane	0.00	0.00	0.00
total	8.69	10.99	-2.30

[a] Strain energy difference: (Λ-β) − (Δ-β).

Equilibrium Study. Thermodynamic equilibrium between the two isomers, Λ-β- and Δ-β-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$, has been attained at room temperature in the presence of a catalytic amount of the cobalt(II) analogue and activated charcoal. Dwyer et al. reported[12] that, in the [Co(ox)(*R*-pn)$_2$]$^+$ system, the thermodynamic equilibrium had been attained after 12 h under similar conditions. In the present case, however, much longer times (72 h) have been necessary in order to achieve the equilibrium.

In the ^{1}H NMR spectrum of the equilibrium mixture, a pair of doublets with almost equal intensities due to *C*-methyl groups was observed. This suggests that almost equal amounts of the two isomers exist in the solution. However, the two doublets were not separated sufficiently to estimate the accurate value of the equilibrium ratio between the two isomers. Then the ratio was calculated on the basis of the CD and AB strengths according to eq 1 and 2 given in the Experimental Section. The resulting ratio was Λ-β/Δ-β = 54/46 (at 20 °C).[8] The free energy difference calculated from these values is -0.1 kcal/mol. The equilibrium could also be achieved after a few days' boiling in the presence of activated charcoal in contact with the atmosphere.

The thermodynamic equilibrium of Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ has also been examined. Under conditions similar to those described above, no change in the CD spectrum was observed. This observation is consistent with the stereospecific formation of this complex and indicates that the free energy difference between the Λ-β and the Δ-β isomers is very large in this system.

Strain Energy Minimization Calculations. As a tool in the examination of the optimum conformation of a molecule and its relative stability, the calculations of strain energy minimization have been developed. In our investigation, in order to evaluate factors of the remarkable Λ-β selectivity in the *cis*-[Co(ox)-(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ system, the calculations have been performed for four complex ions:[8] Λ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Δ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$, and Δ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$.

The final values for each energy term are listed in Table I. The total energy differences between the two isomers, Λ-β and Δ-β, were 0.53 and -2.30 kcal/mol in the *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$ and *cis*-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ systems, respectively. The equilibrium constants at 20 °C estimated from these values are K = 0.40 (Λ-β/Δ-β = 29/71)[8] for the former and 52.0 (98/2) for the latter, respectively. The perspective views of the final structures are drawn in Figure 4. Dotted lines indicated the nonbonded interactions with energies greater than 0.40 kcal/mol.

Discussion

Two obtained isomers of *cis*-[Co(ox)(5*S*-Me-2,3,2-tet)]$^+$ have been characterized to have Λ-β and Δ-β geometries, in which the *C*-methyl groups are equatorially orientated. They have the structures that may result from removing the axially orientated *C*-methyl groups from the corresponding isomers of *cis*-[Co-

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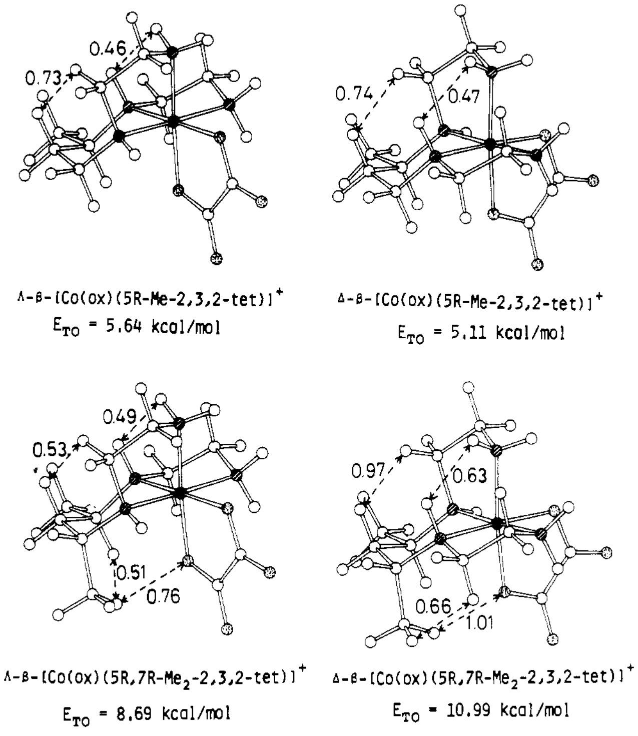

Λ-β-[Co(ox)(5R-Me-2,3,2-tet)]$^+$ E_{TO} = 5.64 kcal/mol

Δ-β-[Co(ox)(5R-Me-2,3,2-tet)]$^+$ E_{TO} = 5.11 kcal/mol

Λ-β-[Co(ox)(5R,7R-Me$_2$-2,3,2-tet)]$^+$ E_{TO} = 8.69 kcal/mol

Δ-β-[Co(ox)(5R,7R-Me$_2$-2,3,2-tet)]$^+$ E_{TO} = 10.99 kcal/mol

Figure 4. Perspective views of the strain energy minimized cations. Dotted lines indicate nonbonded interactions whose energies are greater than 0.40 kcal/mol.

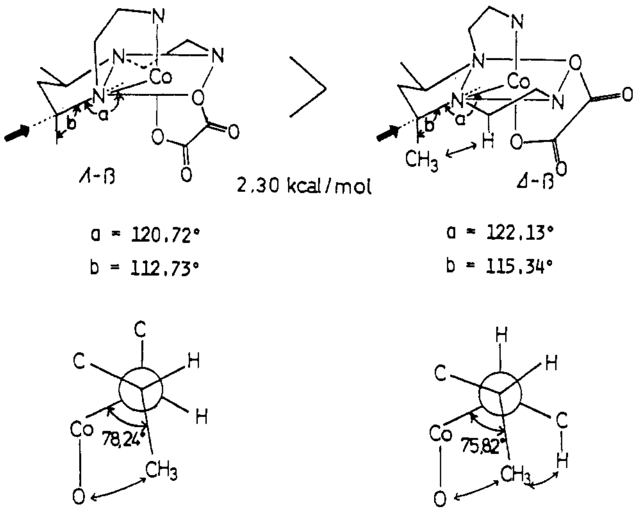

Figure 5. Two isomers of *cis*-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$.

(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$. Thermodynamic equilibrium studies have revealed that the energy difference between the two isomers, Λ-β and Δ-β, is very small in the *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$ system[8] but that the difference is fairly large in the *cis*-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ system. This indicates that the existence of the axially orientated *C*-methyl group causes a large energy difference between the two geometries, Λ-β and Δ-β, but the existence of the equatorially orientated *C*-methyl group does not affect remarkably the energy difference.

These experimental findings could be sufficiently reproduced in the strain energy minimization calculations. The estimated energy difference between the two isomers is small in the *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$ system and is large enough in the *cis*-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ system. The estimated large energy difference in the latter system is mainly caused by the strain energy terms concerning the axially orientated *C*-methyl group. The most characteristic feature appeared in the nonbonded interactions (Figure 4). In the Δ-β isomer, a nonbonded interaction energy of 0.66 kcal/mol exists between a proton on the axially orientated *C*-methyl group and a proton of the methylene in the adjacent five-membered chelate ring. On the other hand, in the Λ-β isomer, this kind of repulsion does not exist because the vicinal five-membered chelate ring links to the apical position.

Figure 5 shows the Newman projections viewed from the directions indicated by the arrows. The largest nonbonded interaction is observed between the oxygen atom coordinated to the cobalt atom and the axially orientated *C*-methyl group. In the Λ-β form, this repulsion can be relieved by the rotation around the axis of the projection. The torsional angle is considerably larger (78.24°) than in the usual gauche conformation. On the other hand, in the Δ-β form, the strain relieving by this rotation is limited by another repulsion between a proton of the axially orientated *C*-methyl group and one of the methylene protons in the adjacent five-membered chelate ring. Therefore, the value of the torsional angle cannot be so large as in the Δ-β form (75.82°). This repulsion is alternatively released by locating the axially orientated *C*-methyl group far from the cobalt center. This is reflected in the angles of *a* and *b*, which are considerably enlarged compared with those in the Λ-β form. These features, however, appear with some mild modifications, because the distortion energies are dispersed around the whole molecule as a result of the optimization. Alternatively, the summation of each energy term sufficiently reflects these features. The energy of the torsional constraint in the Λ-β form is larger than in the Δ-β form by 0.37 kcal/mol. The energies of the bond angle deformations and the nonbonded interatomic interactions are larger in the Δ-β form than in the Λ-β form by 2.09 and 0.51 kcal/mol, respectively. In the whole, the total strain energy of the Λ-β form is 2.30 kcal/mol smaller than that of the Δ-β form.

This difference does not appear if the axially orientated *C*-methyl group does not exist. Therefore, in the *cis*-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$ system, the energy difference was estimated to be very small.

Conclusion

An axially orientated *C*-methyl group on the carbon adjacent to the secondary nitrogen in the central six-membered chelate ring of 2,3,2-tet brings about a considerable energy difference between the Λ-β and Δ-β geometries in the cis cobalt(III) system, and its existence is the essential factor of the stereospecific formation of the complex. In order to provide the axially orientated *C*-methyl group, two chiral *C*-methyl groups are necessary at least.

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Registry No. Λ-β-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO$_4$, 98218-62-3; Δ-β-[Co(ox)(5*S*-Me-2,3,2-tet)]ClO$_4$, 98301-39-4; Λ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]ClO$_4$, 55683-81-3; Δ-β-[Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$, 98301-40-7; Λ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, 98301-41-8; Δ-β-[Co(ox)(5*R*-Me-2,3,2-tet)]$^+$, 98301-42-9; 5*S*-Me-2,3,2-tet, 34776-69-7; *N*-*t*-Boc-gly, 4530-20-5; (*S*)-1,3-butanediamine, 590-88-5; potassium tris(oxalato)cobaltate(III), 14239-07-7.