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Mechanism for Chiral Recognition of a Prochiral Center and for Asymmetric Induction in Asymmetric Syntheses of α-Amino Acids Using Chiral Cobalt(III) Complexes. Crystal and Molecular Structures of $(+)_{577}$-(α-Amino-α-methylmalonato)((4*R*,6*R*)-4,6-dimethyl-1,9-diamino-3,7-diazanonane)cobalt(III) Perchlorate Monohydrate and $(-)_{546}$-(α-Amino-α-methylmalonato)((6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane)-cobalt(III) Bromide Trihydrate

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Two X-ray structure determinations of $(+)_{577}$-[Co(AMM)((4*R*,6*R*)-4,6-dimethyl-1,9-diamino-3,7-diazanonane)]$ClO_4 \cdot H_2O$ (**1**) and $(-)_{546}$-[Co(AMM)((6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane)]$Br \cdot 3H_2O$ (**2**), where AMM represents an α-amino-α-methylmalonate ion, are reported. For **1**: formula $CoC_{13}H_{29}N_5O_8Cl \cdot H_2O$, space group $P2_12_12_1$ (orthorhombic); a = 13.766 (4) Å, b = 14.068 (5) Å, c = 10.762 (3) Å, Z = 4, R = 0.0432. For **2**: formula $CoC_{15}H_{33}N_5O_4Br \cdot 3H_2O$, space group $P2_12_12_1$ (orthorhombic); a = 14.041 (2) Å, b = 16.158 (2) Å, c = 9.997 (1) Å, Z = 4, R = 0.0511. Although the CD patterns of the two AMM complexes are quite different from each other, the two complex ions take approximately identical structures except for the existence of the terminal *N*-methyl groups on the tetraamine part in **2**. The absolute configurations of the two complex ions are both Λ in the β_2 form. The prochiral center of the AMM ion is highly recognized in each complex, as a result of the three-point attachment including intramolecular hydrogen bond formation. Each absolute configuration of the chiral α-carbon of the AMM moiety is *S*, as a result of the coordination of the pro-*S* carboxyl group, and the uncoordinated carboxyl group forms an intramolecular hydrogen bond to one of the secondary nitrogens of the tetraamine. Of the two terminal *N*-methyl groups on the tetraamine ligand of **2**, one on the "out-of-plane" five-membered chelate ring takes an equatorial orientation and the other on the "in-plane" five-membered chelate ring takes an axial orientation with regard to each chelate ring. On decarboxylation, **1** resulted in 34% (*R*)-alaninato and 66% (*S*)-alaninato, while **2** resulted in 83% (*R*)-alaninato and 17% (*S*)-alaninato. The results suggest that the important factor which governs the stereoselectivity on decarboxylation is not the coordination geometry of AMM in the starting complex, but the asymmetric environment around the AMM chelate. The terminal *N*-methyl group on the tetraamine can be an effective steric hindrance that regulates the direction of the proton attack.

Introduction

It is an interesting subject to design ligands suitable for metal-assisted asymmetric syntheses. From this standpoint, X-ray crystal structure investigations of metal complexes that are intermediates in asymmetric syntheses should play an important role in elucidating the relationship between the structures and the observed properties of the complexes.

Previously, we have developed a novel cyclic system for the asymmetric synthesis of α-alanine by using a chiral cobalt(III) complex containing 1,5*R*,7*R*,11-Me_4-2,3,2-tet as a ligand (1,5*R*,7*R*,11-Me_4-2,3,2-tet = (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane).[2] In the system, decarboxylation of an α-amino-α-methylmalonato (AMM) complex in acidic conditions has been employed to yield an α-alaninato complex. Since AMM is itself achiral, the asymmetry of the resulting alanine is induced by a chiral metal complex. During our research to elucidate the important factor for the effective asymmetric induction, we have observed that the stereoselectivity on decarboxylation differs significantly between the two cases using the following optical active tetraamines: 5*R*,7*R*-Me_2-2,3,2-tet and 1,5*R*,7*R*,11-Me_4-2,3,2-tet (5*R*,7*R*-Me_2-2,3,2-tet = (4*R*,6*R*)-4,6-dimethyl-1,9-diamino-3,7-diazanonane). The decarboxylation of $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$ClO_4 \cdot H_2O$ (**1**) yielded 34% (*R*)-alaninato and 66% (*S*)-alaninato, while the decarboxylation of $(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$Br \cdot 3H_2O$ (**2**) yielded 83% (*R*)-alaninato and 17% (*S*)-alaninato.

In order to discuss the factor that caused this large difference in stereoselectivity on the decarboxylation, it is very important to establish the structures of the AMM complexes. However, it is difficult to speculate on their structures by spectroscopic means, such as electronic absorption (AB), circular dichroism (CD), or NMR spectra. Therefore, their detailed stereochemistries should be established by means of X-ray diffraction studies.

Experimental Section

Electronic absorption (AB) spectra were obtained on a Shimadzu UV-210 double-beam spectrophotometer. Circular dichroism (CD) spectra were obtained on a JASCO J-500A spectropolarimeter. These measurements were made on aqueous solutions at concentrations near 2 × 10^{-3} M. FT ^1H NMR spectra were obtained on a JEOL GX-400 spectrometer (400 MHz) with sodium 3-(trimethylsilyl)propanesulfonate (DSS) as an internal reference in D_2O. FT ^{13}C NMR spectra in D_2O solutions were obtained on a JEOL PS-100 spectrometer (25 MHz) with Me_4Si sealed in a capillary as an external reference.

Preparations. All materials used were of reagent grade. Ammonium α-amino-α-methylmalonate (NH_4AMM) was prepared by the method of Thanassi.[3] 5*R*,7*R*-Me_2-2,3,2-tet and *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 were prepared by the methods of Mizukami.[4] 1,5*R*,7*R*,11-Me_4-2,3,2-tet and *trans*-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 were prepared by the methods described previously.[5]

$(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$ClO_4 \cdot H_2O$ (1). *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 (0.72 g, 1.66 mmol), NH_4AMM (0.22 g, 1.5 mmol), and dried triethylamine (1.21 g) were refluxed in 100 mL of absolute methanol for 3 h. A reddish orange solution was obtained. After the triethylamine and the methanol had been removed on a rotary evaporator, the residue was dissolved in 100 mL of water. The solution was poured on a column of SP-Sephadex C-25 cation-exchange resin in the sodium form (h = 70 cm, o.d. = 4.5 cm). The complexes were eluted with 0.01 N $NaClO_4$. Two trace bands and one main band were developed on the column. Concentration of the eluant from the main band gave reddish orange crystals. They were collected by filtration, washed with methanol and ether, and air-dried. Anal. Calcd for $C_{13}H_{29}N_5O_8ClCo \cdot H_2O$: C, 31.49; H, 6.30; N, 14.13; Cl, 7.15. Found: C, 31.89; H, 6.27; N, 14.18; Cl, 6.62.

$(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$ClO_4 \cdot 2.5H_2O$ (2) was prepared from *trans*-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 (0.74 g,

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1.66 mmol) and NH_4AMM (0.22 g, 1.5 mmol) in the same manner as the preparation of **1**. Two trace bands and one main band were developed on the column. Concentration of the eluant from the main band gave red crystals. Anal. Calcd for $C_{15}H_{33}N_5O_8ClCo \cdot 2.5H_2O$: C, 32.71; H, 6.95; N, 12.71. Found: C, 32.85; H, 6.50; N, 12.25.

Λ-β_2-[Co(*R*- or *S*-ala)(5*R*,7*R*-Me_2-2,3,2-tet)]$ZnClO_4$ (3_R or 3_S) was prepared from (*R*)- or (*S*)-alanine and *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 by the method used for the synthesis of *cis*-β_2-[Co(gly)-(3,2,3-tet)]$^+$,[6] with slight modifications. The solution of (*R*)- or (*S*)-alanine and *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 was adjusted to pH 5.5 with 0.1 N NaOH, and heated for 1 h at 50 °C. The pH was then adjusted to 8.0, and heating was continued for an additional 3 h. The reaction mixture was passed through a column of anion-exchange resin (DOWEX 2-X8, Cl^- form) and treated with $ZnCl_2$ to obtain red crystals. Anal. Calcd for $C_{12}H_{30}N_5O_2Cl_4CoZn$ ($\mathbf{3}_R$): C, 26.57; H, 5.57; N, 12.91. Found: C, 26.43; H, 6.06; N, 13.07. Calcd for $C_{12}H_{30}N_5O_2Cl_4CoZn \cdot H_2O$ ($\mathbf{3}_S$): C, 25.71; H, 5.75; N, 12.49. Found: C, 25.95; H, 5.56; N, 12.56.

Λ-β_2-[Co(*R*- or *S*-ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$(ClO_4)_2$ (4_R or 4_S) was prepared from (*R*)- or (*S*)-alanine and *trans*-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4 in the same manner as the preparation of $\mathbf{3}_R$ or $\mathbf{3}_S$. The reaction mixture was poured on a column of SP-Sephadex C-25 cation-exchange resin in the sodium form. The complexes were eluted with 0.1 N $NaClO_4$. Concentration of the eluant from the main band gave red crystals. Anal. Calcd for $C_{14}H_{34}N_5O_{10}Cl_2Co \cdot H_2O$ ($\mathbf{4}_R$): C, 28.98; H, 6.25; N, 12.07. Found: C, 28.96; H, 6.56; N, 12.20. Calcd for $C_{14}H_{34}N_5O_{10}Cl_2Co \cdot H_2O$ ($\mathbf{4}_S$): C, 28.98; H, 6.25; N, 12.07. Found: C, 28.88; H, 6.00; N, 12.46.

Decarboxylation of 1. 1 (300 mg) was dissolved in 1 N HCl (30 mL) and heated to 70 °C for 1 h. After the solvent had been removed on a rotary evaporator, the residue was dissolved in water and was poured on a column of SP-Sephadex C-25 cation-exchange resin in the sodium form. Elution with 0.1 N $NaClO_4$ produced two bands. The complex in the eluant for each band was characterized on the basis of its AB, CD, and ^1H NMR spectra by comparison with those of the authentic (*R*)- and (*S*)-alaninato complexes ($\mathbf{3}_R$, $\mathbf{3}_S$). The amount of each complex was determined on the basis of its AB and CD strengths by comparison with those of the authentic $\mathbf{3}_R$ and $\mathbf{3}_S$. Then the formation ratio on the decarboxylation was determined. (*Caution*! Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities.)

Decarboxylation of 2. 2 was decarboxylated by the same procedure as described above. The reaction mixture could not be separated into diastereomers by the chromatographic technique. Then the formation ratio of alaninato complexes was determined through the isolation of alanine from the complex, followed by the measurement of the optical rotation of its DNP derivative.[2] The optical rotation of the DNP derivative of alanine isolated from Λ-β_2-[Co(*R*- or *S*-ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^{2+}$ ($\mathbf{4}_R^{2+}$ or $\mathbf{4}_S^{2+}$) showed almost the same value as those of the authentic DNP–(*R*)-alanine or DNP–(*S*)-alanine, respectively, which indicates no racemization occurs during the isolation of alanine from the complex. Then the optical rotation of the DNP derivative of alanine isolated from the decarboxylated mixture was measured, and the ratio of the product on the decarboxylation was determined from its value: $[\alpha]_{546}$ −146° (in 1% $NaHCO_3$); for authentic DNP–(*R*)-alanine $[\alpha]_{546}$ −219° (in 1% $NaHCO_3$). Further details of this technique will be dealt with in a subsequent paper.

X-ray Data Collection. Since the perchlorate crystals of **2** obtained above were unsuitable for the X-ray crystallography, a bromide crystal was newly prepared as follows. The perchlorate obtained above was dissolved in water and converted to the bromide form by allowing it to pass through a column of Dowex 2-X8 anion exchange resin (100–200 mesh, Br^- form). The pure bromide salt was obtained upon evaporation of the resultant solution to near dryness. A red powder was obtained, which yielded good red crystals upon recrystallization from a minimum amount of a water–ethanol–ether solution. The AB, CD, and ^1H NMR spectra of the bromide were identical with those of the perchlorate. Anal. Calcd for $C_{15}H_{33}N_5O_4BrCo \cdot 3H_2O$: C, 33.34; H, 7.27; N, 12.96; Br, 14.79. Found: C, 33.42; H, 7.65; N, 12.68; Br, 15.90.

Crystal data and experimental conditions for **1** and **2** are listed in Table I. Measured densities were obtained by flotation in dichloroethane–dibromoethane mixtures. The intensity data were collected on a Rigakudenki four-circle automated diffractometer. Three standard reflections were monitored every 50 reflections for each compounds and showed no systematic decrease in intensity, for which no correction was made. Totals of 2895 reflections (for **1**) and 4962 reflections (for **2**) were measured. If $|F_o|$ was less than $3\sigma(F_o)$, the reflection was considered to be unobserved. The intensities were corrected for Lorentz–polarization effects. Absorption corrections (μ = 1.041 and 2.696 mm^{-1} for **1** and **2**, respectively) were applied.

Table I. Crystal Data and Experimental Conditions for $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$ClO_4 \cdot H_2O$ (**1**) and $(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$Br \cdot 3H_2O$ (**2**)

	1	**2**
formula	$CoC_{13}H_{29}N_5O_8Cl \cdot H_2O$	$CoC_{15}H_{33}N_5O_4Br \cdot 3H_2O$
M_r	495.80	540.34
cryst size, mm	0.31 × 0.30 × 0.27	0.48 × 0.48 × 0.32
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	13.766 (4)	14.041 (2)
b, Å	14.068 (5)	16.158 (2)
c, Å	10.762 (3)	9.997 (1)
V, $Å^3$	2084 (1)	2268.2 (6)
d(obsd), Mg m^{-3}	1.58	1.58
d(calcd), Mg m^{-3}	1.58	1.58
Z	4	4
λ, Å	0.7107 (Mo Kα)	0.7107 (Mo Kα)
abs coeff, mm^{-1}	1.041	2.696
monochromator	LiF	graphite
take-off angle, deg	3	5
method	θ–2θ	θ–2θ
scan speed, deg min^{-1}	2	3
bkgd counts, s	10	10
stds	3 every 50 reflections	3 every 50 reflections
2θ max, deg	60	60
no. of data	2895	4962 (*hkl*, 3728; $\bar{h}kl$, 1234)
no. of obsd data	2374 ($F_o \geq 3\sigma(F_o)$)	3666 ($F_o \geq 3\sigma(F_o)$)
R	0.0432	0.0511
R′	0.0428	0.0551

Structure Determination and Refinement. Compound 1. The initial position of the cobalt atom was determined from a Patterson map. The positions of the remaining nonhydrogen atoms were determined by successive structure factor and electron density map calculations. Isotropic followed by anisotropic least-squares refinement gave values of $R = \sum||F_o| - |F_c|/\sum|F_o| = 0.0597$ and $R' = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.0703$. A weighting scheme, $1/w = \sigma_c^{\,2} + (0.015|F_o|)^2$, was employed, where σ_c defined as $\sigma_c = (\bar{N})^{1/2}$ is a counting statistics error with Gaussian distribution function $P(N) = (^1/_2\bar{N})^{1/2} \exp[-(N - \bar{N})^2/2\bar{N}]$. Since the tetraamine was prepared from (*R*,*R*)-2,4-pentanediamine, the known absolute configurations of the two asymmetric carbon atoms[7] were used as internal reference asymmetric centers to determine the absolute configuration of the whole complex ion. The effects of anomalous dispersion were introduced in F_c, and values of f' and f'' for Co, Cl, O, N, and C were taken from Cromer's tabulation.[8]

The positions of all hydrogen atoms except those of the water molecule of crystallization were determined from a difference map. Least-squares refinement, allowing all the atoms except for hydrogen atoms to vibrate anisotropically, with hydrogen atoms isotropic, converged to *R* and *R′* values of 0.0432 and 0.0428, respectively.

When the f'' values were reversed in sign in order to test the final structure, convergence was reached with *R* = 0.0526 and *R′* = 0.0526, which are significantly larger than the corresponding values of 0.0432 and 0.0428 for the final structure. Final atomic parameters are listed in Table II.

Compound 2. The initial positions of the cobalt and the bromine atoms were determined from a Patterson map. The positions of the remaining non-hydrogen atoms were determined by successive structure factor and electron density map calculations. Isotropic followed by anisotropic least-squares refinement gave values of *R* = 0.0675 and *R′* = 0.0788.

Since the tetraamine was prepared from (*R*,*R*)-2,4-pentanediamine, the known absolute configurations of the two asymmetric carbon atoms[7] were used as internal reference asymmetric centers to determine the absolute configuration of the whole complex ion. The effects of anomalous dispersion were introduced in F_c.

The positions of all hydrogen atoms except those of the water molecules of crystallization were determined by a difference map. Least-squares refinement, allowing all the atoms except for hydrogen atoms to vibrate anisotropically, with hydrogen atoms isotropic, converged to *R*

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Table II. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses) for $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$ClO_4 \cdot H_2O$ (**1**)

atom	*x*	*y*	*z*
Co	0.21489 (4)	0.19380 (4)	0.03901 (5)
O(1)	0.34873 (23)	0.21302 (20)	0.00201 (28)
O(2)	0.48423 (22)	0.14426 (24)	−0.06482 (35)
O(3)	0.40730 (27)	−0.04700 (27)	−0.19666 (35)
O(4)	0.26158 (26)	0.02034 (24)	−0.21331 (31)
N(1)	0.07918 (28)	0.16422 (28)	0.07588 (36)
N(2)	0.17332 (27)	0.19659 (29)	−0.13871 (33)
N(3)	0.19809 (26)	0.33277 (24)	0.06060 (34)
N(4)	0.24556 (30)	0.19147 (30)	0.21642 (33)
N(5)	0.24844 (25)	0.05800 (25)	0.02971 (34)
C(1)	0.03498 (35)	0.12120 (34)	−0.03483 (55)
C(2)	0.06604 (35)	0.18088 (36)	−0.14346 (46)
C(3)	0.20161 (42)	0.27800 (32)	−0.22212 (43)
C(4)	0.17971 (40)	0.37381 (36)	−0.16211 (46)
C(5)	0.23200 (34)	0.39698 (31)	−0.04339 (48)
C(6)	0.24253 (38)	0.35897 (34)	0.18247 (46)
C(7)	0.21529 (46)	0.28211 (34)	0.27460 (43)
C(8)	0.34840 (31)	0.04258 (31)	−0.02208 (42)
C(9)	0.39939 (32)	0.13925 (30)	−0.02964 (42)
C(10)	0.33964 (35)	0.00293 (32)	−0.15782 (45)
C(C3)	0.30569 (44)	0.26966 (40)	−0.26959 (51)
C(C5)	0.21746 (48)	0.50156 (34)	−0.00886 (49)
C(C8)	0.40637 (36)	−0.02530 (36)	0.05968 (51)
Cl	0.45491 (11)	0.16501 (10)	0.42826 (14)
O(5)	0.45635 (42)	0.13177 (47)	0.30492 (48)
O(6)	0.54334 (47)	0.14742 (67)	0.48130 (68)
O(7)	0.37840 (39)	0.11826 (34)	0.49151 (48)
O(8)	0.43723 (54)	0.26232 (37)	0.42339 (74)
O(9)	−0.07906 (32)	−0.00903 (36)	0.18523 (48)
H1(N1)	0.079 (4)	0.117 (4)	0.147 (5)
H2(N1)	0.046 (4)	0.206 (4)	0.102 (5)
H1(N2)	0.200 (3)	0.146 (3)	−0.160 (4)
H1(N3)	0.139 (3)	0.345 (3)	0.067 (4)
H1(N4)	0.218 (4)	0.140 (3)	0.247 (4)
H2(N4)	0.295 (4)	0.182 (4)	0.223 (5)
H1(N5)	0.241 (3)	0.033 (3)	0.112 (4)
H2(N5)	0.218 (3)	0.028 (3)	−0.010 (4)
H1(C1)	0.058 (4)	0.056 (3)	−0.036 (5)
H2(Cl)	−0.037 (3)	0.121 (3)	−0.025 (4)
H1(C2)	0.046 (4)	0.232 (4)	−0.135 (5)
H2(C2)	0.053 (4)	0.150 (3)	−0.220 (5)
H1(C3)	0.167 (4)	0.268 (4)	−0.302 (5)
H1(C4)	0.110 (3)	0.379 (3)	−0.149 (4)
H2(C4)	0.205 (4)	0.423 (4)	−0.223 (5)
H1(C5)	0.302 (3)	0.388 (3)	−0.054 (4)
H1(C6)	0.221 (4)	0.416 (3)	0.212 (4)
H2(C6)	0.312 (3)	0.360 (3)	0.161 (4)
H1(C7)	0.246 (3)	0.292 (3)	0.360 (4)
H2(C7)	0.149 (5)	0.272 (4)	0.292 (6)
H1(CC3)	0.314 (5)	0.318 (5)	−0.339 (6)
H2(CC3)	0.321 (4)	0.206 (4)	−0.310 (5)
H3(CC3)	0.361 (5)	0.285 (5)	−0.215 (6)
H1(CC5)	0.153 (6)	0.513 (5)	0.017 (7)
H2(CC5)	0.228 (5)	0.547 (4)	−0.087 (6)
H3(CC5)	0.254 (5)	0.526 (5)	0.066 (6)
H1(CC8)	0.409 (3)	−0.007 (3)	0.149 (4)
H2(CC8)	0.464 (4)	−0.032 (3)	0.035 (5)
H3(CC8)	0.373 (4)	−0.076 (4)	0.074 (5)

and *R′* values of 0.0511 and 0.0551, respectively. When the *f″* values were reversed in sign in order to test the final structure, convergence was reached with $R = 0.0684$ and $R' = 0.0811$, which are significantly larger than the corresponding values of 0.0511 and 0.0551 for the final structure. Final atomic parameters are listed in Table III.

Table III. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses) for $(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]Br$\cdot 3H_2O$ (**2**)

atom	*x*	*y*	*z*
Co	0.10465 (4)	0.12388 (4)	0.17353 (6)
O(1)	0.17177 (24)	0.06482 (19)	0.30767 (30)
O(2)	0.30718 (26)	0.00206 (23)	0.35764 (35)
O(3)	0.43747 (31)	0.15946 (29)	0.28693 (49)
O(4)	0.32671 (29)	0.24312 (22)	0.20252 (42)
N(1)	0.04148 (30)	0.18809 (24)	0.02604 (40)
N(2)	0.13222 (32)	0.23397 (24)	0.25580 (40)
N(3)	−0.01399 (29)	0.11302 (25)	0.28246 (39)
N(4)	0.06757 (30)	0.01593 (24)	0.08782 (39)
N(5)	0.22855 (27)	0.12282 (26)	0.07995 (36)
C(1)	0.08160 (39)	0.27370 (30)	0.03283 (57)
C(2)	0.08484 (38)	0.29945 (28)	0.17443 (62)
C(3)	0.11649 (47)	0.25039 (35)	0.40267 (51)
C(4)	0.01700 (48)	0.22403 (37)	0.44447 (57)
C(5)	−0.00730 (41)	0.13359 (35)	0.42897 (50)
C(6)	−0.05177 (40)	0.02821 (36)	0.25940 (59)
C(7)	−0.03531 (40)	0.00658 (34)	0.11454 (59)
C(8)	0.30769 (32)	0.09495 (28)	0.16905 (52)
C(9)	0.26200 (36)	0.05031 (29)	0.28771 (45)
C(10)	0.36305 (38)	0.17333 (34)	0.22584 (54)
C(N1)	0.04304 (43)	0.15802 (35)	−0.11434 (53)
C(N4)	0.11860 (42)	−0.06092 (30)	0.12871 (58)
C(C3)	0.19504 (51)	0.21400 (40)	0.48937 (61)
C(C5)	−0.10102 (49)	0.11423 (44)	0.50022 (61)
C(C8)	0.37671 (41)	0.04027 (35)	0.09470 (55)
Br	0.82314 (4)	0.24998 (4)	0.16254 (6)
O(5)	0.78593 (49)	0.08661 (40)	0.84918 (104)
O(6)	0.08231 (70)	0.45068 (54)	0.69120 (103)
O(7)	0.77688 (50)	−0.07265 (45)	0.61104 (106)
H1(N1)	−0.014 (4)	0.192 (3)	0.051 (6)
H1(N2)	0.201 (4)	0.239 (4)	0.245 (6)
H1(N3)	−0.047 (3)	0.143 (2)	0.249 (4)
H1(N4)	0.074 (3)	0.019 (3)	0.002 (4)
H1(N5)	0.239 (4)	0.173 (3)	0.039 (5)
H2(N5)	0.232 (5)	0.084 (4)	0.020 (7)
H1(C1)	0.051 (4)	0.315 (3)	−0.024 (6)
H2(C1)	0.149 (4)	0.267 (3)	−0.010 (5)
H1(C2)	0.027 (4)	0.303 (3)	0.213 (5)
H2(C2)	0.123 (4)	0.355 (3)	0.189 (5)
H1(C3)	0.125 (4)	0.315 (3)	0.397 (5)
H1(C4)	−0.035 (4)	0.258 (3)	0.397 (5)
H2(C4)	0.016 (4)	0.235 (4)	0.523 (6)
H1(C5)	0.050 (3)	0.101 (2)	0.469 (4)
H1(C6)	−0.120 (3)	0.024 (3)	0.281 (4)
H2(C6)	−0.014 (4)	−0.009 (4)	0.328 (7)
H1(C7)	−0.058 (3)	−0.045 (3)	0.098 (4)
H2(C7)	−0.076 (4)	0.036 (3)	0.063 (5)
H1(CN1)	0.012 (4)	0.193 (3)	−0.167 (6)
H2(CN1)	0.004 (3)	0.104 (3)	−0.122 (5)
H3(CN1)	0.110 (3)	0.151 (3)	−0.136 (4)
H1(CN4)	0.098 (4)	−0.104 (3)	0.083 (5)
H2(CN4)	0.180 (3)	−0.058 (3)	0.110 (4)
H3(CN4)	0.112 (3)	−0.069 (3)	0.234 (4)
H1(CC3)	0.184 (4)	0.155 (3)	0.487 (5)
H2(CC3)	0.192 (5)	0.237 (5)	0.564 (8)
H3(CC3)	0.270 (5)	0.255 (4)	0.441 (7)
H1(CC5)	−0.129 (6)	0.140 (5)	0.576 (8)
H2(CC5)	−0.154 (4)	0.130 (4)	0.460 (6)
H3(CC5)	−0.119 (5)	0.053 (4)	0.492 (8)
H1(CC8)	0.407 (4)	0.072 (3)	0.016 (5)
H2(CC8)	0.351 (4)	−0.008 (3)	0.072 (5)
H3(CC8)	0.412 (4)	0.017 (4)	0.144 (6)

All refinements were carried out by the block-diagonal least-squares technique. Atomic scattering factors were taken from ref 9 and 10. All calculations were performed on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with Universal Program System UNICS III.[11] The perspective views were drawn by using the program ORTEP 2.

Results

Spectra. The ^1H NMR spectral data for the two AMM complexes (**1**, **2**) are listed in Table IV. Complex **1** shows two doublets at δ 1.13 and 1.43 due to the two *C*-methyl groups on the tetra-

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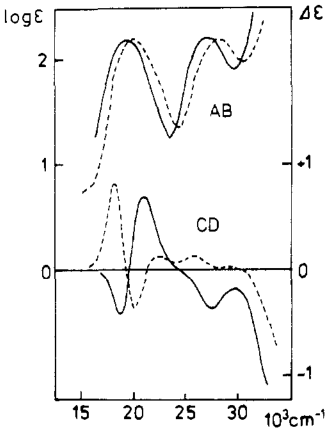


Figure 1. Electronic absorption (AB) and circular dichroism (CD) spectra: i (- -), $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$ (**1**); ii (—), $(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ (**2**).

Table IV. ^{1}H NMR Spectral Data Observed in D_2O[a]

	δ(H)			
no.	N–CH_3 of tet	C–CH_3 of AMM	C–CH_3 of ala	C–CH_3 of tet
1		1.64 s		1.43 d, 1.13 d
2	2.20 s, 1.95 s	1.75 s		1.41 d, 1.10 d
3$_R$			1.47 d	1.44 d, 1.22 d
3$_S$			1.50 d	1.45 d, 1.28 d
4$_R$	2.16 s, 1.90 s		1.53 d	1.45 d, 1.20 d
4$_S$[b]	(2.45–2.03		1.62–1.45	1.27–1.22)

[a] Chemical shifts are given in referenced to DSS (s = singlet, d = doublet). [b] Mixture of stereoisomers, probably due to the configurational isomerization concerning the orientation of the two terminal *N*-methyl groups on the tetraamine moiety.

amine ligand and a singlet at δ 1.64, which can be assigned to the methyl protons of the AMM moiety. Complex **2** shows a pair of doublets at δ 1.10 and 1.41 and a pair of singlets at δ 1.95 and 2.20, which can be ascribed to the two *C*-methyl groups and two *N*-methyl groups on the tetraamine, respectively. A singlet at δ 1.75 is due to the methyl protons of the AMM moiety. The ^{13}C NMR spectrum of **1** shows 13 signals, and that of **2** shows 15 signals, including two signals due to the carboxyl groups (at δ 174 and 185 for **1** and δ 179 and 189 for **2**). The ones at δ 174 for **1** and δ 179 for **2** can be ascribed to the uncoordinated carboxyl groups and the others at δ 185 for **1** and δ 189 for **2** can be ascribed to the coordinated carboxyl groups by comparison with the ^{13}C NMR spectra of decarboxylated products. These spectral features indicate that a stereoisomer of C_1 symmetry was obtained in each AMM complex in a high selectivity. These steric features are in good agreement with those obtained from the present X-ray studies.

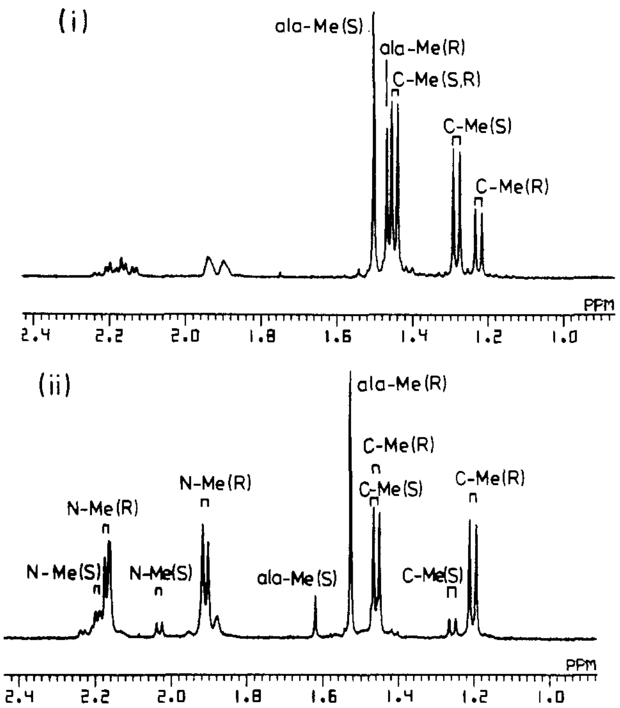
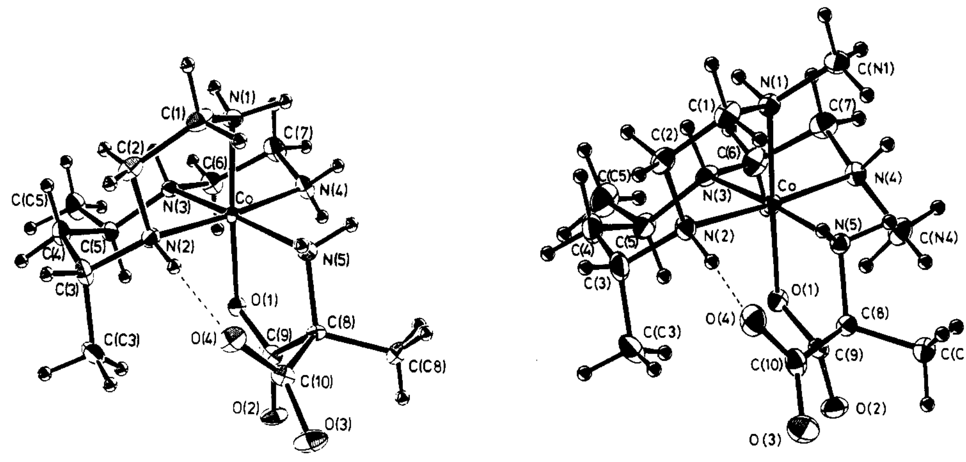


Figure 2. FT ^{1}H NMR spectra of decarboxylation mixtures obtained from (i) $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$ (**1**) and (ii) $(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ (**2**) by treatment with DCl. (R) or (S) represents resonances due to the (*R*)-alaninato complex or to the (*S*)-alaninato complex, respectively. C-Me or N-Me represents resonances due to the *C*-methyl groups or to the *N*-methyl groups in the tetraamine part, respectively. ala-Me represents resonances due to the methyl group in the alanine part.

The AB and CD spectra of the two AMM complexes (**1**, **2**) are shown in Figure 1, and their spectral data are summarized in Table V. Each absorption spectrum shows a typical pattern for an N_5O-type Co(III) complex. The absorption maxima of **2** are slightly shifted toward lower energy when compared with those of **1**. The CD patterns of the two AMM complexes are quite different from each other. The CD spectrum of **1** shows larger positive, smaller negative, and even smaller positive Cotton effects from lower to higher enery in the first absorption region, while

Table V. Electronic Absorption (AB) and Circular Dichroism (CD) Spectral Data

no.	complex	AB $\tilde{\nu}/10^3$, cm^{-3} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-3} (Δε)
1	Λ-β_2-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$	20.0 (2.20)	18.5 (+0.81)
			20.3 (−0.37)
			22.5 (+0.13)
		28.0 (2.20)	26.1 (+0.17)
			29.2 (+0.04)
2	Λ-β_2-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$	19.3 (2.18)	18.8 (−0.44)
			21.0 (+0.70)
		27.0 (2.18)	27.5 (−0.36)
3$_R$	Λ-β_2-[Co(*R*-ala)(5*R*,7*R*-Me_2-2,3,2-tet)]$^{2+}$	20.0 (2.20)	18.7 (+1.33)
			20.7 (−0.64)
		28.0 (2.20)	26.9 (+0.35)
3$_S$	Λ-β_2-[Co(*S*-ala)(5*R*,7*R*-Me_2-2,3,2-tet)]$^{2+}$	20.0 (2.20)	19.0 (+1.17)
			21.5 (−0.98)
		28.0 (2.19)	26.7 (+0.23)
4$_R$	Λ-β_2-[Co(*R*-ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^{2+}$	19.5 (2.15)	17.9 (+0.24)
			19.3 (−0.20)
			21.0 (+0.67)
		27.3 (2.18)	25.5 (+0.10)
			28.0 (−0.08)
4$_S$	Λ-β_2-[Co(*S*-ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^{2+}$	19.3 (2.12)	18.1 (+0.78)
			20.5 (−0.84)
		27.1 (2.17)	26.0 (+0.26)



1^+ 2^+

Figure 3. ORTEP drawing and atomic numbering scheme for the $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$^+$ (1^+) ion and the $(-)_{546}$-[Co(AMM)-(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$^+$ (2^+) ion.

the CD spectrum of **2** shows smaller negative and dominant positive Cotton effects from lower energy.

The AB and CD spectral data of the alaninato complexes $\mathbf{3}_R$, $\mathbf{3}_S$, $\mathbf{4}_R$, and $\mathbf{4}_S$ are summarized in Table V. Their ^{1}H NMR spectral data are listed in Table IV.

Decarboxylation. The AMM complexes **1** and **2** were decarboxylated in acidic solutions (1 N HCl) at 70 °C for 1 h. The ^{1}H NMR spectra of decarboxylation mixtures treated with DCl are shown in Figure 2. The spectra indicate that the AMM complexes converted completely to mixtures of the (*R*)- and (*S*)-alaninato complexes. It is important to note that each *C*-methyl signal of the alaninato moiety appears as a sharp singlet. These observations indicate that α-deuterated alanine could be prepared by decarboxylation using DCl.

The formation ratios on the decarboxylation were determined by the procedure described in the Experimental Section. The decarboxylation of **1** resulted in 34% (*R*)-alaninato ($\mathbf{3}_R$) and 66% (*S*)-alaninato ($\mathbf{3}_S$), while **2** resulted in 83% (*R*)-alaninato ($\mathbf{4}_R$) and 17% (*S*)-alaninato ($\mathbf{4}_S$). The stereoselectivities for the two cases are very different from each other. Further the order of asymmetry is reversed.

Description of the Structures. $(+)_{577}$-[Co(AMM)(5*R*,7*R*-Me_2-2,3,2-tet)]$ClO_4\cdot H_2O$ (1). The perspective view of the complex ion for compound **1** is shown in Figure 3 along with that for compound **2**. The tetraamine coordinates to the slightly distorted octahedral cobalt center in the Λ-cis-β geometry. The absolute configurations around the secondary nitrogen atoms, N(2) and N(3), are both *S*. The conformations of the two five-membered chelate rings are both δ. The central six-membered chelate ring takes a chair conformation with one methyl group (C(C3)) axial and the other (C(C5)) equatorial. The distances between the cobalt atom and the nitrogen atoms for Co–N(2) and Co–N(3) (1.997 (4) and 1.982 (4) Å, respectively) are larger than those for Co–N(1) and Co–N(4) (1.955 (4) and 1.956 (4) Å, respectively). The angles for Co–N(2)–C(3) and Co–N(3)–C(5) (120.8 (3) and 117.8 (3)°, respectively) are slightly larger than the usual tetrahedral angles. These features can be ascribed to the distortion of the six-membered ring due to the nonbonded interactions between the two *C*-methyl groups (C(C3) and C(C5)) and the oxygen atom in the apical position (O(1)). The angles around the cobalt center for the five-membered chelate rings, N(1)–Co–N(2) and N(3)–Co–N(4), are 85.7 (2) and 85.8 (2)°, respectively, and that for the six-membered ring, N(2)–Co–N(3), is 93.4 (2)°. These steric features of the tetraamine ligand are quite similar to those in Λ-β-[Co(ox)(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4 previously established crystallographically.[12]

The AMM ion coordinates to the cobalt atom through N(5) and O(1) bidentately in the β_2-form. The five-membered chelate ring takes a pseudo-envelope conformation. The distances of Co–N(5) and Co–O(1) are 1.968 (4) and 1.904 (3) Å, respectively. The absolute configuration around the asymmetric carbon center of the AMM moiety is *S*, as a result of the coordination of the pro-*S* carboxyl group. The distances in the corrdinated carboxyl group, O(1)–C(9) and O(2)–C(9), are 1.296 (5) and 1.230 (6) Å, respectively. These differences in the bond lengths indicate that the C–O bond containing the coordinated oxygen atom (O(1)) has single-bond character and that containing the uncoordinated oxygen atom (O(2)) has double-bond character. The distances for O(3)–C(10) and O(4)–C(10) in the uncoordinated carboxyl group are 1.239 (6) and 1.254 (6) Å, respectively, which suggests a resonance structure of the uncoordinated carboxyl group. However, the distance O(4)–C(10) containing O(4), which forms the intramolecular hydrogen bond to N(2), is slightly larger than the distance O(3)–C(10).

An internal hydrogen bond is observed between the uncoordinated carboxyl group of the AMM moiety (O(4)) and the proton on the secondary nitrogen of the tetraamine (H–N(2)). The distance N(2)···O(4) is 2.876 (5) Å and the angle N(2)–H···O(4) is 180.0°.

$(-)_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$Br\cdot 3H_2O$ (2). The steric features are quite similar to those of compound **1**. The tetraamine coordinates to the slightly distorted cobalt atom in the Λ-cis-β geometry. The absolute configurations around the secondary nitrogen atoms N(1), N(2), N(3), and N(4) are *R*, *S*, *S*, and *S*, respectively. The conformations of the two five-membered chelate rings are both δ. The central six-membered chelate ring takes a chair conformation with one methyl group (C(C3)) axial and the other (C(C5)) equatorial. Of the two terminal *N*-methyl groups on the tetraamine moiety, one on the "out-of-plane" five-membered chelate ring takes an equatorial orientation and the other on the "in-plane" five-membered chelate ring takes an axial orientation with regard to each chelate ring. The same arrangement of *N*-methyl groups has been found in Δ-β-[Co(ox)(1,5*R*,7*S*,11-Me_4-2,3,2-tet]$ClO_4\cdot H_2O$[13] and in Λ-β_2-[Co(*R*-ala)(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]$Br_2\cdot 3H_2O$.[2,14] The distances between the cobalt atom and the nitrogen atoms (Co–N(1), Co–N(2), Co–N(3), and Co–N(4)) are all about 2.0 Å. The distances Co–N(1) and Co–N(4) are considerably larger than those of the compound **1**. The angles Co–N(2)–C(3) and Co–N(3)–C(5) (121.9 (3) and 117.3 (3)°, respectively) are slightly larger than usual tetrahedral angles, which indicates distortion of the six-membered ring as discussed for the compound **1**. The angles for the two terminal *N*-methyl groups (Co–N(1)–C(N1)

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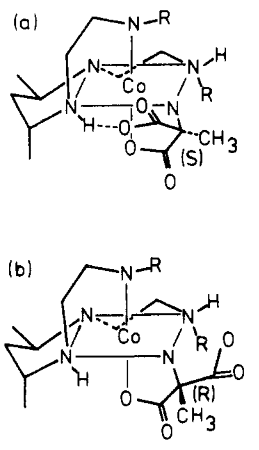


R = -H or $-CH_3$

Figure 4. Two stereoisomers that may result from the coordination of the pro-*S* or pro-*R* carboxyl group of the AMM ion.

and Co–N(4)–C(N4)) are 121.2 (3) and 118.8 (3)°, respectively, which are larger than the usual tetrahedral angles. The angles around the cobalt center for the five-membered chelate rings, N(1)–Co–N(2) and N(3)–Co–N(4), are 85.9 (2) and 86.6 (2)°, respectively, and that for the six-membered ring, N(2)–Co–N(3), is 90.9 (2)°.

The AMM ion coordinates to the cobalt atom through N(5) and O(1) bidentately in the β_2-form. The five-membered chelate ring takes a pseudo-envelope conformation. The absolute configuration around the asymmetric carbon center of the AMM moiety is *S*. The distances Co–N(5) and Co–O(1) are 1.975 (4) and 1.897 (3) Å, respectively. The distances for the C–O bonds in the coordinated carboxyl group (O(1)–C(9), O(2)–C(9)) and in the uncoordinated carboxyl group (O(3)–C(10), O(4)–C(10)) are 1.304 (6), 1.224 (6), 1.231 (7), and 1.259 (7) Å, respectively. The tendencies of their bond lengths are quite similar to those of compound **1**.

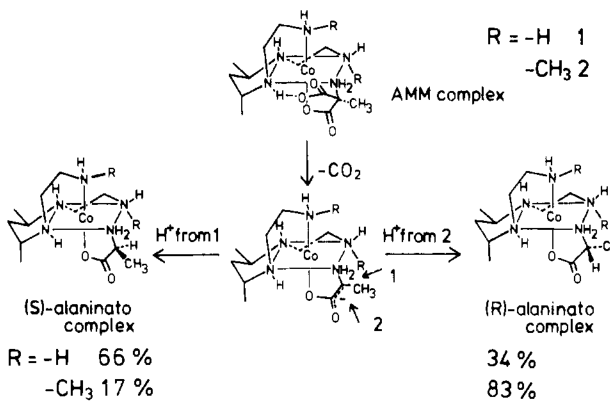
An internal hydrogen bond is also observed between the uncoordinated carboxyl group of the AMM moiety (O(4)) and the proton on the secondary nitrogen of the tetraamine (H–N(2)). The distance N(2)···O(4) is 2.786 (6) Å and the angle N(2)–H···O(4) is 172.1°.

Discussion

CD Spectra. It is well-known that the shape of the CD spectrum in the first absorption region closely correlates to the absolute configuration and conformation of a cobalt(III) complex. The shapes of the CD spectra of the two AMM complexes (**1** and **2**) in this region are very different from each other (Figure 1). The present X-ray studies revealed that both complex ions take a Λ-cis-β_2 geometry and the absolute configurations of the asymmetric carbons in the AMM moieties are both *S*. The two complex ions are different only in the substituents on the terminal nitrogen atoms of the tetraamine. Since absolute configurations around the two nitrogen atoms of **2** (N(1) and N(4)) are *R* and *S*, respectively, their vicinal effects should cancel each other. Therefore, it is difficult to explain the large difference in the CD spectra between the two AMM complexes in terms of the vicinal effects of the asymmetric nitrogen atoms. It can be assumed that the two components of the first absorption region are inversed in order by an effect that may be caused by distortion of the complex ion.

Chiral Recognition. The two crystal structures revealed that the absolute configuration of the chiral α-carbon of the AMM moiety in each complex is *S* as a result of the coordination of the pro-*S* carboxyl group, and the uncoordinated carboxyl group forms an intramolecular hydrogen bond to one of the secondary nitrogens of the tetraamine. This type of hydrogen bond seems to play an important role in the chiral recognition of a prochiral center of the AMM ion. The hydrogen bond angles N(2)–H···O(4) in the complex ions of **1** and **2** are 180.0 and 171.1°, respectively. The linear arrangement of the three atoms forms the stable hydrogen bond. In contrast, in the possible isomer in which the absolute configuration of the chiral carbon of the AMM moiety is *R*, which may result from the coordination of the pro-*R* carboxyl group, the linear arrangement is impossible (Figure 4). Thus, the complex ion is not able to be stabilized by the formation of the hydrogen bond. Other binding modes of AMM than β_2 are expected to be less stable due to the steric repulsion between the tetraamine and AMM. Consequently, only the stereoisomers found in the present crystal structures can be stabilized significantly due to the hydrogen bond formation. As a result, the two carboxyl groups of AMM are chirally recognized effectively by so-called three-point attachment,[15] and this is the important factor that caused the stereospecific formation of each complex.

Scheme I



Glusker et al. have reported this type of hydrogen bond in the structure of an AMM Co(III) complex with a trien derivative Λ-β_2-[Co(AMM)((2*S*,9*S*)-2,9-diamino-4,7-diazadecane)]-$ClO_4 \cdot H_2O$.[16] The present two structure determinations suggest the generality of the three-point attachment in the course of the incorporation of AMM into a chiral cobalt(III) complex with a tetraamine of the 2,3,2-tet type as well as of the trien type.

Asymmetric Induction on Decarboxylation. The present X-ray studies revealed that coordination geometries of the AMM moieties in the reaction precursors (**1** and **2**) are quite similar to each other. However, the decarboxylation of **1** (R/S = 34/66) showed very different stereoselectivity from that of **2** (R/S = 83/17). These observations indicate that the stereoselectivity on the decarboxylation is not governed by the chirality of the coordinated AMM ion but by the asymmetric environment constructed around the AMM chelate by the chiral tetraamine. The important factor seems to be the direction of the attack of proton. The plausible mechanism is drawn in Scheme I. In the decarboxylation of **2**, the axially oriented *N*-methyl group (C(N4)) hinders the attack from direction 1. Consequently, the attack from direction 2 is relatively dominant. This caused the remarkable displacement to (*R*)-alaninato (about 50%) on the decarboxylation of **2**, compared with the case of **1**.

In conclusion, we have found that the terminal *N*-methyl group on the tetraamine can be an effective steric hindrance that regulates the direction of the proton attack. The stereoselectivity on the decarboxylation of AMM is largely governed by this environmental factor. This information would be very useful in designing a molecule with a high degree of asymmetric induction.

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Registry No. **1**, 100570-27-2; **2**, 101400-34-4; 3_R, 101248-47-9; 3_S,

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101540-69-6; 4_R, 77818-88-3; 4_S, 101248-50-4; *trans*-[$CoCl_2$(5*R*,7*R*-Me_2-2,3,2-tet)]ClO_4, 55683-80-2; *trans*-[$CoCl_2$(1,5*R*,7*R*,11-Me_4-2,3,2-tet)]ClO_4, 77818-90-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond distances and angles, nonbonded interactions less than 3.4 Å between methyl groups and other atoms, intra- and intermolecular hydrogen bonds, and observed and calculated structure factor amplitudes and stereoscopic illustrations of the unit cell contents (40 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Inorganic Chemistry and Magnetism, Indian Association for the Cultivation of Science, Calcutta 700032, India, and Department of Physics, Jadavpur University, Calcutta 700032, India

Ruthenium Complexes of N,S- and C,N,S-Coordinating Azo Ligands: Synthesis, Reactions, and Structure

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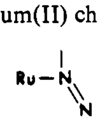
The reaction of ruthenium trichloride with 2-(arylazo)phenyl thioethers ($ArNNC_6H_4SR$: Ar = Ph, *p*-tolyl; R = Me, CH_2Ph) (HL, **4**) in methanol affords blue-violet Ru(HL)(L)Cl (**8**) and red-violet RuL_2 (**6**), the former being the major product. If lithium bromide is added to the reaction mixture, the bromo analogue of **8** is formed. Both **8** and **6** contain pseudooctahedral ruthenium(II): HL is bidentate, coordinating via thioether sulfur and an azo nitrogen, but L is meridionally tridentate (coordination at sulfur, nitrogen, and the ortho carbon of Ar). All chelate rings are five-membered. The dissimilar binding of HL and L is reflected in infrared and ^1H NMR data. Considerable lowering of $\nu_{N=N}$ occurs in going from HL to **6** and **8** due to Ru–azo π-back-bonding. The conversion **8** → **6** is very effectively catalyzed (yield of **6** 60%) by a mildly hot (323 K) silica gel surface. The same conversion can be achieved but in poorer yield by reaction with silver perchlorate in methanol solution. A mechanism is suggested involving ortho-metalative edge displacement assisted by electrophilic (silver(I), silica gel) halide displacement. With two HL-like moieties bridged as in $ArNNC_6H_4S(CH_2)_3SC_6H_4NNAr$ (Ar = Ph, *p*-tolyl, *m*-tolyl; H_2LL, **9**), octahedral hexadenticity of the type $RuC_2N_2S_2$ is readily achieved in violet Ru(LL) (**10**). The ortho metalation of the Ar groups (i.e. absence of two ortho protons) in **10** is unequivocally revealed by the spin–spin structure of the ^1H NMR spectrum of **10**. All three types of complexes (**6**, **8**, and **10**) exhibit reversible or nearly reversible ruthenium(III)/ruthenium(II) couples in cyclic voltammetry (platinum electrode, MeCN solvent). The formal potentials are as follows: RuL_2^+/RuL_2, ~0.52 V; $Ru(LL)^+/Ru(LL)$, ~0.60 V; $Ru(HL)(L)Cl^+/Ru(HL)(L)Cl$, ~0.70 V. The oxidized complexes are relatively unstable and have not been isolated in the pure state. However the electronic structure of coulometrically produced $Ru(HL)(L)Cl^+$ and RuL_2^+ in solution could be studied with the help of EPR and near-IR spectra. In frozen dichloromethane (77 K) the EPR spectrum of $Ru(HL)(L)Cl^+$ is rhombic ($g_x = 2.291$, $g_y = 2.173$, and $g_z = 1.963$ in the case Ar = Ph and R = CH_2Ph) and corresponds to axial (Δ) and rhombic (V) splitting parameters of 10 200 and 4700 cm^{-1} respectively. On the other hand the spectrum of the corresponding RuL_2^+ complex is axial ($g_\perp = 2.213$ and $g_\parallel = 1.965$), with $\Delta = 9800$ cm^{-1}. The predicted near-IR absorptions due to transitions within Kramers doublets are experimentally observable. The ruthenium(II) complexes **6**, **8**, and **10** show multifeatured absorptions in the region 450–750 nm believed to be due to MLCT excitations. The axial splittings here (estimated to be <4000 cm^{-1}) are much less than those in the oxidized complexes.

Introduction

This work stems from our interest[2-5] in the chemistry of ruthenium coordinated to azo ligands. A persistent feature of the azo–ruthenium(II) chromophore (**1**) is the presence of substantial $Ru(t_2) \rightarrow azo(\pi^*)$ back-bonding as reflected in short Ru–N and long N–N distances.[3,5] Associated with such bonding are the red-shift[4,6] of $\nu_{N=N}$ and the display of strong MLCT transitions[2-6] in the visible region—a property that can be useful in protein labeling via azo functionalization.[7] Also associated is the multiple-electron-transfer activity[2,4] of the chromophore occurring at relatively high potentials—a property that can help in mediating energetic electroprotic transformations such as the oxidation of water to dioxygen.[8]



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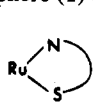

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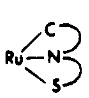

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Such results have encouraged us to explore newer azo–ruthenium chemistry. Ligands examined thus far are mostly[2-6] of the bidentate N,N type where one of the nitrogen atoms is of the azo type. Herein we describe the binding of ruthenium by a group of N(azo),S(thioether) ligands viz., 2-(arylazo)phenyl thioethers. The motive behind this choice was to ascertain the effect of attaching two π-acceptor sites—azo and sulfur[9]—to the same ruthenium center on the nature of the compounds produced. In practice two modes of chelation, N,S (**2**) and C,N,S (**3**, via ortho metalation), are observed with a preponderance of the latter. The spectra, reactions, and structure of selected species including a

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