Table II. Comparison of Metal-Oxygen Bond Lengths[a]

metal	M-O bond lengths, Å range	av	ref
Mn(II)	2.125-2.369	2.208	25
Ni(II)	2.048-2.081	2.065	26
Co(III)	1.936-1.953	1.944	27
Cr(III)	1.940-1.980	1.965	28

[a] The references given are examples from the recent literature. Many other reports exist for each of these metals, with the values shown being typical.

least in the case of nonenzymatic hydrolysis. Following the oxyphosphorane intermediate model of Ramirez et al.,[23,24] we can write a simple mechanism that can give rise to either breakdown of the metal-nucleotide complex to give free ATP or hydrolysis to ADP (Scheme IV).

While this mechanism is written for the β,γ-bidentate metal-nucleotide complex, it could apply equally well to the tridentate Co(III) and Cr(III) complexes. In the latter case, chelate ring strain due to the coordination of the α-phosphorus could make steps 1, 2, and 3 (the hydrolysis pathway) more likely relative to steps 4, 5, and 6 (decomposition to free ATP). This induced strain model also provides an explanation for the failure to observe substantial hydrolysis in the putative tridentate complexes of Mn(II) and Ni(II).[13] From model-building studies it is apparent that increasing the metal-oxygen bond lengths in the tridentate metal-nucleotide complex reduces the inherent chelate ring strain. As shown in Table II, Cr(III)-O and Co(III)-O bond lengths are substantially shorter than those of Mn(II) and Ni(II). Further support for this model is found in the fact that Ni(II), with a bond length to oxygen intermediate between that of Co(III) and Cr(III) on the one hand and Mn(II) on the other, shows a low level of hydrolysis in 1:1 Ni:ATP systems that is increased sixfold as the pH is increased from pH 7 to pH 10. Mn(II), on the other hand, with the longest metal-oxygen bond length in Table II, shows a very low level of hydrolysis in 1:1 complexes with ATP that is insensitive to pH between pH 5 and pH 9.5.

The notion of nucleophilic attack on phosphorus facilitated by ring strain has been put forth in a slightly different manner by Martin and Mariam[29] to explain the enhancement of hydrolysis of ATP by Cu(II) in weakly acidic and neutral solutions. In this case it is proposed that the metal ion may induce strain by chelating two oxygens bound to the γ-phosphorus. Several crystal structures in fact show a metal ion chelating two oxygens of a single phosphate to produce a (strained) four-membered ring.[30-32] The resulting reduction of the OPO bond angle facilitates the conversion from tetrahedral to trigonal-bipyramidal geometry in forming the pentacovalent phosphorus intermediate. The strain produced by the formation of the tridentate Co(III) and Cr(III) complexes examined here can produce much the same effect and can set the stage for release of free nucleotides and hydrolysis of bound ATP, both of which will relieve this strain.

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Registry No. $Co(NH_3)_4ATP$, 63915-26-4; $Co(NH_3)_3ATP$, 83214-28-2; $Cr(H_2O)_4ATP$, 58682-54-5; $Cr(H_2O)_3ATP$, 83214-29-3; ATP, 56-65-5; ADP, 58-64-0; AMP, 61-19-8; ATP, Cr salt, 69381-95-9; ATP, Co salt, 78738-35-9.

(23) Ramirez, F.; Hansen, B.; Desai, N. *J. Am. Chem. Soc.* **1962**, *84*, 4588.
(24) Ramirez, F.; Chaw, Y.; Maracek, J. *Phosphorus Sulfur* **1979**, *7*, 241.
(25) Lis, T. *Acta Crystallogr. Sect. B* **1977**, *B33*, 2964.
(26) Downie, T. C.; Harrison, W.; Raper, E. S. *Acta Crystallogr., Sect. B* **1971**, *B27*, 706.
(27) Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D.; Cleland, W. W. *Biochemistry* **1978**, *17*, 3274.
(28) Dugué, P. J.; Vovan, T.; Villers, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1291.
(29) Martin, R. B.; Mariam, Y. *Met. Ions Biol. Syst.* **1979**, *8*, 57.
(30) Shiba, J. K.; Bau, R. *Inorg. Chem.* **1978**, *17*, 3484.
(31) Aoki, K. *J. Chem. Soc., Chem. Commun.* **1978**, 748.
(32) Anderson, B.; Milburn, R.; Harrowfield, J.; Robertson, G.; Sargeson, A. *J. Am. Chem. Soc.* **1977**, *99*, 2652.

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Asymmetric Transformation of α-Amino Acids Promoted by Optically Active Cobalt(III) Complexes. 3.[1] Importance of Side-Chain Intramolecular Interligand Hydrogen Bonding to Stereoselectivity

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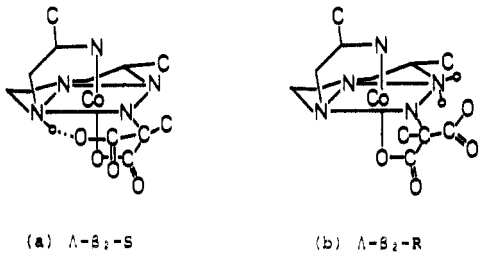
The Λ-β_2-$[Co(aa)(N_4)]^{n+}$ complexes, where aa refers to aspartate, asparaginate, and glutamate and N_4 to chiral derivatives of 3,7-diazanonane-1,9-diamine (2,3,2-tet), were prepared, and the hydroxide ion catalyzed epimerizations of these complexes were examined at pH 11.2 in water or pH 12.3 in water-methanol (1/1), to give rise to equilibrium mixtures of diastereomers (Λ-*R* and Λ-*S*). The equilibrated isomeric ratios for Λ-*S*/Λ-*R* ranged from 80/20 to 91/9 except for that of the glutamato complex (68/32). Higher stereoselectivity was observed in water-methanol than in water. Hydrogen bonding between the side-chain β-carboxylate or β-amide group and the secondary amine nitrogen explains the preference for the (*S*)-amino acidato isomer in the examined systems.

Introduction

Metal ions increase the reactivity of the α-proton of chelated α-amino acids.[2] It has been known that chelated α-amino acidates in chiral cobalt(III) complexes undergo hydroxide ion catalyzed epimerization,[1,3,4] which is considered as an example of a "first-order asymmetric transformation"[5] of racemic α-amino acids.[1,4] No remarkable stereoselectivity has been observed in the case of the C-substituted tetraamine complexes

(1) Part 2: Yamaguchi, M.; Yano, S.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 691.
(2) (a) Sato, M.; Okawa, K.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 937. (b) Williams, D. H.; Busch, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 4644.
(3) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133.
(4) Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1980**, *19*, 2010.
(5) Turner, E. E.; Harris, M. M. *Q. Rev., Chem. Soc.* **1947**, *1*, 299.

0020-1669/82/1321-4138$01.25/0



(a) Λ-β₂-S (b) Λ-β₂-R

Figure 1. Possible isomers of the Λ-β_2-[Co(α-methyl-α-aminomalonato)(2(*S*),9(*S*)-Me_2trien)]$^+$ complex.

with alaninate, valinate, or phenylalaninate ligands.[4] It was expected that a functional group on the side chain such as the carboxylate of aspartic acid or the amide of asparagine has a possibility to produce significant effects on stereoselectivity by interligand interactions.[6-8]

An aspartate or asparaginate as a bidentate ligand forms a five-membered glycinate ring and leaves its β-carboxylate or β-amide group uncoordinated.[6-8] Exhaustive studies by Shibata and co-workers on mixed-ligand (α-amino acidato)-cobalt(III) complexes containing (*S*)-aspartic acid or (*S*)-asparagine as a bidentate chelate revealed that the isomers having an ability of interligand hydrogen bonding between the uncoordinated β-carboxylate or β-amide group and the amino group of the other amino acidate moiety were highly stabilized.[6,7] The intramolecular interligand hydrogen bondings including the uncoordinated β-amide group and adjacent amino group were observed in an X-ray crystallographic study of Δ-*fac*-[Co((*S*)-asn)$_3$]·3H_2O.[9] In a study of (trimethylenediamine-*N*,*N*'-diacetato)((*S*)-aspartato)cobaltate-(III) ion similar high stereoselectivity attributed to the interligand hydrogen bonding was observed.[8]

Although both β-carboxyl and β-amide groups introduced in amino acidato complexes showed considerable effects on the stereoselectivity, as mentioned above, the γ-carboxylate group of glutamato complexes seemed to be less effective.[6,8] In the case of the bis(ethylenediamine)((*S*)-glutamato)cobalt(III) complex kinetically controlled[10] and thermodynamically controlled[11] stereoselectivities with regard to the absolute configuration (Λ and Δ isomers) had once been reported and explained on the basis of intramolecular hydrogen bonding involving an uncoordinated γ-carboxylate group. These results were reexamined carefully by subsequent workers, and the absence of such stereoselectivities was reported.[12]

The mechanism for racemization of an amino acid moiety in the [Co(amino acidato)$(en)_2$]$^{2+}$ ion in basic solution involving a planar enolate intermediate has been proposed from the fact that the rate of deuteration of the α-proton of the amino acidate is almost equal to that of racemization.[3,13] For [Co((*S*)-asp)$(en)_2$]$^+$ ion, however, it was found that the rate of deuteration is faster than that of racemization.[14] The preference for retention of configuration on deuteration of the α-proton in the above system is ascribed to the interligand hydrogen bonding between the β-carboxylate and the diamine nitrogen.[14]

Job and Bruice reported that a single isomer was obtained in the synthesis of an α-amino-α-methylmalonato complex with the optically active triethylenetetramine (trien) derivative,[15] the structure of which was determined to be Λ-β_2-*S* (Figure 1a) by an X-ray analysis study.[15b] Preference for the Λ-β_2-*S* isomer over the Λ-β_2-*R* was explained by the intramolecular interligand hydrogen bonding between the uncoordinated carboxylate and the secondary amino nitrogen, as was observed in the crystal. Such stereoselectivity was also observed in a variety of α-amino-α-alkylmalonato complexes with various optically active tetraamine derivatives.[16a] Recently, an X-ray analysis study revealed that the α-amino-α-methylmalonato complex with a 2,3,2-tet derivative was also a Λ-β_2-*S* isomer having interligand hydrogen bonding.[16b] Though such a stereoselectivity observed in the α-amino-α-alkylmalonato complexes is considered to be kinetically controlled, the Λ-β_2-*S* isomers involving interligand hydrogen bonding are assumed to be thermodynamically more stable than the Λ-β_2-*R* isomer.

In a previous paper,[4] we have examined the OH^--catalyzed epimerization of chelated alaninate, valinate, or phenylalaninate in the Λ-β_2-[Co(amino acidato)(tetraamine)]$^{2+}$ complexes. This paper reports the results on a study of the asymmetric transformation of aspartic acid, asparagine, and glutamic acid chelated to chiral cobalt(III) ion to gain insight into the influence of the side-chain carboxylate or amide group of the amino acid upon stereoselectivity.

Experimental Section

All materials used were of reagent grade. The ligands 2(*S*),10-(*S*)-4,8-diazaundecane-2,10-diamine (=2(*S*),10(*S*)-Me_2-2,3,2-tet)[17] and 2(*S*),8(*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (=3(*S*),9-(*S*)-Me_2-2,3,2-tet)[4] were prepared by methods described previously. The *trans*-dichlorocobalt(II) complexes with the tetraamine were prepared by a method described previously.[4]

Λ-β_2-[Co(*R*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4·4H_2O (1_R) and **Λ-β_2-[Co(*S*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4·H_2O (1_S)** were prepared from *trans*-[$CoCl_2$(2(*S*),10(*S*)-Me_2-2,3,2-tet)]ClO_4 and (*R*)- or (*S*)-aspartic acid by the method used for the preparation of Λ-β_2-[Co(ala)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$·H_2O.[4] The resulting solution was diluted with water and poured on a column of SP-Sephadex C25 cation-exchange resin (4.0 × 50 cm) in the sodium form. Four bands were developed on the column during the elution with 0.04 M $NaClO_4$, which moved at a rate of monopositive charged species. The ^1H NMR spectra of each band showed that the first band did not contain the aspartate moiety and the second, third, and fourth bands were aspartato complexes. The minor third band and the major fourth band were assigned to the Λ-β_1- and Λ-β_2-aspartato complexes on the basis of their circular dichroism spectra. The second band, which was a very small amount, was assigned to the Δ-aspartato complex. The fourth band was concentrated on a rotary evaporator below 50 °C to about 50 mL. After the solution stood several hours at room temperature, the orange-red crystals were collected, washed with methanol and ether, and air-dried; yield 0.61 g (49%) for 1_R and 0.53 g (43%) for 1_S. Anal. Calcd for [$Co(C_4H_5NO_4)(C_9H_{24}N_4)$]-$ClO_4$·4$H_2O$ (1_R): C, 28.40; H, 6.78; N, 12.74. Found: C, 28.57; H, 6.63; N, 12.80. Calcd for [$Co(C_4H_5NO_4)(C_9H_{24}N_4)$]$ClO_4$·$H_2O$ (1_S): C, 31.49; H, 6.30; N, 14.13. Found: C, 31.13; H, 6.39; N, 13.91.

Λ-β_2-[Co(*R*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$·3H_2O (2_R) and **Λ-β_2-[Co(*S*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2$·2H_2O (2_S)**

(6) (a) Kawasaki, K.; Yoshii, J.; Shibata, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3819. (b) Matsuda, T.; Okumoto, T.; Shibata, M. *Ibid.* **1972**, *45*, 802. (c) Matsuda, T.; Shibata, M. *Ibid.* **1973**, *46*, 3104. (d) Takeuchi, M.; Shibata, M. *Ibid.* **1974**, *47*, 2797.
(7) (a) Kojima, Y.; Shibata, M. *Inorg. Chem.* **1971**, *10*, 2382. (b) Kojima, Y.; Shibata, M. *Ibid.* **1973**, *12*, 1009. (c) Kojima, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2033.
(8) Okabayashi, M.; Igi, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 753.
(9) Sekizaki, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 403.
(10) (a) Dunlop, J. H.; Gillard, R. D.; Payne, N. C. *J. Chem. Soc. A* **1967**, 1469. (b) Gillard, R. D.; Payne, N. C.; Robertson, G. B. *Ibid.* **1970**, 2579. (c) Gillard, R. D.; Maskill, R.; Pasini, A. *Ibid.* **1971**, 2268.
(11) Legg, J. I.; Steele, J. *Inorg. Chem.* **1971**, *10*, 2177.
(12) Buckingham, D. A.; Dekkers, J.; Sargeson, A. M.; Marzilli, L. G. *Inorg. Chem.* **1973**, *12*, 1207.
(13) Sudmeier, J. L.; Occupati, G. *Inorg. Chem.* **1968**, *7*, 2524.
(14) (a) Keyes, W. E.; Legg, J. I. *J. Am. Chem. Soc.* **1973**, *95*, 3431. (b) Keyes, W. E.; Caputo, R. E.; Willett, R. D.; Legg, J. I. *Ibid.* **1976**, *98*, 6939.
(15) (a) Job, R. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 809. (b) Glusker, J. P.; Carrell, H. L.; Job, R. C.; Bruice, T. C. *Ibid.* **1974**, *96*, 5741.
(16) (a) Yamaguchi, M.; Yamamatsu, S.; Oikawa, H.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1981**, *20*, 3179. (b) Yashiro, M.; Toriumi, K.; Ito, T.; Yano, S.; Yoshikawa, S., manuscript in preparation.
(17) Goto, M.; Makino, T.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1879.

Table I. 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_R	Λ-β_2-[Co(*R*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·$4H_2O$	496 (138) 353 (139)	526 (1.61), 470 (−0.43) 374 (0.11), 337 (0.19)
1_S	Λ-β_2-[Co(*S*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·H_2O	492 (143) 352 (153)	520 (1.83), 455 (−0.60) 357 (−0.09)
2_R	Λ-β_2-[Co(*R*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·$3H_2O$	494 (149) 352 (150)	525 (1.74), 467 (−0.45) 376 (0.07), 336 (0.15)
2_S	Λ-β_2-[Co(*S*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·$2H_2O$	492 (137) 352 (147)	520 (2.06), 456 (−0.78) 356 (−0.08), 328 (0.02)
3_R	Λ-β_2-[Co(*R*-glu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·$3H_2O$	496 (137) 354 (144)	525 (1.58), 468 (−0.31) 375 (0.10), 339 (0.13)
3_S	Λ-β_2-[Co(*S*-glu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]·$3H_2O$	494 (142) 353 (153)	515 (1.56), 451 (−0.38) 354 (−0.21)
4_R	Λ-β_2-[Co(*R*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]·$^3/_2H_2O$	495 (135) 353 (134)	528 (1.37), 471 (−0.52) 375 (0.12), 337 (0.21)
4_S	Λ-β_2-[Co(*S*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]·H_2O	491 (131) 352 (140)	520 (1.94), 458 (−0.55) 356 (−0.16)
5_R	Λ-β_2-[Co(*R*-asn)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]·$^5/_2H_2O$	493 (130) 352 (139)	523 (1.43), 463 (−0.46) 386 (0.03), 360 (−0.22) 333 (0.07)
5_S	Λ-β_2-[Co(*S*-asn)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]·$3H_2O$	492 (131) 352 (139)	520 (1.60), 460 (−0.47) 361 (−0.08), 327 (0.02)

were prepared from (*R*)- or (*S*)-asparagine by the above procedure except that the bands on the column that contained asparaginato complexes moved at a rate of dipositive charged species. Orange-red crystals were obtained; yield 0.30 g (24%) for $\mathbf{2}_R$ and $\mathbf{2}_S$. Anal. Calcd for $[Co(C_4H_7N_2O_3)(C_9H_{24}N_4)](ClO_4)_2 \cdot 3H_2O$ ($\mathbf{2}_R$): C, 24.73; H, 5.91; N, 13.31. Found: C, 24.66; H, 5.43; N, 12.97. Calcd for $[Co(C_4H_7N_2O_3)(C_9H_{24}N_4)](ClO_4)_2 \cdot 2H_2O$ ($\mathbf{2}_S$): C, 25.46; H, 5.75; N, 13.70. Found: C, 25.59; H, 5.74; N, 13.64.

Λ-β_2-[Co(*R*- or *S*-glu)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$ClO_4 \cdot 3H_2O$ ($\mathbf{3}_R$ or $\mathbf{3}_S$) was prepared from (*R*)- or (*S*)-glutamic acid in the same manner as **1** except that the Δ isomer was not found. Pinkish orange powder was obtained; yield 0.33 g (27%) for $\mathbf{3}_R$ and $\mathbf{3}_S$. Anal. Calcd for $[Co(C_5H_7NO_4)(C_9H_{24}N_4)]ClO_4 \cdot 3H_2O$: C, 30.80; H, 6.83; N, 12.83. Found: C, 30.87; H, 6.76; N, 12.85 ($\mathbf{3}_R$). Found: C, 30.72; H, 6.82; N, 12.91 ($\mathbf{3}_S$).

Λ-β_2-[Co(*R*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$ClO_4 \cdot {}^3/_2H_2O$ ($\mathbf{4}_R$) and **Λ-β_2-[Co(*S*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$ClO_4 \cdot H_2O$** ($\mathbf{4}_S$) were prepared from *trans*-$[CoCl_2(3(S),9(S)\text{-}Me_2\text{-}2,3,2\text{-}tet)]ClO_4$ and (*R*)- or (*S*)-aspartic acid in the same manner as **1** except that the length of the column was not sufficient for the complete separation in the case of the (*R*)-aspartato complex. After the eluate was recycled twice by a rotary pump, the Λ-β_2-(*R*)-aspartato complex was separated from the Λ-β_1 isomer. Orange-red crystals were obtained; yield 0.19 g (19%) for $\mathbf{4}_R$ and 0.24 g (24%) for $\mathbf{4}_S$. Anal. Calcd for $[Co(C_4H_5NO_4)(C_9H_{24}N_4)]ClO_4 \cdot {}^3/_2H_2O$ ($\mathbf{4}_R$): C, 30.93; H, 6.39; N, 13.87. Found: C, 31.04; H, 6.43; N, 13.80. Calcd for $[Co(C_4H_5NO_4)(C_9H_{24}N_4)]ClO_4 \cdot H_2O$ ($\mathbf{4}_S$): C, 31.49; H, 6.30; N, 14.13. Found: C, 31.70; H, 6.39; N, 14.10.

Λ-β_2-[Co(*R*-asn)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot {}^5/_2H_2O$ ($\mathbf{5}_R$) and **Δ-β_2-[Co(*S*-asn)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$(ClO_4)_2 \cdot 3H_2O$** ($\mathbf{5}_S$) were prepared in the same manner as **2**. Orange-red crystals were obtained; yield 0.16 g (13%) for $\mathbf{5}_R$ and 0.11 g (9%) for $\mathbf{5}_S$. Anal. Calcd for $[Co(C_4H_7N_2O_3)(C_9H_{24}N_4)](ClO_4)_2 \cdot {}^5/_2H_2O$ ($\mathbf{5}_R$): C, 25.09; H, 5.83; N, 13.50. Found: C, 24.88; H, 6.12; N, 13.97. Calcd for $[Co(C_4H_7N_2O_3)(C_9H_{24}N_4)](ClO_4)_2 \cdot 3H_2O$ ($\mathbf{5}_S$): C, 24.73; H, 5.91; N, 13.31. Found: C, 24.77; H, 5.81; N, 13.47.

Measurements. The pH was measured by using a Hitachi-Horiba F-7_{DE} digital pH meter. Visible absorption spectra were measured with a Hitachi 340 recording spectrophotometer. Circular dichroism curves were obtained with a JASCO J20 or JASCO J-500A recording spectropolarimeter. Proton magnetic resonance (^1H NMR) spectra (90 MHz) were obtained on a Hitachi R-40 spectrometer using sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) as an internal standard reference.

The perchlorate salts (50–70 mg) were 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.

Deuteration. Deuterations were carried out in D_2O with the pD adjusted to 10.1 by addition of a small quantity of Na_2CO_3. The solutions were allowed to stand at 30 °C until the ^1H NMR signal (a triplet) of the methine proton of the coordinated amino acidate was no longer detectable (ca. 30 days).

Measurements of Isomer Ratios for Epimerization Reactions. Weighed samples (100 mg) of Λ-β_2-[Co(*R*- or *S*-amino acidato)(tetraamine)]$^{n+}$ were dissolved in an H_2O solution (100 mL) of 0.02 M Na_2CO_3 buffer (pH 11.2) or in a 1/1 MeOH–H_2O solution (100 mL) of 0.02 M Na_2CO_3–0.02 M $NaHCO_3$ buffer (pH 12.3), and the solution was warmed at 37 °C for 20 h. At this stage, the CD curve of the solution for the (*R*)-amino acidato complex and that for the (*S*)-amino acidato complex became identical within the experimental error. After neutralization by 1 M HCl, the solution was reduced to near dryness with a rotary evaporator. After most of the NaCl was removed by addition of ethanol and filtration, the resulting solution was poured onto a column of SP-Sephadex C25 cation-exchange resin (2.5 × 50 cm) in the sodium form. The complexes were eluted with 0.01 M Na_2HPO_4–0.01 M NaH_2PO_4 for the asparato or glutamato complexes or with 0.05 M Na_2HPO_4–0.05 M NaH_2PO_4 for the asparaginato complexes. Small amounts of decomposed products were observed. The amino acidato complexes were clearly separated into two monopositive (asparato or glutamato complexes) or dipositive (asparaginato complexes) bands. The first major (bottom) and the second minor (top) bands were assigned to the (*S*)-amino acidato and (*R*)-amino acidato complexes, respectively. After the separation was completed, the bands were washed with 500 mL of water and eluted with 0.02 or 0.07 M NaCl. The addition of a small amount of $NaHCO_3$ was required for the elution of the aspartato or glutamato complexes. The eluates were collected and evaporated to near dryness, and excess NaCl was filtered off. After most of the NaCl was removed by addition of ethanol and filtration, the concentrations of each band were spectrophotometrically determined.[4]

The recoveries of the amino acidato complexes were about 97–98, 75–88, and 86–99% for the asparato, asparaginato, and glutamato complexes, respectively. Isomer ratios were reproducible to better than ±1%.

Results and Discussion

The β_2-[Co(amino acidato)(tetraamine)]$^{n+}$ complexes were prepared from *trans*-$[CoCl_2(tetraamine)]^+$ complexes by modification of the method described previously.[1,4] The absolute configurations of these complexes were assigned to be Λ on the basis of their circular dichroism spectra.[4] The electronic and circular dichroism spectral data are tabulated in Table I. These spectra were similar to those of the corresponding Λ-β_2-$[Co(aa)(tetraamine)]^{2+}$ complexes (aa = alaninate, valinate, or phenylalaninate),[4] which indicated the formation of the N–O-bound chelate ring.

As shown in Figure 2 and Table II, the ^1H NMR spectra of the aspartato complexes exhibit a triplet at 3.6–3.8 ppm and a doublet at 2.7–2.8 ppm corresponding to the ABX

Table II. ^{1}H NMR Spectral Data and Fractional Populations of Rotational Isomers of Aspartate and Asparaginate in the Tetraamine Complexes

no.	complex	chem shifts[a] CH	chem shifts[a] CH_2	$\lvert J_{AX} + J_{BX}\rvert$[b]	$P_I + P_{II}$	P_{III}
1_R	Λ-β$_2$-[Co(*R*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$	3.81	2.71	7.5	0.21	0.79
1_S	Λ-β$_2$-[Co(*S*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$	3.63	2.79	6.9	0.16	0.84
2_R	Λ-β$_2$-[Co(*R*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$	3.97	2.95	9.8	0.42	0.58
2_S	Λ-β$_2$-[Co(*S*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^{2+}$	3.73	2.98	7.5	0.21	0.79
4_R	Λ-β$_2$-[Co(*R*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^+$	3.83	2.71	7.5	0.21	0.79
4_S	Λ-β$_2$-[Co(*S*-asp)(3(*S*),9(*S*)-Me_2-2,3,2-tet)]$^+$	3.57	2.76	7.5	0.21	0.79

[a] ppm from DSS. [b] The sum of the coupling constants (Hz). See text.

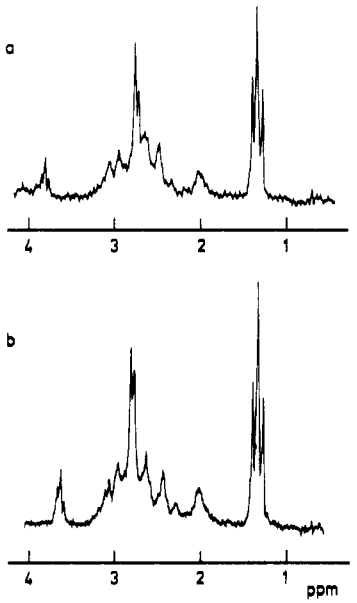


Figure 2. ^{1}H NMR spectra of (a) the Λ-β$_2$-[Co(*R*-asp)(2(*S*),10-(*S*)-Me_2-2,3,2-tet)]$^+$ ion and (b) the Λ-β$_2$-[Co(*S*-asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion.

portion of the aspartate moiety, the methine proton (X of ABX) and the methylene protons (AB of ABX), respectively. The ^{1}H NMR spectra of the asparaginato complexes (Figure 3) exhibit a triplet at 3.7–4.0 ppm and a doublet at 3.0 ppm. The chemical shifts of these signals are in good accordance with data in the literature.[6b-d,7,11,18] As Takenaka and Shibata reported,[18] the signal of the methine proton of the asparaginate resonates 0.10–0.16 ppm downfield from that of the aspartate having the same absolute configuration. Furthermore, the methine proton of the (*R*)-amino acidato complex resonates 0.1–0.5 ppm downfield from that of the (*S*)-amino acidato complex in the Λ-β$_2$-[Co(amino acidato)(tetraamine)]$^{n+}$ system, as was observed in the alaninato, valinto, and phenylalaninato complexes.[4]

In the case of the aspartato and glutamato complexes, there was the possibility of a six- or seven-membered chelate ring involving the β- or γ-carboxylate group coordinated to a metal ion. The fact that the methine proton of the aspartate moiety was subject to the deuterium exchange in basic solution confirmed the formation of a five-membered glycinate ring.[2b,3,11]

From the signal of an ABX system we could obtain the sum of the vicinal coupling constants, $|J_{AX} + J_{BX}|$ (Table II).[19] Since the vicinal coupling constant depends on the dihedral angle,[20] the $|J_{AX} + J_{BX}|$ value gives information about the orientation of the side-chain functional group of aspartate or asparaginate in the complexes. Shibata and co-workers reported[6c,d,17] that the $|J_{AX} + J_{BX}|$ value in (aspartato)- or (asparaginato)cobalt(III) complexes is 7.0–8.0 Hz when an adjacent coordination site is occupied by an NH_2 group, while the $|J_{AX} + J_{BX}|$ value is 10.0–14.0 Hz when an adjacent coordination site is occupied by an O atom. In the former case the side-chain carboxylate or amide group was assumed to be directed toward the adjacent NH_2 group, making an intramolecular hydrogen bond.

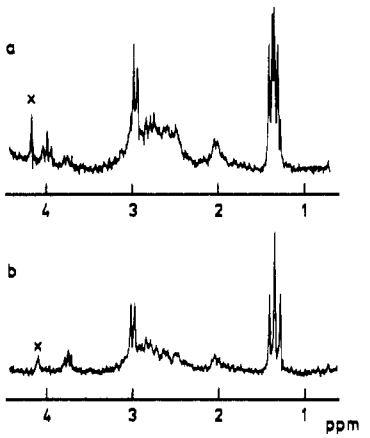


Figure 3. ^{1}H NMR spectra of (a) the Λ-β$_2$-[Co(*R*-asn)(2(*S*),10-(*S*)-Me_2-2,3,2-tet)]$^+$ ion and (b) the Λ-β$_2$-[Co(*S*-asn)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion.

It is assumed that the J_{AX} and J_{BX} values are the statistical averages of the contribution from the three rotational isomers I, II, and III of staggered forms as shown in Figure 4

$$J_{AX} = P_I J_g + P_{II} J_t + P_{III} J_g \quad (1)$$

$$J_{BX} = P_I J_t + P_{II} J_g + P_{III} J_g \quad (2)$$

$$P_I + P_{II} + P_{III} = 1 \quad (3)$$

where P_I, P_{II}, and P_{III} are the fractional populations and J_t and J_g are the coupling constants between trans and gauche proton pairs, respectively. The isomer III is assumed to make an interligand hydrogen bond between the side-chain functional group and the secondary amino nitrogen atom of the tetraamine, judging from the molecular model examination (Figure 4). Because the coupling constants between the α- and β-protons both in free alanine and in [Co(ala)(tetraamine)]$^{2+}$ have the same value of 7.2 Hz at pD 6.0,[21] it can be assumed that the J_t (=13.56 Hz) and J_g (=2.60 Hz) values[22] do not change when the amino acid coordinates to the cobalt(III) ion. This assumption has also been shown to hold in Zn(II)[23] and Pd(II) complexes.[24] The P_I, P_{II}, and P_{III} values can be calculated according to eq 4–6, which follow from eq 1–3.[22,24]

(18) Takenaka, H.; Shibata, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2133.
(19) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance"; Pergamon Press: London, 1965; Vol. 1.
(20) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
(21) Yamaguchi, M.; Saburi, M.; Yoshikawa, S., unpublished results.
(22) Pachler, K. G. R. *Spectrochim. Acta* **1964**, *20*, 581.
(23) Ishizuka, H.; Yamamoto, T.; Arata, Y.; Fujiwara, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 468.

$$P_I = (J_{BX} - J_g)/(J_t - J_g) \quad (4)$$

$$P_{II} = (J_{AX} - J_g)/(J_t - J_g) \quad (5)$$

$$P_{III} = [(J_t + J_g) - (J_{AX} + J_{BX})]/(J_t - J_g) \quad (6)$$

Since J_{AX} and J_{BX} for α-amino acids are positive,[25] eq 6 gives P_{III}, and then eq 3 gives $P_I + P_{II}$ (Table II). The P_{III} values are significantly high. It suggests that the intramolecular interligand hydrogen bonding between the uncoordinated carboxylate or amide group and the amine nitrogen atom of the tetraamine exists in solution.

As described in the Introduction, the hydroxide ion catalyzed epimerization of the chelated α-amino acid occurs in basic solution without change in the configuration about the Co(III) center and gives rise to a mixture of diastereomers after the equilibrium has been established (eq 7). The epimerization

$$\Lambda\text{-}\beta_2\text{-}[Co(R\text{-aa})(N_4)]^{n+} \rightleftharpoons \Lambda\text{-}\beta_2\text{-}[Co(S\text{-aa})(N_4)]^{n+} \quad (7)$$

in Λ-β_2-[Co(*R*- or *S*-aa)(N_4)]$^{n+}$ complexes is considered as an example of a "first-order asymmetric transformation"[5] of a racemic α-amino acid.[1,4] The diastereomeric ratios (Λ-*S*/Λ-*R*) of the asparato, asparaginato, and glutamato complexes at equilibrium are summarized in Table III.

The (*S*)-amino acidato isomer was the predominant isomer over (*R*)-amino acidato in each complex. The aspartato and asparaginato complexes showed considerable stereoselectivities in the epimerization reaction: Λ-*S*/Λ-*R* ranged from 80/20 to 91/9 ($|\Delta G|$ = 0.9–1.4 kcal/mol). On the other hand, the glutamato complex showed no significant stereoselectivity (Λ-*S*/Λ-*R* = 68/32, $|\Delta G|$ = 0.5 kcal/mol). The selectivity in the equilibrium decreased in the order asp > asn >> glu ≃ ala ≃ phe ≃ leu.[26] The improved chiral selectivity suggests that the uncoordinated β-carboxylate or β-amide group of the side chain plays a significant role in the selectivity. The contribution from the side-chain functional group is estimated to be 0.6–1.1 kcal/mol for the carboxylate and 0.4–0.9 kcal/mol for the amide group, on the basis of the selectivity of the corresponding alaninato complexes. A possibility that the bulkiness of the side chain causes steric repulsions and influences the selectivity can be excluded, because the leucinato complex, the side chain of which is as bulky as the β-carboxylate or β-amide, showed no significant stereoselectivity. Furthermore, the glutamato complex having a bulkier substituent, γ-carboxylate, showed less significant stereoselectivity, which supported the above assumption. In a 1/1 MeOH–H_2O solution the stereoselectivity increased. The fact that less polar solvent enhances the selectivity suggests that there is an effect of solvation on stereoselectivity.[4]

As Figure 5 shows, the presence of the intramolecular interligand hydrogen bonding is assumed between the side chain β-carboxylate or β-amide group and the amino group of the tetraamine. Since the ^{1}H NMR spectrum showed no significant change with respect to the ABX pattern even in basic solution (pD 10.1), the orientation of the side chain suggested by the analysis of the ^{1}H NMR spectra described above seems not to change in the reaction condition. Such types of interligand interaction were assumed to exist in the various (amino acidato)cobalt(III) complexes with side-chain carboxylate or amide groups as described earlier.[6-9,14,15,17,27] In ternary (amino acidato)copper(II)[28] or -palladium(II)[24] complexes the importance of the intramolecular interligand hydrogen bonding between the side chains was suggested.

Table III. Isomeric Ratios (Λ-*S*/Λ-*R*) of Λ-β_2-[Co(amino acidato)(N_4)]$^{n+}$ Complexes[a]

amino acid	N_4: $(en)_2$	N_4: 2(*S*),10(*S*)-Me_2-2,3,2-tet	N_4: 3(*S*),9(*S*)-Me_2-2,3,2-tet
asp	60/40[b]	84/16	88/12 (91/9)[g]
asn		80/20	87/13
glu	50/50[c]	68/32	
ala	50/50[d]	66/34[e]	61/39 (67/33)[g]
val	37/63[d]	47/53[e]	30/70[e]
phe		61/39[e]	64/36[e]
leu		65/35[f]	

[a] At 37 °C and pH 11.2 unless stated otherwise. [b] Reference 11; formation ratio (Λ-*S*/Δ-*S*) in the presence of activated carbon. [c] Reference 12; at 25 °C and 0.05 M NaOH. [d] Reference 3; at 34.3 °C and 0.02 M NaOH. [e] Reference 4; at 40 °C and pH 11.2. [f] Reference 16a; at 40 °C and pH 11.2. [g] In 1/1 MeOH-H_2O, at 37 °C in 0.02 M $NaHCO_3$–0.02 M Na_2CO_3 (1/1) buffer.

In the case of the Λ-β_2-(*R*)-aspartato complex, the β-carboxylate group is directed at the middle of the two hydrogen atoms of the primary amino group of the tetraamine. On the other hand, in the case of the Λ-β_2-(*S*)-aspartato complex, the β-carboxylate group can take the direction toward the hydrogen atom of the angular secondary amino group of the tetraamine. It is expected that such interligand hydrogen bonding in the (*S*)-aspartato complex is stronger than that in the (*R*)-aspartato complex.[7a] Furthermore, in the aspartato complexes having β-carboxylate side chains, the electrostatic interaction may enhance such a tendency, comparing to the case for the asparaginato complexes.

Since appropriate stereochemistry is necessary for interligand hydrogen bonding, it is supposed from a molecular model that the γ-carboxylate side chain is too long to form an effective interligand hydrogen bond or the hydrogen bonding in the (*R*)-glutamato complex is as strong as that in the (*S*)-glutamato complex. Therefore, it can be concluded that the β-carbonyl group in the side chain is essential for higher stereoselectivity.

No considerable stereoselectivity is shown in the [Co(asp)$(en)_2$]$^+$ system but in the Λ-β_2-[Co(asp or asn)(tetraamine)]$^{n+}$ system. The structure of the tetraamine is considered to be an important factor of the selectivity. Kojima and Shibata reported that the formation ratio (Λ/Δ) at equilibrium in the presence of activated charcoal was 12/88 in the [Co(gly)(*R*-pn)$_2$]$^{2+}$ ion[29] and 50/50 in the [Co(*S*-asp)(*R*-pn)$_2$]$^+$ ion.[7a] The selectivity observed in the glycinato complex is attributed to the difference in stability between the $(lel)_2$ form and $(ob)_2$ form (the $(ob)_2$ form is less stable than the $(lel)_2$ form[30]), while in the aspartato complexes the Λ-$(ob)_2$ isomer is assumed to be stabilized by interligand hydrogen bonding. The diastereomeric ratio of Λ-$\lambda\lambda$- and Δ-$\lambda\lambda$-[Co(*S*-asp)(*R*-pn)$_2$]$^+$ ions, however, cannot be compared with that of asymmetric transformation, since the (*R*)-propylenediamine (=*R*-pn) is fixed to the λ gauche conformation. (Asymmetric transformation should be examined for the Λ-$\lambda\lambda$-[Co(*S*- and *R*-asp)(*R*-pn)$_2$]$^+$ system or the Δ-$\lambda\lambda$-[Co(*S*- and *R*-asp)(*R*-pn)$_2$]$^+$ system.) Since the ethylenediamine chelate ring can take both δ and λ conformations, the diastereomeric ratio of Λ- and Δ-[Co(*S*-asp)$(en)_2$]$^+$ is considered to be equal to that of Λ-[Co(*S*- and *R*-asp)$(en)_2$]$^+$ ions. It is assumed that the lower stereoselectivity in the [Co(asp)$(en)_2$]$^+$ system is due to the stabilization of the conformationally less stable $(ob)_2$ isomer by the hydrogen bonding between the β-carboxylate group and the amino group of the ethylenediamine. In the chiral 2,3,2-tet derivatives employed in this work, both of the

(24) Yamauchi, O.; Odani, A. *J. Am. Chem. Soc.* **1981**, *103*, 391.
(25) Fujiwara, S.; Arata, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 344.
(26) Since the Λ-*S*/Λ-*R* value of the valinato complexes was contrary to the others, the valinato complex was the exceptional case.
(27) (a) Jursik, F. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3811. (b) Jursik, F.; Archer, R. D.; Hajek, B. *Ibid.* **1978**, *43*, 819.
(28) Yamauchi, O.; Sakurai, T.; Nakahara, A. *J. Am. Chem. Soc.* **1979**, *101*, 4164 and references cited therein.
(29) Kojima, Y.; Shibata, M. *Inorg. Chem.* **1970**, *9*, 238.
(30) Corey, J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2620.

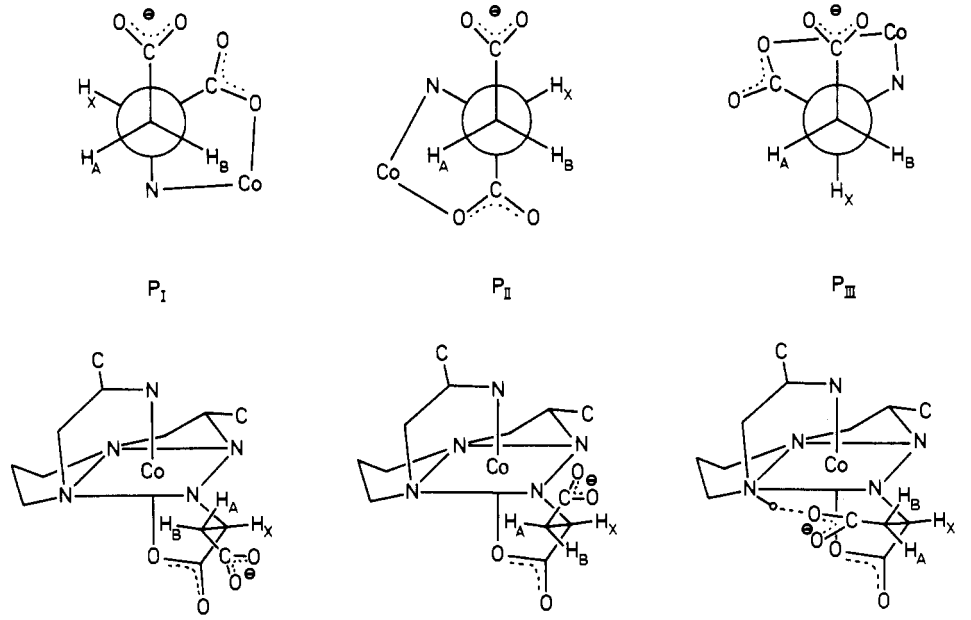


Figure 4. Views of the three rotational isomers of the Λ-β_2-$[Co(asp)(N_4)]^+$ ion through the bond (top) and in perspective (bottom).

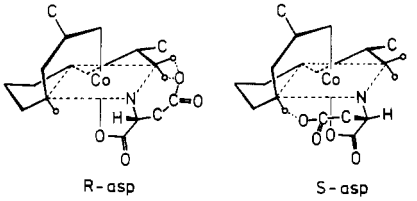


Figure 5. Possible structures of the Λ-β_2-[Co(asp)(2(*S*),10(*S*)-Me_2-2,3,2-tet)]$^+$ ion.

two outer five-membered chelate rings are fixed to the δ-(lel) conformation, and higher stereoselectivities were observed in these systems. Therefore, it is an important factor for the high stereoselectivity in the Λ-[Co(asp or asn)$(N_4)]^{n+}$ systems that the conformations of the two outer five-membered chelate rings are fixed rigidly to the $\delta\delta$-$(lel)_2$ conformation.

Thus, from the viewpoint of asymmetric transformation, the β-carbonyl carbon in the side chain of the amino acidate results in a striking improvement in the chiral selectivity of the α-amino acidate.[4] These results suggest the importance of intramolecular interligand hydrogen bonding. In previous papers, we have obtained considerable selectivities in some complexes, which were considered to be due mostly to interligand nonbonded repulsions.[1,4] Such steric repulsions, however, cause not only selectivity but also destabilization of the system. In fact, the recovery of the alaninato complex, which showed high selectivity, was about 50%. On the contrary, the recovery of aspartato and asparaginato complexes was satisfactory, because an attractive force such as hydrogen bonding causes stabilization. The high stereoselectivity brought about through the interligand hydrogen bonding seems to be observed only in the complex having the appropriate structure with respect to the (N_4) part. Furthermore, the fact that only the aspartato and asparaginato complexes showed high chiral selectivities is thought to be a kind of substrate specificity, which is of interest in connection with enzyme systems.

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X-ray Crystallographic Characterization of an Iron Porphyrin with a Vinylidene Carbene Inserted into an Iron–Nitrogen Bond

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The complex TpTP[$(p$-$ClC_6H_4)_2C$=C]FeCl·$2CH_2Cl_2$, where TpTP is the dianion of *meso*-tetra-*p*-tolylporphyrin, has been characterized by single-crystal X-ray structural analysis. The compound crystallizes in the space group $P2_1/n$ with cell dimensions (140 K) of a = 19.653 (5) Å, b = 12.418 (2) Å, c = 23.473 (5) Å, and β = 103.10 (2)°. The structure was refined by blocked-cascade least-squares methods to a final R of 0.061 for the 6106 reflections which had $I > 3\sigma(I)$. The vinylidene carbene ligand has inserted into an iron–nitrogen bond. The iron atom is five-coordinate with approximate trigonal-bipyramidal geometry. Its donor set consists of three of the four porphyrin nitrogen atoms, the carbene atom, and the chlorine atom.

Introduction

The reactions of potential carbene sources with metalloporphyrins have led to the synthesis of a variety of substances in which a R_2C fragment has been added to various portions of metalloporphyrin. A number of iron porphyrins with axial carbene ligands, **1**, are known[1-3] and one of these, (TPP)Fe-$(CCl_2)H_2O$, (TPP is the dianion of *meso*-tetraphenyl-

(1) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781.

0020-1669/82/1321-4143$01.25/0