comparable amounts of two such products, we infer that the oxidizing species attacking N_2H_2 (or $N_2H_3^+$) in the final rapid step (9) has the same ligand environment as that attacking $N_2H_5^+$ in the rate-determining steps.

One point continues to concern us. The proposed mechanism includes a dissociation equilibrium involving departure of the ligand $HOLig^-$ from the Cr^V center and its return, with the rate constants for forward (k_1) and reverse (k_{-1}) components much greater than that for the subsequent formation of the precursor complex, P (k_2). Even if it is assumed that the labile carboxyl is attached to Cr(V) through only one donor site (i.e., $-COO^-$), the implication is that both formation and breakage of a Cr^V–O bond are much more rapid than formation of a Cr^V–N bond. Such a conclusion would appear to be inadmissible if applied to octahedral complexes of the first-row transition-metal ions in their +2 and +3 states, for these undergo substitution by variants of a dissociative process with rates determined, in large part, by the metal–ligand bond being broken rather than by the bond formed.[24] The story is much less clear for substitution reactions at centers derived from metals in very high oxidation states (e.g., Ti(IV), V(V), Cr(V), and Cr(VI)). Here, nonoctahedral geometries, angular distortion of coordination polyhedra, and unusually strong polarization of the metal–ligand bonds complicate the picture, and broad mechanistic generalizations have not yet emerged.[25] However, rates of substitution at Cr(VI) have been shown to be highly sensitive to the structure of the attacking nucleophile,[26] and it would not be astonishing to find an analogous sensitivity for reactions of the pentapositive state as well.

(23) E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).
(24) See, for example, F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, Chapter 3.
(25) See, however: (a) A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **65**, 2098 (1961); **69**, 1736 (1965); (b) H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, 2700 (1966).

Appendix

Derivation of Equations 10. The steady-state equations applied to the precursor, P, and the monocarboxylato intermediate $(OLig^{2-})Cr(O)OH$ (abbreviated CrCl below) in the sequence (5)–(7) are

$$d[CrL]/dt = 0 = k_1[CrL_2] - k_{-1}[CrL][L^-] - k_2[CrL][N_2H_5^+] + k_{-2}[P][H^+] \quad (a)$$

$$d[P]/dt = 0 = k_2[CrL][N_2H_5^+] - k_{-2}[P][H^+] - k_3[P] \quad (b)$$

Addition of (a) and (b) and then rearranging give (c) whereas

$$[P] = (k_1[CrL_2] - k_{-1}[CrL][L^-])/k_3 \quad (c)$$

simple rearrangement of (b) gives (d). Equating (c) and (d)

$$[P] = k_2[CrL][N_2H_5^+]/(k_{-2}[H^+] + k_3) \quad (d)$$

and then solving for [CrL] lead to (e). The proposed two-path

$$[CrL] = \frac{k_1[CrL_2]}{\frac{k_2k_3[N_2H_5^+]}{k_{-2}[H^+] + k_3} + k_{-1}[L^-]} \quad (e)$$

reaction sequence implies the rate expression (f). Substitution

$$\text{rate} = k_3[P] + k_{OS}[CrL][N_2H_5^+] \quad (f)$$

of (d) and (e) into (f) and then rearranging give equation 10 in the text.

Registry No. I, 70132-29-5; $N_2H_5^+$, 18500-32-8.

(26) P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 220 (1966).

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Asymmetric Induction on Decarboxylation of α-Amino-α-alkylmalonic Acids Chelated to Chiral Cobalt(III) Complexes

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The Λ-β_2-[Co(α-amino-α-alkylmalonato)(N_4)]$^+$ complexes, where α-amino-α-alkylmalonato = α-amino-α-methylmalonato (AMM), α-amino-α-isopropylmalonato (AIPM), α-amino-α-benzylmalonato (ABzM), and α-amino-α-isobutylmalonato (AIBM) and N_4 = chiral derivatives of 3,7-diazanonane-1,9-diamine (2,3,2-tet) and triethylenetetramine (trien), were prepared from *trans*-$[CoCl_2(N_4)]^+$. The chelated α-amino-α-alkylmalonate stereospecifically took the *R* configuration. Decarboxylations of the α-amino-α-alkylmalonato complexes in acidic aqueous or methanolic solution gave rise to a diastereomeric mixture of the corresponding (*R*)- and (*S*)-amino acidato complexes (Λ-*R* and Λ-*S* isomers). Considerable asymmetric induction was observed. In the most favorable case, the formation ratio (Λ-*S*/Λ-*R*) on decarboxylation was 2/98 of the AIPM complex with N_4 = 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane (abbreviated as *SS*-pyht).

Introduction

α-Amino-α-alkylmalonic acids are useful intermediary compounds for syntheses of a variety of α-amino acids.[1] α-Amino-α-alkylmalonic acids have a prochiral center since it contains two enantiotopic carboxyl groups. Asperger and Liu[2] reported that α-amino-α-methylmalonic acid ($AMMH_2$) coordinated to a chiral cobalt(III) complex with its amino and one of the carboxylate groups decarboxylated (at pH 7.5–8.0) yielded stereoselectively the corresponding (*S*)-alaninato complex and that the alanine liberated from the decarboxylated complex showed a 14% excess of (*S*)-alanine over (*R*)-alanine, even though the decarboxylation product seemed to be the

(1) Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids"; Wiley: New York, 1961; Vol. 3
(2) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1967**, *6*, 796.
(3) The abbreviation for this tetraamine, L,L-α,α′-dimethyltrien, used by Asperger and Liu[2] is not appropriate because the positions of the substituents are not clearly indicated. The tetraamine is newly abbreviated according to the system shown in Table I.

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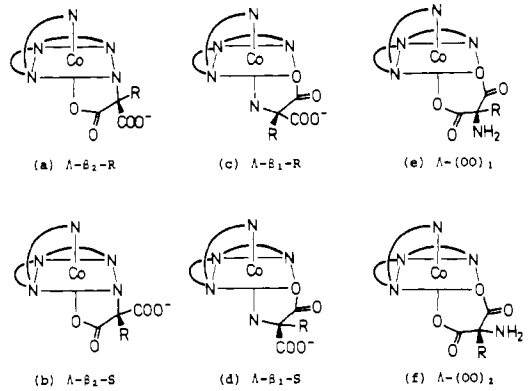
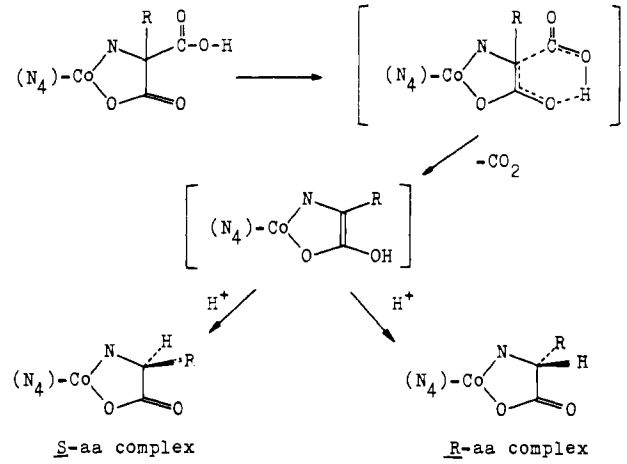


Figure 1. Possible isomers of α-amino-α-alkylmalonato complex with tetraamine.

Scheme I[a]



[a] aa = amino acidato.

Δ-β_1-(*S*)-alaninato complex on the basis of its ORD curve. However, their conclusions were suspected to be erroneous by subsequent workers[4] because their (*S*)-alaninato complexes seemed to be impure and, further, the AMM complex employed in the decarboxylation reaction could be a mixture of Λ-β_1, Λ-β_2, Δ-β_1, and Δ-β_2 isomers, each of which could decarboxylate to yield a mixture of isomers of the alaninato complexes. Further, it was revealed that decarboxylation did not occur in neutral but in acidic condition.[4]

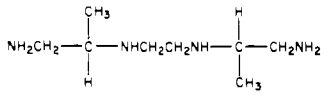
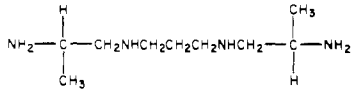
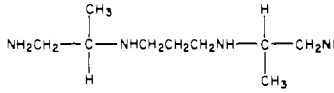
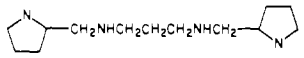
Job and Bruice[4] reported the stereospecific synthesis of Λ-β_2-[Co(AMM)(2(*S*),9(*S*)-Me$_2$trien)]$^+$,[3] the structure of which was determined to be Λ-β_2-*R* (Figure 1a)[5] by an X-ray analysis study.[6] Preference for the Λ-β_2-*R* isomer over the Λ-β_2-*S* isomer was explained by the intramolecular hydrogen bonding between the uncoordinated carboxylate group and the secondary nitrogen, as was observed in the crystal.[4,6] This metal system provided special features capable of accepting only one configuration and of being regarded as analogous to the model suggested by Ogston[7] in his three-point hypothesis for enzyme systems.

Further, upon decarboxylation in acidic solution, this AMM complex gave rise to a mixture of the corresponding diastereomers as expected. The formation ratio of the (*R*)-alaninato and (*S*)-alaninato complex (Λ-*S*/Λ-*R*) was 65/35. Job et al. proposed[4] Scheme I involving a cyclic transition state that converted to an "enol"-like intermediate. The selectivity was thought to be affected by the stereochemical factors of the dissymmetric cobalt center upon protonation of the intermediate. Though methyl substitutents on the tetraamine ligand were replaced by isopropyl groups, the extent of assymmetric induction unexpectedly did not improve very much (Λ-*S*/Λ-*R* = 68.5/31.5).

On the other hand, they also reported[4] that the Λ-β_2-(*R*)-aminoisopropylmalonato (AIPM) complex decarboxylated yielded a mixture of the (*R*)- and (*S*)-valinato complexes, the formation ratio of which (Λ-*S*/Λ-*R*) was 36/64. The predominant valinato complex has the (*R*)-amino acidate, contrary to the case of the AMM and alaninato complex system. This reversion in the selectivity between the AMM and AIPM complexes has not yet been explained.

In order to elucidate the effect of the α substituent of the aminomalonate moiety on the formation ratio (Λ-*S*/Λ-*R*), we investigated α-amino-α-methylmalonato (AMM), α-amino-α-isopropylmalonato (AIPM), α-amino-α-benzylmalonato (ABzM), and α-amino-α-isobutylmalonato (AIBM) complexes. To gain an insight into the influence of the structure of the tetraamine on asymmetric induction, we employed a few chiral derivatives of triethylenetetraamine (trien) and 3,7-diazanonane-1,9-diamine (2,3,2-tet) for the N_4 ligand and prepared the Λ-β_2-*R*-type complexes (Figure 1a). The structure and abbreviations for these tetraamines are summarized in Table I. The 1,7-(2(*S*)-pyrrolidyl)-1,6-diazaheptane (*SS*-pyht) containing pyrrolidyl groups on terminal amines was especially expected to have the ability to bring about significant steric effects toward other ligand(s) in the remaining two coordination sites of the octahedron,[8] and actually such stereoselectivity has been observed on the asymmetric transformation of the α-amino acid.[9] The decarboxylations of α-amino-α-alkylmalonato complexes were carried out in acidic aqueous or methanolic solutions, and the formation ratios of the corresponding (*R*)- and (*S*)-amino acidato complexes were obtained by chromatographic separation.

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

Experimental Section

All materials used were of reagent grade. The ligands 2(*S*), 7-(*S*)-dimethyl-3,6-diazaoctane-1,8-diamine (=3(*S*),8(*S*)-Me$_2$trien),[10] 2(*S*),10(*S*)-4,8-diazaundecane-2,10-diamine (=2(*S*),10(*S*)-Me$_2$-2,3,2-tet),[11] 2(*S*),8(*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (=3(*S*),9(*S*)-Me$_2$-2,3,2-tet),[9] and 1,7-bis(2(*S*)-pyrrolidyl)-2,6-dia-

(4) Job, R. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 809.
(5) According to ref 4, the aminoalkylmalonato complex shown in Figure 1a will be referred to in this paper as the "(*R*)-malonato complex" in the sense that if the uncoordinated carboxylate group were replaced by a proton with retention of configuration, (*R*)-amino acidato complex would result, though the asymmetric carbon of the chelated malonate moiety has the *S* configuration.
(6) Glusker, J. P.; Carrell, H. L.; Job, R. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 5741.
(7) Ogston, A. G. *Nature (London)* **1948**, *162*, 963.
(8) Jun, M. J.; Liu, C. F. *J. Coord. Chem.* **1975**, *5*, 1.
(9) Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1980**, *19*, 2010.
(10) Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 806.
(11) Goto, M.; Makino, T.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1879.

zaheptane (=*SS*-pyht)[9] were prepared by methods described previously. The *trans*-dichlorocobalt(III) complexes with the tetraamine were prepared by a method described previously.[9]

Ammonium α-amino-α-methylmalonate (NH_4AMM) was prepared in a manner similar to that reported by Asperger and Liu.[2] Ammonium α-amino-α-isopropylmalonate (NH_4AIPM), ammonium α-amino-α-benzylmalonate (NH_4ABzM), and ammonium α-amino-α-isobutylmalonate (NH_4AIBM) were prepared from diethyl formamidomalonate and isopropyl iodide, benzyl chloride, or isobutyl chloride, respectively, by the method of Thanassi and Fruton.[12]

Λ-β$_2$-[Co(*R*-AMM)(3(*S*),8(*S*)-Me$_2$trien)]ClO$_4$ (1) was prepared from *trans*-[$CoCl_2$(3(*S*),8(*S*)-Me_2trien)]ClO_4[9] and α-amino-α-methylmalonic acid by the method of Job and Bruice;[6] yield 0.46 g (36%). Anal. Calcd for [Co($C_4H_5NO_4$)($C_8H_{22}N_4$)]ClO_4: C, 29.92; H, 6.13; N, 14.54. Found: C, 30.16; H, 5.73; N, 14.94.

The other chiral cobalt(III) complexes with the alkylaminomalonates were prepared from the corresponding *trans*-dichloro complexes by the method of Job and Bruice[6] with slight modifications, as follows.

Λ-β$_2$-[Co(*R*-AIPM)(3(*S*),8(*S*)-Me$_2$trien)]ClO$_4$·$^3/_2$H$_2$O (2). Ammonium α-amino-α-isopropylmalonate (0.266 g), *trans*-[$CoCl_2$(3(*S*),8(*S*)-Me_2trien)]ClO_4[9] (0.80 g), and 4 mL of 1 M KOH in methanol were placed in 200 mL of methanol (dried over Mg) and heated to reflux. After 3 h of refluxing, the resulting orange-brown solution was concentrated to near dryness with a rotary evaporator, and the residue was diluted with water (200 mL) 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 0.04 M sodium perchlorate. The six bands were developed on the column. The eluant for each band was collected separately, and their electronic, circular dichroism, and ^1H NMR spectra were examined. The first pink band (bottom of the column) was chargeless. The second pink band, which moved at a rate of monopositive-charged species, was assumed to be the carbonato complex. The third and fourth eluted orange 1+ bands contained the aminoisopropylmalonate moiety (from their ^1H NMR spectra). The minor third band and the major fourth band were assigned to the β_1- and β_2-aminoisopropylmalonato complexes, respectively. The fifth orange band and the sixth brown band (top) were eluted at rates consistent with dipositive- and tripositive-charged species, respectively. The former was assumed to be a decarboxylation product (valinato complex), while the latter contained no malonate or aminoacidate moiety. The fourth eluate was concentrated on a rotary evaporator until orange crystals began to precipitate. After standing overnight at room temperature, the orange crystals were collected by filtration, washed with methanol and ether, successively, and air dried; yield 0.26 g (25%). Anal. Calcd for [Co($C_6H_9NO_4$)($C_8H_{22}N_4$)]ClO_4·$^3/_2H_2O$: C, 32.41; H, 6.61; N, 13.50. Found: C, 32.39; H, 6.48; N, 13.38.

Λ-β$_2$-[Co(*R*-AMM)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·H$_2$O (3), Λ-β$_2$-[Co(*R*-AIPM)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·$^3/_2$H$_2$O (4), Λ-β$_2$-[Co(*R*-ABzM)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·2H$_2$O (5), and **Λ-β$_2$-[Co(*R*-AIBM)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·4H$_2$O (6)** were prepared from *trans*-[$CoCl_2$(2(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4[9] and NH_4AMM, NH_4AIPM, NH_4ABzM, or NH_4AIBM by the above procedure. Anal. Calcd for the AMM complex [Co($C_4H_5NO_4$)($C_9H_{24}N_4$)]ClO_4·H_2O: C, 31.49; H, 6.30; N, 14.13. Found: C, 31.59; H, 6.52; N, 14.36. Anal. Calcd for the AIPM complex [Co($C_6H_9NO_4$)($C_9H_{24}N_4$)]ClO_4·$^3/_2H_2O$: C, 33.81; H, 6.81; N, 13.14. Found: C, 33.94; H, 6.86; N, 13.23. Anal. Calcd for the ABzM complex [Co($C_{10}H_9NO_4$)($C_9H_{24}N_4$)]ClO_4·$2H_2O$: C, 38.69; H, 6.32; N, 11.87. Found: C, 38.65; H, 5.85; N, 11.74. Anal. Calcd for the AIBM complex [Co($C_7H_{11}NO_4$)($C_9H_{24}N_4$)]ClO_4·$4H_2O$: C, 32.44; H, 7.33; N, 11.83. Found: C, 32.58; H, 7.69; N, 11.89.

Λ-β$_2$-[Co(*R*-AMM)(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·2H$_2$O (7), Λ-β$_2$-[Co(*R*-AIPM)(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·2H$_2$O (8), and **Λ-β$_2$-[Co(*R*-ABzM)(3(*S*),9(*S*)-Me$_2$-2,3,2-tet)]ClO$_4$·$^3/_2$H$_2$O (9)** were prepared from *trans*-[$CoCl_2$(3(*S*),9(*S*)-Me_2-2,3,2-tet)]ClO_4[9] and NH_4AMM, NH_4AIPM, or NH_4ABzM in the same manner as above. Anal. Calcd for the AMM complex [Co($C_4H_5NO_4$)($C_9H_{24}N_4$)]ClO_4·$2H_2O$: C, 30.39; H, 6.47; N, 13.63. Found: C, 30.90; H, 6.41; N, 13.65. Anal. Calcd for the AIPM complex [Co($C_6H_9NO_4$)($C_9H_{24}N_4$)]ClO_4·$2H_2O$: C, 33.25; H, 6.88; N, 12.92. Found: C, 33.23; H, 7.03; N, 12.84. Anal. Calcd for the ABzM complex [Co($C_{10}H_9NO_4$)($C_9H_{24}N_4$)]ClO_4·$^3/_2H_2O$: C, 39.28; H, 6.25; N, 12.06. Found: C, 39.20; H, 6.00; N, 11.89.

Λ-β$_2$-[Co(AMM)(*SS*-pyht)]ClO$_4$ (10) and **Λ-β$_2$-[Co(*R*-AIPM)(*SS*-pyht)]ClO$_4$·$^3/_2$H$_2$O (11)** were prepared from *trans*-[$CoCl_2$(*SS*-pyht)]ClO_4[9] and NH_4AMM or NH_4AIPM in a similar manner. Since the ^1H NMR spectrum of the AMM complex showed two singlets at about 1.7 ppm (intensity ratio was ca. 4:1) arising from the α-methyl group of the malonate, the complex was assumed to contain two species assigned to Λ-β$_2$-*R* (major) and Λ-β$_2$-*S* (minor). Attempts to separate these isomers failed. Anal. Calcd for the AMM complex [Co($C_4H_5NO_4$)($C_{13}H_{28}N_4$)]ClO_4: C, 38.53; H, 6.28; N, 13.22. Found: C, 38.31; H, 6.31; N, 12.92. Anal. Calcd for the AIPM complex [Co($C_6H_9NO_4$)($C_{13}H_{28}N_4$)]ClO_4·$^3/_2H_2O$: C, 39.01; H, 6.89; N, 11.97. Found: C, 39.12; H, 6.66; N, 12.04.

Λ-β$_2$-[Co(*R*-leu)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)](ClO$_4$)$_2$·3H$_2$O (12), Λ-β$_2$-[Co(*S*-leu)(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)](ClO$_4$)$_2$·2H$_2$O (13), Λ-β$_2$-[Co(*R*-val)(*SS*-pyht)](ClO$_4$)$_2$·H$_2$O (14), and **Λ-β$_2$-[Co(*S*-val)(*SS*-pyht)](ClO$_4$)$_2$·H$_2$O (15)** were prepared from their *trans*-dichloro complexes by the method described previously.[9] Anal. Calcd for **12**, [Co($C_6H_{12}NO_2$)($C_9H_{24}N_4$)]$(ClO_4)_2$·$3H_2O$: C, 28.58; H, 6.72; N, 11.11. Found: C, 28.59; H, 6.23; N, 11.24. Anal. Calcd for **13**, [Co($C_6H_{12}NO_2$)($C_9H_{24}N_4$)]$(ClO_4)_2$·$2H_2O$: C, 29.42; H, 6.58; N, 11.44. Found: C, 29.92; H, 6.83; N, 11.20. Anal. Calcd for **14** and **15**, [Co($C_5H_{10}NO_2$)($C_{13}H_{28}N_4$)]$(ClO_4)_2$·H_2O: C, 34.18; H, 6.38; N, 11.08. Found for **14**: C, 34.16; H, 6.09; N, 10.82. Found for **15**: C, 34.32; H, 6.19; N, 10.74.

Measurements. Visible absorption spectra were measured with a Hitachi 340 recording spectrophotometer. Circular dichroism curves were obtained with a JASCO J-20 recording spectropolarimeter. Proton magnetic resonance (^1H NMR) spectra were obtained on a Hitachi R-40 spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard reference. FT ^{13}C NMR spectra were obtained at 25.03-MHz with broad-band proton decoupling on a JEOL PS-100 spectrometer (at 99.5 MHz) employing the solvent deuterium signal as an internal lock. A pulse angle of 45° was employed with no pulse delay. The ambient temperature was 39 °C. Me_4Si sealed in a capillary was used as an external reference.

The perchlorate salt of the α-amino-α-alkylmalonato complexes (50–100 mg) was dissolved in a minimal amount of water and passed through a small column of anion-exchange resin (Dowex 1-X8, 200-400 mesh, Cl^- form). The resulting solution containing chloride salt was concentrated to dryness with a rotary evaporator, and its NMR spectrum in D_2O was measured. So that the change of the spectrum on decarboxylation of the complex could be examined, the above solution was made acidic with 20% DCl (below pD 1) and heated to 70 °C for about 3 h. Then the ^1H NMR spectrum of the decarboxylation product was measured.

Measurements of Formation Ratios for Decarboxylation Reactions. Weighed samples (100 mg) of the α-amino-α-alkylmalonato complex were dissolved in 100 mL of 1 M HCl aqueous or methanolic solution (the latter was prepared by bubbling dry HCl gas into MeOH (dried over Mg)), and the solution was heated at 70 °C (or the methanolic solution was refluxed) for 2 h. A longer reaction time in methanol resulted in a slight decomposition of the complexes. After neutralization by 1 M NaOH, the solution was reduced to near dryness with a rotary evaporator, and excess NaCl was filtered off. After most of NaCl was removed by addition of methanol and filtration, the resulting solution was poured onto a column of SP-Sephadex C25 cation-exchange resin (2.5 × 40 cm) in the sodium form. The remainder of the procedure was similar to the method described previously[9] except that only two bands were developed on the column. The (*R*)- and (*S*)-amino acidato complexes were obtained quantitatively.

Measurements of Isomer Ratio for Epimerization Reaction. The isomer ratio for the Λ-β$_2$-[Co(*R*- and *S*-leu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$ ions was measured by the method described previously.[9]

Kinetics. The complex **3** or **4** (10 mg) was dissolved in 1, 3, or 6 N hydrochloric acid or buffer (10 mL) prepared from 1 N hydrochloric acid and 1 N sodium acetate. The ionic strength was adjusted at 1.0 with KCl in the pH range. The solution was placed in a 10-cm water-jacketed cell with thermostated water circulating. The H_0 scale[13] was used for acid concentrations of 1.0 M and above,

(12) (a) Thanassi, J. W.; Fruton, J. S. *Biochemistry* **1962**, *1*, 975. (b) Thanassi, J. W. *Biochemistry* **1970**, *9*, 525.

(13) Paul, M. A.; Long, F. A. *Chem. Rev.* **1957**, *57*, 1.

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})
1	Λ-β_2-[Co(*R*-AMM)(3(*S*),8(*S*)-Me_2trien)]ClO_4	477 (161), 348 (176)	466 (1.24), 345 (−0.44)
2	Λ-β_2-[Co(*R*-AIPM)(3(*S*),8(*S*)-Me_2trien)]$ClO_4\cdot{}^3/_2H_2O$	476 (169), 348 (171)	465 (1.22), 343 (−0.37)
3	Λ-β_2-[Co(*R*-AMM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot H_2O$	497 (153), 353 (160)	527 (1.51), 476 (−0.05), 443 (0.11), 357 (−0.25)
4	Λ-β_2-[Co(*R*-AIPM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot{}^3/_2H_2O$	495 (155), 354 (176)	528 (1.38), 450 (0.19), 357 (−0.19)
5	Λ-β_2-[Co(*R*-ABzM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot 2H_2O$	494 (151), 353 (172)	529 (1.61), 476 (−0.23), 430 (0.07), 392 (0.06), 357 (−0.07), 335 (0.03)
6	Λ-β_2-[Co(*R*-AIBM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot 4H_2O$	498 (188), 353 (187)	530 (1.30), 481 (−0.03), 444 (0.18), 359 (−0.25)
7	Λ-β_2-[Co(*R*-AMM)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot 2H_2O$	495 (148), 353 (155)	527 (1.43), 470 (−0.05), 438 (0.06), 360 (−0.23)
8	Λ-β_2-[Co(*R*-AIPM)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot 2H_2O$	496 (137), 354 (157)	530 (1.24), 476 (−0.05), 440 (0.06), 396 (0.03), 360 (−0.15), 333 (0.02)
9	Λ-β_2-[Co(*R*-ABzM)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$ClO_4\cdot{}^3/_2H_2O$	495 (137), 354 (153)	530 (1.26), 477 (−0.27), 390 (0.06), 359 (−0.06), 333 (0.09)
10	Λ-β_2-[Co(AMM)(*SS*-pyht)]ClO_4	513 (171), 363 (205)	545 (1.25), 479 (0.67), 372 (−0.37)
11	Λ-β_2-[Co(*R*-AIPM)(*SS*-pyht)]$ClO_4\cdot{}^3/_2H_2O$	522 (153), 368 (164)	558 (1.32), 480 (0.52), 378 (−0.18)
12	Λ-β_2-[Co(*R*-leu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2\cdot 3H_2O$	495 (164), 352 (175)	526 (2.25), 466 (−0.26), 377 (0.14), 342 (0.14)
13	Λ-β_2-[Co(*S*-leu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2\cdot 2H_2O$	493 (142), 352 (153)	514 (1.82), 452 (−0.63), 352 (−0.22)
14	Λ-β_2-[Co(*R*-val)(*SS*-pyht)]$(ClO_4)_2\cdot H_2O$	515 (176), 363 (192)	549 (1.52), 498 (−0.04), 461 (0.32), 353 (0.22)
15	Λ-β_2-[Co(*S*-val)(*SS*-pyht)]$(ClO_4)_2\cdot H_2O$	518 (169), 364 (186)	540 (1.07), 477 (−0.49), 350 (0.05)

while, for the other solutions, the pH was determined by a glass electrode. The decarboxylation reactions were followed at 55–70 °C on a JASCO DIP-4 digital polarimeter. The final rotation changes averaging 0.3° were observed at 546 nm.

Results and Discussion

The β_2-[Co(α-amino-α-alkylmalonato)(N_4)]$^+$ complexes were prepared from *trans*-[$CoCl_2(N_4)$]$^+$ complexes by modification of the method described by Job and co-workers.[4,6] The complexes **1-9** contain a chiral derivative of tetraamine ligand with primary terminal amines, while the complexes **10** and **11** contain a tetraamine having secondary terminal amines.

The absolute configurations of these complexes were assigned to be Λ on the basis of their circular dichroism spectra.[9] With respect to the aminomalonate moiety, the complexes prepared by the present method were anticipated to adopt stereospecifically the β_2-*R* configuration[5] as long as the quadridentate ligand took the Λ configuration.[4,6] The electronic and circular dichroism spectral data of the Λ-β_2-[Co(α-amino-α-alkylmalonato)(N_4)]$^+$ complexes are tabulated in Table II, and the spectra of the Λ-β_2-[Co(aminomalonato)-(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ complexes (aminomalonato = AMM, AIPM, ABzM, or AIBM) are shown in Figure 2. The positions of the electronic absorption maxima were similar to those of the corresponding amino acidato complexes,[9] which indicated the formation of the N–O-bound aminomalonato complexes. The CD spectra of the aminomalonato complexes were similar to those of the corresponding (*R*)-amino acidato complexes[9] and to that of the Λ-β_2-[Co(*R*-AMM)(2(*S*),9-(*S*)-Me_2trien)]$^+$ complex, the structure of the latter having been determined by an X-ray crystallographic study.[6]

The complex, which was assumed to be the *S*-AMM complex,[5] was also obtained[4] and showed a CD spectrum similar to that of the (*S*)-amino acidato complex. This indicates that the AMM complexes show similar vicinal effects in the CD to the amino acidato complexes. (The absolute configuration of the α-carbon is, however, reversed between the AMM and amino acidato complexes which show the same vicinal effect.[5]) These similarities in CD suggest that the aminomalonato complexes isolated in this study have the same configuration around the α-carbon as the AMM complex with 2(*S*),9-(*S*)-Me_2trien. Consequently, the aminomalonate moiety is assumed to coordinate to the cobalt center with the pro-*S* carboxylate group and the amino group. As described in the Introduction, the preference for the Λ-β_2-*R* complex is attributed to the intramolecular hydrogen bonding between the uncoordinated carboxylate group and the trigonal secondary amine.[6] The change of the α substituent did not alter this selectivity, although yields of the complex with AMM, AIPM, and ABzM decreased in this order.

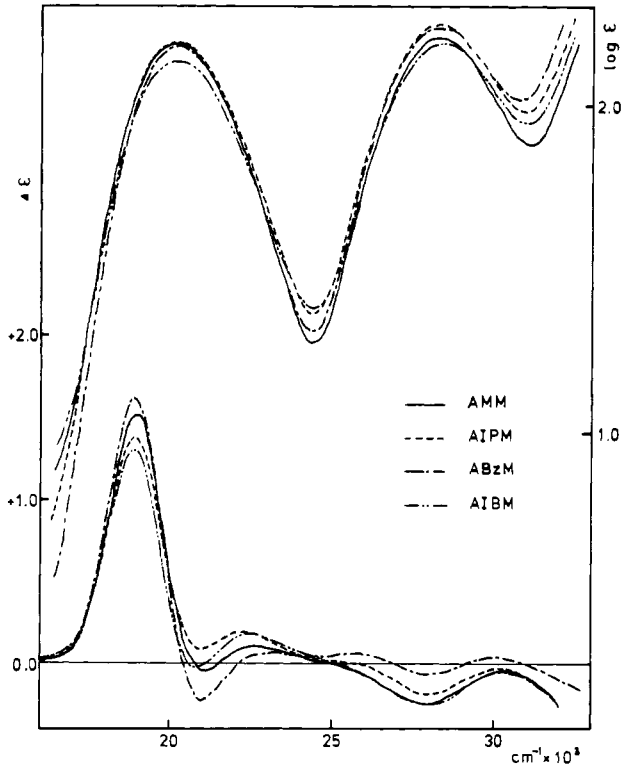


Figure 2. Electronic absorption and CD spectra of Λ-β_2-[Co(*R*-AMM)(L)]$ClO_4\cdot H_2O$ (—), Λ-β_2-[Co(*R*-AIPM)(L)]$ClO_4\cdot{}^3/_2H_2O$ (- - -), Λ-β_2-[Co(*R*-ABzM)(L)]$ClO_4\cdot 2H_2O$ (- - -), and Λ-β_2-[Co(*R*-AIBM)(L)]$ClO_4\cdot 4H_2O$ (- · - ·); L = 2(*S*),10(*S*)-Me_2-2,3,2-tet.

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 the tetraamine ligands for complexes **1–9**. The ^1H NMR spectra of the AMM complexes exhibit a singlet at 1.63–1.72 ppm due to the α-methyl group of the aminomalonate moiety (Figure 3a), and those of the AIPM complexes (Figure 4a) and the AIBM complex (Figure

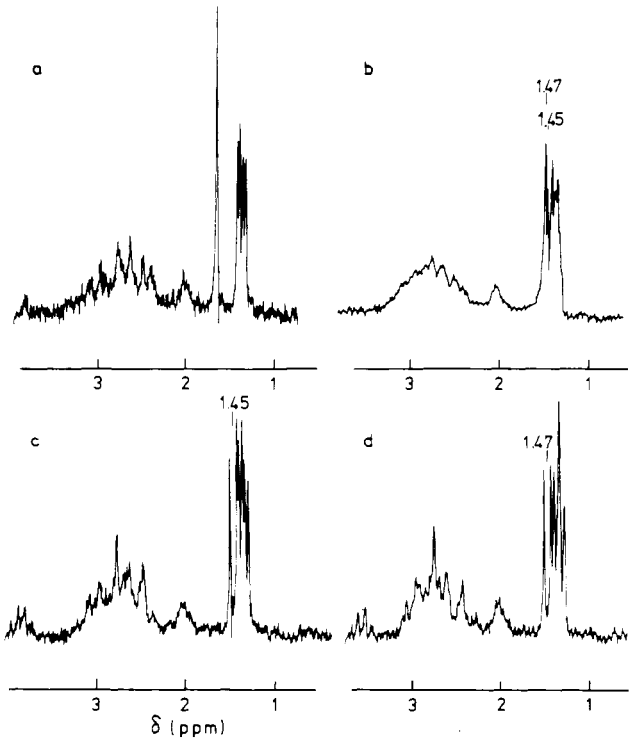


Figure 3. ^{1}H NMR spectra of (a) Λ-β_2-[Co(*R*-AMM)(L)]$^+$ ion, (b) the decarboxylation product of a, (c) Λ-β_2-[Co(*R*-ala)(L)]$^{2+}$ ion, and (d) Λ-β_2-[Co(*S*-ala)(L)]$^{2+}$ ion. L = 2(*S*),10(*S*)-Me_2-2,3,2-tet. a, c, and d in D_2O; b in DCl.

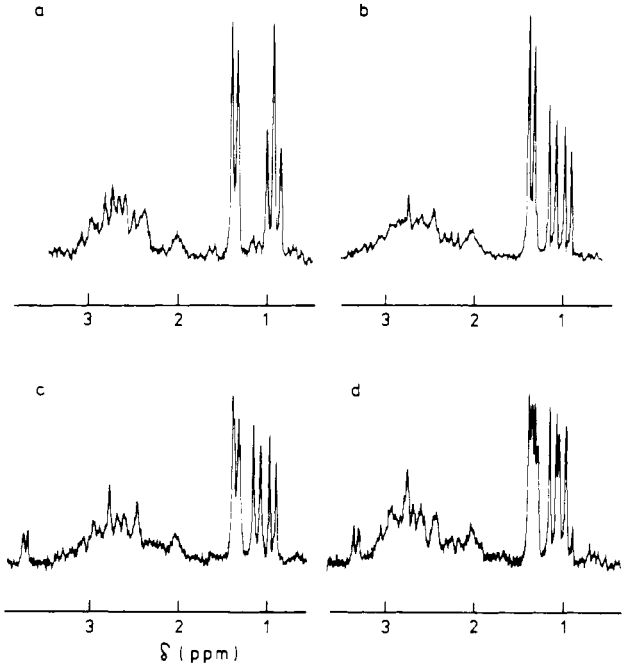


Figure 4. ^{1}H NMR spectra of (a) Λ-β_2-[Co(*R*-AIPM)(L)]$^+$ ion, (b) the decarboxylation product of a, (c) Λ-β_2-[Co(*R*-val)(L)]$^{2+}$ ion, and (d) Λ-β_2-[Co(*S*-val)(L)]$^{2+}$ ion. L = 2(*S*),10(*S*)-Me_2-2,3,2-tet. a, c, and d in D_2O; b in DCl.

5) exhibit a pair of doublets at 0.87–1.03 ppm due to the nonequivalent methyl groups in the isoproyl or isobutyl group. The ^{1}H NMR spectra of the ABzM complexes show signals for an AB system at 3.4 ppm, which can be ascribed to the methylene protons in the benzyl group (Figure 6). The $^2J_{AB}$ values for **5** and **9** are both 14 Hz. The ^{1}H NMR spectrum of the Λ-β_2-[Co(AMM)(*SS*-pyht)]$^+$ complex exhibited two singlets with the approximate ratio 4:1 as the signals for the α-methyl group of the aminomalonato moiety, which suggested

Table III. Assignments of Proton Resonance Shifts[a]

no.	CH_3[b]	CH_3[c]	CH_2[d]	phenyl[d]
1	1.38 d[e]	1.65 s		
2	1.38 d[e]	0.89 d, 0.99 d		
3	1.33 d, 1.36 d	1.63 s		
4	1.36 d[e]	0.89 d, 0.96 d		
5	1.04 d, 1.31 d		3.39 q[f]	7.4 m
6	1.34 d[e]	0.90 d, 0.96 d		
7	1.41 d, 1.46 d	1.67 s		
8	1.35 d, 1.40 d	0.87 d, 0.96 d		
9	1.33 d[e]		3.40 q[f]	7.4 m
10		1.72 s[g], 1.69 s[h]		
11		0.97 d, 1.03 d		
12	1.24 d, 1.29 d	0.97 d[e]		
13	1.33 d, 1.36 d	0.94 d, 0.98 d		
14		1.02 d, 1.16 d		
15		1.05 d, 1.14 d		

[a] Given in ppm from DSS (s = singlet, d = doublet, q = quartet, m = multiplet). [b] Tetraamine. [c] Aminomalonate or amino acidate. [d] ABzM. [e] Resonances overlapping. [f] Quartet of AB system. [g] Major. [h] Minor.

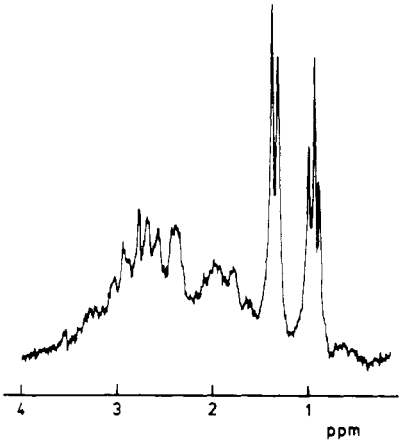


Figure 5. ^{1}H NMR spectrum of Λ-β_2-[Co(*R*-AIBM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion in D_2O.

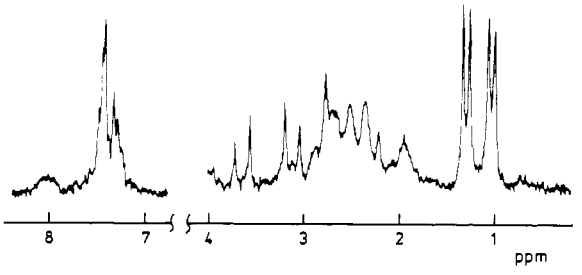


Figure 6. ^{1}H NMR spectrum of Λ-β_2-[Co(*R*-ABzM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion in D_2O.

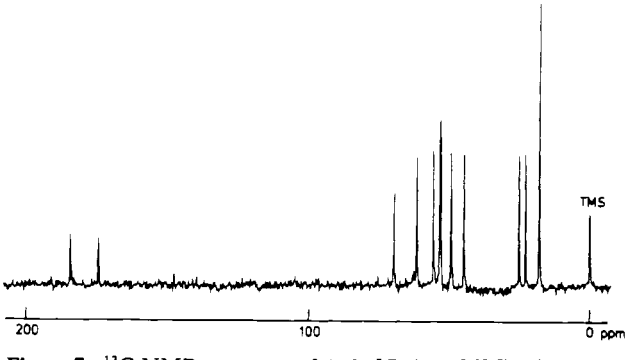


Figure 7. ^{13}C NMR spectrum of Λ-β_2-[Co(*R*-AMM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion in D_2O.

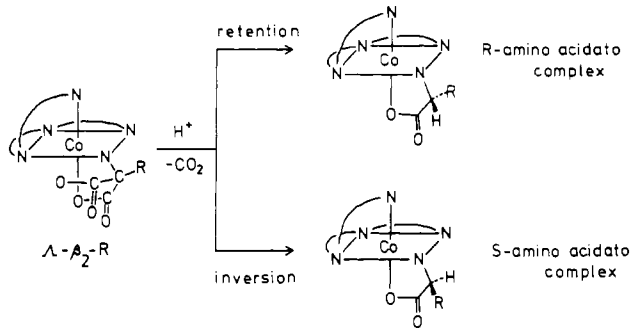


Figure 8. Stereochemistry of decarboxylation of Λ-β_2-[Co(α-amino-α-alkylmalonato)(N_4)]$^+$ complex.

that the product obtained was a mixture of the *R*-AMM (major component) and the *S*-AMM (minor component) complexes.

The ^{13}C NMR spectrum of the AMM complex (Figure 7) exhibits 12 peaks with one overlapping peak, which is consistent with the number of the carbons expected for the single isomer. Two signals at about 180 ppm are attributed to the carbons of the carboxylate groups. The signal at 174.7 ppm is assigned to the uncoordinated carboxylate, while the signal at 184.8 ppm, 10 ppm downfield from that of the free one, is assigned to the coordinated carboxylate.[14]

When an acidic solution of the α-amino-α-alkylmalonato complex is heated at 70 °C, decarboxylation occurs without change in the configuration about the Co(III) center and gives rise quantitatively to a diastereomeric mixture of the corresponding amino acidato complexes.[4,6] On decarboxylation of the AMM complex (in DCl), the signal for the α-methyl group of the aminomethylmalonate moiety disappeared and two singlets corresponding to the α-methyl groups of the (*R*)- and (*S*)-alaninate appeared (Figure 3). The ^1H NMR spectrum of the decarboxylation product of the AIPM complex (in DCl) exhibited a pair of doublets at 0.89 and 0.96 ppm that resembled that of the (*R*)-valinato complex (Figure 4b). As Figure 8 shows, the (*R*)-amino acidato complex is formed with retention of configuration about the C center and the (*S*)-amino acidato complex with inversion.

Decarboxylation took place in acidic aqueous solution (1 M HCl in H_2O) in the same manner as indicated by Job and Bruice[4] and also in the acidic methanolic solution (1 M HCl in methanol). After the chromatographic separation of the diastereomers of the resulting amino acidato complexes, the formation ratios (Λ-*S*/Λ-*R*) were determined spectrophotometrically on the basis of ε values of the first absorption band. The spectral data of most of amino acidato complexes were reported previously.[9] The diastereomeric ratios (Λ-*S*/Λ-*R*) of the alaninato, valinato, phenylalaninato, and leucinato complexes formed through the decarboxyaltion of the α-amino-α-alkylmalonato complexes are summarized in Table IV.

It is noteworthy that in aqueous solution the direction of stereoselectivity of decarboxylation for the AMM complexes, except for the case with *SS*-pyht ligand, is opposite to that of the AIPM, ABzM, and AIBM complexes (Table IV(a)). The complexes, which have the isopropyl, benzyl, or isobutyl group in the aminomalonate, tend to decarboxylate with retention of configuration, while the AMM complexes decarboxylated preferably with inversion of configuration.

On the other hand, with the *SS*-phyt ligand, a higher preference for the retention of configuration upon decarboxylation was observed for both the AMM and the AIPM complexes. With respect to the degree of stereoselectivity, the Λ-*S*/Λ-*R* value for Λ-β_2-[Co(*R*-AIPM)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^+$ ion was 13/87 ($|\Delta\Delta G^{\ddagger}|$ = 1.30 kcal/mol), which

(14) Ama, T.; Yasui, T. *Chem. Lett.* **1974**, 1295.

Table IV. Formation Ratios (Λ-*S*/Λ-*R*) for Λ-β_2-[Co(amino acidato)(N_4)]$^{2+}$ on Decarboxylation

N_4	Λ-*S*/Λ-*R* ala	val	phe	leu
(a) In 1 N HCl/H_2O (70 °C)				
2(*S*),9(*S*)-Me_2trien[a]	65/35[b]	36/64[b]		
2(*S*),9(*S*)-$^i Pr_2$trien[a]	68.5/31.5[b]			
3(*S*),8(*S*)-Me_2trien	56/44[b]	28/72[b]		
2(*S*),10(*S*)-Me_2-2,3,2-tet	54/46	22/78	39/61	41/59
3(*S*),9(*S*)-Me_2-2,3,2-tet	55/45	13/87	35/65	
SS-pyht	15/85	4/96		
(b) In 1 N HCl/MeOH (Reflux)				
3(*S*),8(*S*)-Me_2trien		22/78[b]		
2(*S*),10(*S*)-Me_2-2,3,2-tet		16/84	50/50	44/56
3(*S*),9(*S*)-Me_2-2,3,2-tet	45/55	9/91	23/77	
SS-pyht	14/86	2/98		

[a] Reference 4. [b] These ratios were calculated on the basis of their CD or ORD[4] spectra (see text).

was the maximum for the complexes with tetraamines having primary terminal amines. Apparently, substitutin at the terminal amino groups of the tetraamine improved the selectivity upon decarboxylation to a value of Λ-*S*/Λ-*R* = 4/96 ($|\Delta\Delta G^{\ddagger}|$ = 2.2 kcal/mol) for Λ-β_2-[Co(*R*-AIPM)(*SS*-pyht)]$^+$ ion. The complexes with *SS*-phyt having secondary terminal amines showed a different selectivity effect upon decarboxylation compared to those with other tetraamines. The effect of N substitution on tetraamine will be discussed below.

In methanolic solution the formation of the (*R*)-amino acidato complexes generally increased compared with the results in aqueous solution, as shown in Table IV(b). Decarboxylation proceeds more favorably with retention of configuration in methanol than in H_2O. Reversing of selectivity occurred in the case of the AMM complexes, and, therefore, (*R*)-amino acidato complexes were the predominant products as well as the AIPM, ABzM, and AIBM complexes. The degree of the selectivity with the AIPM and ABzM complexes increased so that the Λ-*S*/Λ-*R* value of 2/98 ($|\Delta\Delta G^{\ddagger}|$ = 2.7 kcal/mol) for Λ-β_2-[Co(*R*-AIPM)(*SS*-pyht)]$^+$ ion, the greatest selectivity in this study, was obtained.

The pH dependence of the decarboxylation rate obtained for the Λ-β_2-[Co(*R*-AIPM)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ complex was similar to that for the Λ-β_2-[Co(*R*-AMM)(2-(*S*),9(*S*)-Me_2trien)]$^+$ ion[4] (Figure 9a). Therefore, the undissociative form, in which the uncoordinated carboxylate group is protonated, is also the reactive species in the AIPM complex. Futher, the kinetics of the decarboxylation of the AMM and AIPM complexes were investigated at constant acidity in the temperature range 55–70 °C. The plots of log k_{obsd} vs. $1/T$ were linear (Figure 9b), and the values of the activation energy for these two systems were nearly equal (E_a = 26 kcal/mol). As Figure 9 shows, the decarboxylation rate of free aminomethylmalonic acid (in the absence of the metal ion) obtained by Thanassi[15] is about 9 times smaller than that of the aminomethylmalonato complex.[16]

Job and Bruice have supposed[4] that the decarboxylation of the AMM complex involves a cyclic transition state (Scheme I) to yield, as a metastable intermediate, an "enol"-like product in which the loss of a carboxyl group brought about a change of the sp^3 state of the asymmetric carbon of AMM to an sp^2 state, and that the selectivity upon protonation of the sp^2 intermediate is affected by the dissymmetric cobalt. According to the above scheme, the α substituents of the aminomalonate

(15) Thanassi, J. W. *J. Org. Chem.* **1971**, *36*, 3019.
(16) Since the pH profile of the decarboxylation of the uncoordinated aminomethylmalonic acid is different from that of the aminomethylmalonato complex (the former had a maximum at about pH 2),[15] the difference in the maximal values of the reaction rate between the former and the latter is smaller than this.

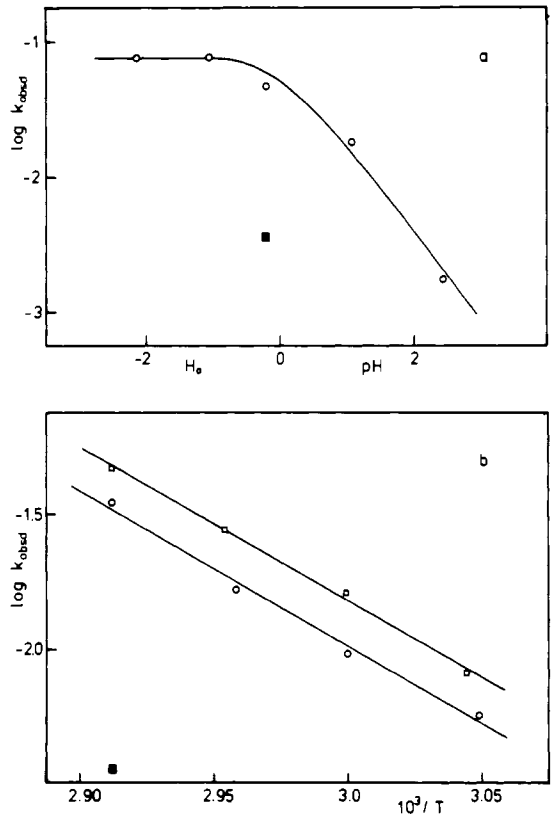


Figure 9. Plots of kinetics data for the decarboxylation: (a) log k_{obsd} vs. pH profile of Λ-β_2-[Co(*R*-AIPM)(L)]$^+$; (b) Arrhenius plots of log k_{obsd} vs. $1/T$ of Λ-β_2-[Co(*R*-AMM)(L)]$^+$ (○) and Λ-β_2-[Co(*R*-AIPM)(L)]$^+$ (□). L = 2(*S*),10(*S*)-Me_2-2,3,2-tet. The ■ was obtained from free aminomethylmalonic acid.[15]

Table V. Isomeric Ratios[a] (Λ-*S*/Λ-*R*) of Λ-β_2-[Co(amino acidato)(N_4)]$^{2+}$ at Equilibrium[b]

	Λ-*S*/Λ-*R*			
N_4	ala	val	phe	leu
3(*S*),8(*S*)-Me_2trien	50/50	34/66		
2(*S*),10(*S*)-Me_2-2,3,2-tet	66/34	47/53	61/39	65/35
3(*S*),9(*S*)-Me_2-2,3,2-tet	61/39	30/70	64/36	
SS-pyht	18/82[c]			

[a] These data are taken from ref 9 except for the leucinato complex. [b] At 40 °C and pH 11.2 unless stated otherwise. [c] At 40 °C and pH 10.1.

must have no influence on the selectivity. In the case of the AIPM complexes, however, the direction of the asymmetric induction was reversed,[4] compared to the results of AMM complexes (Table IV). The AIPM complexes tend to decarboxylate with retention of configuration, contrary to the AMM complexes. (The exceptional case of the *SS*-pyht complexes will be discussed later.) If the planar "enol"-like intermediates were involved in the decarboxylation of both the AMM and AIPM complexes, it would be difficult to explain this reversion of the stereoselectivity.

A possibility that the stereoselectivity reflects the thermodynamic stabilities of the products can be excluded because the direction of the stereoselectivity of the decarboxylation is clearly opposite to that of the epimerization reaction, corresponding to the stabilities of diastereomers (at equilibrium) in the case of the phenylalaninato and leucinato complexes having a secondary β-carbon (Table V). Therefore, we assume that the reaction path is more complicated than that proposed previously.[4]

The ratio of retention of aminoalkylmalonato complexes decreased in the order AIPM > ABzM ≃ AIBM > AMM,

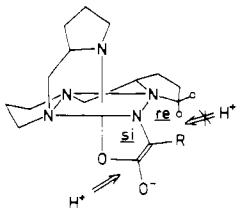


Figure 10. Stereochemistry of the decarboxylation of the Λ-β_2-[Co(α-amino-α-alkylmalonato)(*SS*-pyht)]$^+$ complex.

in which the β-carbon of the aminomalonate moieties are tertiary, secondary, secondary, and primarty, respectively. This suggests that the preference for retention upon decarboxylation is affected by the bulkiness of the α substituent of aminomalonate moiety. In order to explain the strong preference for retention of absolute configuration in the AIPM complexes, it is reasonable to assume an intermediate in which the α-carbon partially holds sp^3 character after the removal of the carboxyl group. Retention of configuration is possibly preferred in the case where the α substituent of the malonate is bulky because the planar intermediate becomes relatively unstable. The fact that in methanolic solution the ratio of retention increases compared to that in aqueous solution suggests that solvation of the intermediate has a considerable influence on selectivity, but details are not yet clear.

With the *SS*-pyht ligand there was no difference in the direction of stereoselectivity between the AMM and AIPM complexes: decarboxylation occurred mainly with retention of configuration. This suggests that N substitution on tetraamine ligand has a much stronger influence on stereoselectivity than the bulkiness of the α substituent of the malonate. This is considered to be due to steric hindrance by the in-plane pyrrolidine ring (Figure 10). Even in the case of the AMM complex, in which decarboxylation occurred with inversion of configuration for the other tetraamine complexes, attack from the *re* face of the planar intermediate was hindered by the in-plane pyrrolidine ring. In the AIPM complex with *SS*-pyht, both such steric hindrance and the preference for the retention by the bulkiness of the α substituent of malonate cooperated and resulted in the highly stereospecific formation of the (*R*)-valinato complex.

Thus, asymmetric induction was observed for the decarboxylation of α-amino-α-alkylmalonic acids chelated to the optically active cobalt(III) ions. It was revealed that modification of a tetraamine ligand such as the pyrrolidine rings of the *SS*-pyht made it possile to obtain a high degree of stereoselectivity upon decarboxylation. It appeared that the decarboxylation mechanism is more complicated than that proposed previously[4] and the solvation of the intermediate plays a significant role in this stereoselectivity. Further investigation to examine the solvent effect and to elucidate the reaction mechanism is now in progress.

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Registry No. **1**, 78149-32-3; **2**, 78149-34-5; **3**, 78149-36-7; **4**, 78149-38-9; **5**, 78149-40-3; **6**, 78149-42-5; **7**, 78306-84-0; **8**, 78246-75-0; **9**, 78478-06-5; **10** (major), 78185-52-1; **10** (minor), 78149-221; **11**, 78149-24-3; **12**, 78149-44-7; **13**, 78185-57-6; **14**, 78215-25-5; **15**, 78166-83-3; Λ-β_2-[Co(*S*-ala)(3(*S*),8(*S*)-Me_2trien)]$^{2+}$, 73453-07-3; Λ-β_2-[Co(*R*-ala)(3(*S*),8(*S*)-Me_2trien)]$^{2+}$, 73493-95-5; Λ-β_2-[Co(*S*-val)(3(*S*),8(*S*)-Me_2trien)]$^{2+}$, 73453-05-1; Λ-β_2-[Co(*R*-val)(3(*S*),8(*S*)-Me_2trien)]$^{2+}$, 73493-93-3; Λ-β_2-[Co(*S*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 68567-18-0; Λ-β_2-[Co(*R*-ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 68531-64-6; Λ-β_2-[Co(*S*-val)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 64387-63-9; Λ-β_2-[Co(*R*-val)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73465-03-9; Λ-β_2-[Co(*S*-phe)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73395-99-0; Λ-β_2-[Co(*R*-phe)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73465-01-7; Λ-β_2-[C_6(*S*-ala)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73453-03-9;

Λ-β_2-[Co(*R*-ala)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-91-1; Λ-β_2-[Co(*S*-val)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73453-01-7; Λ-β_2-[Co(*R*-val)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-89-7; Λ-β_2-[Co(*S*-phe)(3-(*S*),9(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73452-99-0; Λ-β_2-[Co(*R*-phe)(3(*S*),9-(*S*)-Me_2-2,3,2-tet)]$^{2+}$, 73493-87-5; Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$, 64387-61-7; Λ-β_2-[Co(*R*-ala)(*SS*-pyht)]$^{2+}$, 64439-78-7; *trans*-[$CoCl_2$(3(*S*),8(*S*)-Me_2trien)]ClO_4, 60872-59-5; *trans*-[$CoCl_2$(2-(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4, 60801-67-4; *trans*-[$CoCl_2$(3(*S*),9-(*S*)-Me_2-2,3,2-tet)]ClO_4, 73396-02-8; *trans*-[$CoCl_2$(*SS*-pyht)]ClO_4, 59202-14-1.

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Mechanism of Halide Abstraction from (η^5-C_5H_5)$Fe(CO)_2I$ by $AgBF_4$

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The mechanism of halide abstraction from (η^5-C_5H_5)$Fe(CO)_2I$ with $AgBF_4$ was investigated by ^1H NMR ($CDCl_3$ solvent) and infrared (CH_2Cl_2 and $CHCl_3$ solvents) spectroscopic methods. (η^5-C_5H_5)$Fe(CO)_2I$ initially forms a silver(I) adduct formulated as (η^5-C_5H_5)$Fe(CO)_2IAg^+$, which decomposes to yield AgI and, in the presence of excess (η^5-C_5H_5)$Fe(CO)_2I$, the iodine-bridged species [(η^5-C_5H_5)$Fe(CO)_2]_2IBF_4$. This material then reacts with a second 0.5 equiv of $AgBF_4$ to yield (η^5-C_5H_5)$Fe(CO)_2BF_4$, in which tetrafluoroborate is coordinated.

Introduction

Substitution reactions involving the abstraction of halide ion from (η^5-C_5H_5)Fe(CO)(L)X, (L = CO, PR_3, $P(OR)_3$; X = Cl, Br, I) and replacement by a two-electron donor such as PR_3, olefin, alkyne, ketone, H_2O, THF, or CO have been extensively utilized over the past few years.[1-6] In particular, cationic olefin complexes of the type (η^5-C_5H_5)$Fe(CO)_2$(η^2-olefin)$^+$ have been quite thoroughly investigated because of their applications in stoichiometric organic synthesis.[7] In many of the reported syntheses of η^2-olefin complexes, a two-step preparation is utilized: the halide is initially quantitatively abstracted by silver ion, and the resulting solution is then treated with an excess of olefin. The "16-electron" intermediate produced in the halide abstraction step has frequently been postulated to be solvent coordinated, and for reactions done in THF,[6] H_2O,[4,8] or other donor solvents, this is undoubtedly true. For halide abstractions done in CH_2Cl_2, the intermediate has been proposed by several authors,[3,5,9,10] with a degree of speculation, to be the solvent-coordinated (η^5-C_5H_5)$Fe(CO)_2(CH_2Cl_2)^+$.

In our hands, the synthesis of η^2-olefin complexes in CH_2Cl_2 by the literature method[5] always yielded a fairly large amount of the known iodine-bridged species [(η^5-C_5H_5)$Fe(CO)_2]_2I^+$.[11] If excess Ag(I) were used, the amount of this iodine-bridged cationic species could be reduced. However, the resulting excess $AgBF_4$ in solution complicated the next step in which the olefin is added. In order to determine the role of [(η^5-C_5H_5)$Fe(CO)_2]_2I^+$ in the halide abstraction reaction of (η^5-C_5H_5)$Fe(CO)_2I$ with $AgBF_4$ and because of our general interest in weakly coordinated species[12] such as CpFe-$(CO)_2BF_4$, we have undertaken a thorough investigation of the mechanism of halide abstraction with Ag^+ from (η^5-C_5H_5)$Fe(CO)_2I$ in $CHCl_3$ and CH_2Cl_2 solvents. The results of this investigation are reported here.

Experimental Section

All operations were carried out under Ar or dried N_2. Solvents were distilled and purified by established techniques and degassed prior to use. $CDCl_3$ and $CHCl_3$ solvents were passed through a column of Kieselgel 60G silica gel (30 mL of solvent required a 10 cm × 2 cm plug of silica gel) and then degassed. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer, and ^1H NMR spectra were recorded on a Bruker WH 200-MHz spectrometer.

Reagents. (η^5-C_5H_5)$Fe(CO)_2I$, purchased from Strem Chemicals Inc., was used without further purification. $AgBF_4$, purchased from Ozark-Mahoning Co., was dried at room temperature and 0.005 torr for 1 week prior to use.

(η^5-C_5H_5)$Fe(CO)_2BF_4$. A foil-wrapped 100-mL flask with side arm was charged with 0.213 g (0.70 mmol) of $CpFe(CO)_2I$ and 0.146 g (0.74 mmol) of $AgBF_4$. The dry mixture was evacuated to 0.005 torr for 1 h to remove any water absorbed by $AgBF_4$ during transfer. Dichloromethane (20 mL) was then added and the mixture stirred in the dark for 45 min. An infrared spectrum obtained at this point featured broad bands at 2076 (s) with 2065 (sh), 2053 (w), and 2031 (s) with 2020 (sh) cm^{-1} due to $CpFe(CO)_2BF_4$ and [$CpFe(CO)_2]_2IBF_4$. The reaction mixture was cooled to −78 °C and stirred for 30 min. The solution was allowed to settle and was then filtered at −78 °C to remove $AgBF_4$ and [$CpFe(CO)_2]_2IBF_4$. The resulting burgundy-colored CH_2Cl_2 solution was pumped to dryness and dried in vacuo for 1 h. The product, formulated as $CpFe(CO)_2BF_4$, could be stored for short periods of time as a solid microcrystalline material; after a 3-h period only ca. 70% of the material would redissolve in CH_2Cl_2. The solid product is extremely hygroscopic and brief exposure to air caused conversion to the orange $CpFe(CO)_2(OH_2)BF_4$. Data for $CpFe(CO)_2BF_4$: IR (CH_2Cl_2) 2078 (s), 2032 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 5.26 (s); yield 0.154 g (83%). Anal. Calcd: C, 31.88; H, 1.91. Found: C, 30.71; H, 2.22.

[(η^5-C_5H_5)$Fe(CO)_2]_2IBF_4$. $CpFe(CO)_2I$ (0.681 g, 2.25 mmol) and $AgBF_4$ (0.327 g, 1.69 mmol) were placed in a 100-mL side-armed

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