ASYMMETRIC TRANSFORMATION OF α-AMINO ACIDS PROMOTED BY OPTICALLY ACTIVE METAL COMPLEXES

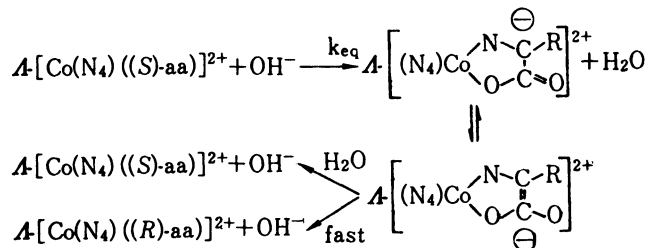Sadao Yoshikawa, Masahiko Saburi, and Motoo Yamaguchi

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Abstract - The hydroxide ion-catalyzed epimerization of the chelated
α-amino acidates in Λ-(or Δ-)$[Co(N_4)(S\text{- or }R\text{-aa})]^{2+}$ ((N_4) represents
four amine nitrogen atoms of bis(diamine) or tetramine ligand and aa
shows the α-amino acidate) was considered as an example of "first order
asymmetric transformation" of α-amino acids promoted by chiral
cobalt (III) complexes.
First, the details on the selection of appropriate linear tetramine
ligands are described with a view to obtain the $[Co(N_4)(aa)]^{2+}$ having
a fixed configuration around the cobalt(III) ion. A few chiral
derivatives of 2,3,2-tet(1,9-diamino-3,7-diazaundecane) were employed
successfully.
The epimerization of the alaninato, valinato, and N-methyl-alaninato
moieties in Λ-$[Co(tetramine)(S\text{- or }R\text{-aa})]^{2+}$ was examined at pH 10-12
mainly in carbonate buffer. In the most favorable case where (N_4)=
SS-pyht, α-alaninate showed the isomer ratio S/R=19/81, N-methyl-
alaninate gave an improved ratio of S/R=85/15, using a chiral trien
derivative as the (N_4) part.

Sargeson and coworkers showed (1) that the OH^--catalyzed racemization of the
α-amino acidate moiety in cobalt complexes, Λ -$[Co(en)_2(R\text{- or }S\text{-aa})]^{2+}$ (and also in
the Δ isomer also occurs in basic aqueous solution (pH∼12), and gives rise to a mixture
of diastereomers (Λ-$[Co(en)_2(R\text{-aa})]^{2+}$ and Λ-$[Co(en)_2(S\text{-aa})]^{2+}$) after the equilibrium
has been established (aa represents the α-amino acidate coordinated as a chelating
ligand, and R and S refer to the absolute configuration of α-carbon atom of amino acids).
The arrangement of three chelate rings around the cobalt(III) ion (represented by Λ or Δ)
does not change under the above reaction condition. The above reaction is applicable
to the amino acidato complexes having the general formula $[Co(N_4)(S\text{-aa})]^{2+}$ and
$[Co(N_4)(R\text{-aa})]^{2+}$, where ($N_4$) indicates four amine nitrogen of diamine (2 moles) or tetramine.

$$\Lambda\text{-}[Co(N_4)((S)\text{-aa})]^{2+}+OH^- \xrightarrow{k_{eq}} \Lambda\text{-}\left[(N_4)Co \overset{N-C-R}{\underset{O-C\text{≈}O}{}}\right]^{2+}+H_2O$$

$$\Lambda\text{-}[Co(N_4)((S)\text{-aa})]^{2+}+OH^- \overset{H_2O}{\underset{\Lambda\text{-}[Co(N_4)((R)\text{-aa})]^{2+}+OH^-}{\diagdown \diagup}} \Lambda\text{-}\left[(N_4)Co \overset{N-C-R}{\underset{O-C-O}{}}\right]^{2+}$$

Scheme. Epimerization process of Λ-$[Co(N_4)(S\text{-aa})]^+$ (Ref. 1)

The overall reaction in the above Scheme is an epimerization with respect to the chiral
complex ion Λ-$[Co(N_4)(S\text{-aa})]^{2+}$, since only one asymmetric center, i.e. the α-carbon
atom, changes in the molecules having two or more chiral centers. If the equimolar
mixture of Λ-S and Λ-R isomers (Λ-S and Λ-R show the combination of the absolute

configuration of two chiral centers in $[Co(N_4)(\underline{S}\text{- or }\underline{R}\text{-aa})]^{2+}$) underwent the same reaction, the equilibrated composition of the isomers (Λ-$\underline{S}$/Λ-$\underline{R}$) should be identical with that obtained for the pure diastereomers. Further, it is naturally expected that the ratio of two isomers at the equilibrium would deviate from 50/50, reflecting the free energy difference between the diastereoisomers. On this basis the epimerization in the Scheme may be considered as an example of "first order asymmetric transformation" (2) of racemic α-amino acid.

This report will show an approach to make the difference of thermodynamic stabilities among the diastereoisomers as large as possible for the $[Co(N_4)(aa)]$ systems.

RESULTS AND DISCUSSION

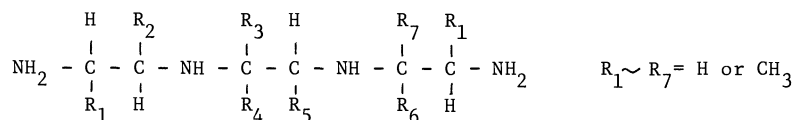1. Construction of the framework of chiral cobalt(III) complexes.

In the first step of the study it was supposed that the (N_4) group must have the function to settle the configuration around the central metal ion regardless of the chirality of the amino acid. It was further desired for the (N_4) to give the expected amino acidato complex in a high yield. The amino acidato complexes could be generally prepared by the reaction of amino acid with trans- or cis-$[Co(N_4)Cl_2]^+$ ion in slightly basic aqueous or alcoholic media. The decomposition, disproportionation, and other stereochemical changes are undesirable in the preparation and the asymmetric transformation reactions for the $[Co(N_4)(\underline{S}\text{- or }\underline{R}\text{-aa})]^{2+}$.

We supposed that the linear tetramines with chiral substituents would be appropriate for the (N_4) ligand which was required to adopt several properties mentioned above.

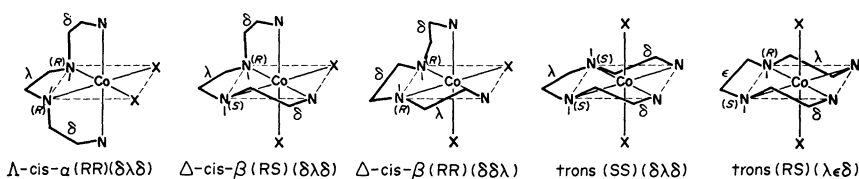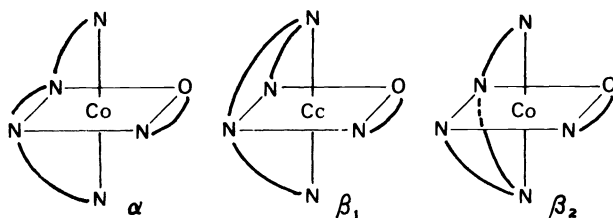TABLE 1. Abbreviation, Structure, and the isolated geometrical isomers of substituted trien

Abbreviation	Structure [a]	Isomers isolated [b]	Ref.
5($\underline{R}$)-metrien	R_4=CH_3	Λ-cis-β ($\underline{SS}$), trans($\underline{SS}$)	3
5($\underline{S}$)6($\underline{S}$)-dimetrien	R_3 & R_5=CH_3	Δ-cis-β ($\underline{RR}$), trans($\underline{RR}$)	3
3($\underline{S}$)8($\underline{S}$)-dimetrien	R_2 & R_6=CH_3	Λ-cis-β ($\underline{SS}$), Δ-cis-β ($\underline{RS}$)	4,5
2($\underline{S}$)9($\underline{S}$)-dimetrien	R_1 = CH_3	Λ-cis-α ($\underline{RR}$), trans($\underline{SS}$) Λ-cis-α ($\underline{RR}$), Λ-cis-β ($\underline{SS}$)	4,5,6
2($\underline{S}$)5($\underline{R}$)9($\underline{S}$)-trimetrien	R_1 & R_4=CH_3	Δ-cis-β ($\underline{RS}$), trans($\underline{SS}$) Δ-cis-β ($\underline{RS}$), Λ-cis-α ($\underline{RR}$)	5
3($\underline{S}$)8($\underline{R}$)-dimetrien	R_2 & R_7=CH_3	Δ-cis-β ($\underline{RR}$)+ Λ-cis-β ($\underline{SS}$) trans($\underline{RS}$)	6
5($\underline{R}$)6($\underline{S}$)-dimetrien	R_4 & R_5=CH_3	Δ-cis-β ($\underline{RS}$)+ Λ-cis-β ($\underline{SR}$) trans($\underline{RS}$), trans($\underline{SS}$)	7

a)

$$NH_2 - \underset{\underset{R_1}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{R_2}{|}}{C}} - NH - \underset{\underset{R_4}{|}}{\overset{\overset{R_3}{|}}{C}} - \underset{\underset{R_5}{|}}{\overset{\overset{H}{|}}{C}} - NH - \underset{\underset{R_6}{|}}{\overset{\overset{R_7}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{R_1}{|}}{C}} - NH_2 \qquad R_1 \sim R_7 = H \text{ or } CH_3$$

b) $\underline{R}$ and $\underline{S}$ shows the configuration of secondary N atoms of trien skeleton, neglecting the methyl groups. (Ref. 4,5)

Table 1 shows the results of stereoisomerism of dianionocobalt(III) complexes coordinated with a variety of methyl-substituted triethylenetetramines (3-8). The geometrical isomers of $[Co(trien)X_2]^{n+}$ (trien-triethylenetetramine) so far proposed are illustrated in Fig.1 (4.5). Details of the steroisomerism of trien complex has been previously discussed (4,5). It is apparent from Table 1 that most of substituted triens adopt preferably the cis-β topology upon coordination, and that the chiral tetramines are able to settle the configuration about the cobalt(III) center for each geometrical isomer.

As exhibited in Fig. 2, a single enantiomer is possible for the α-$[Co(tetramine)(aa)]^{2+}$ while for the β form two geometrical isomers (indicated by β_1 and β_2 (9)) can exist.

Λ-cis-α(RR)(δλδ)   Δ-cis-β(RS)(δλδ)   Δ-cis-β(RR)(δδλ)   trons(SS)(δλδ)   trons(RS)(λεδ)

Fig. 1. Geometrical isomers of $[Co(trien)X_2]^{n+}$

Fig. 2. Possible isomers of $[Co(tetramine)(aa)]^{2+}$

It was intended in an earlier stage of the study to design the substituted trien which adopt preferentially the cis-α configuration (10,11). Though the dichlorocobalt(III) complex of 2(S)9(S)-dimetrien preferred the Λ-cis-α configuration (6), several amino acidato complexes with this ligand were shown to have mainly the Λ-β configuration (10,12). From another point of view, however, it is satisfactory to employ tetramines which lead to the β_1 or β_2 configuration of the amino acidato complexes with good selectivity.

Table 2. Abbreviation, structure and stereoisomerism of cobalt(III) complexes

Abbreviation	Structure [a]	Isomers isolated	Ref.
2,3,2-tet	no CH_3	trans(RS), trans(RR)+(SS)	17
		Λ-cis-β (RR)+ Δ-cis-β (SS)	
5(R)-Me-2,3,2-tet	$R_3=CH_3$	trans(RS), trans(SS)	18
		Δ-cis-β (SS)	
5(R)7(R)-Me$_2$-2,3,2-tet	R_3 & $R_4=CH_3$	trans(RR), trans(RS)	19
		Λ-cis-β (RR)	
2(S)10(S)-Me$_2$-2,3,2-tet	$R_1=CH_3$	trans(RR), trans(RS)	20,21
		Λ-cis-β (RR)	
3(S)9(S)-Me$_2$-2,3,2-tet	$R_2=CH_3$	trans(RR), trans(RS)	22
		Λ-cis-β (RR)	
SS-pyht	b	trans(RR), Λ-cis-β (RR)	23

a)
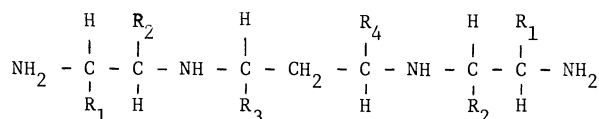
b)
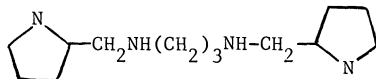
It was very revealing that the reaction of amino acid with trans-$[Co(2,3,2-tet)Cl_2]^+$ or trans-$[Co(3,2,3-tet)Cl_2]^+$ ion (2,3,2-tet=1,9-diamino-3,7-diazanonane; 3,2,3-tet=1,10-diamino-4,7-diazadecane) gave rise to the β_2 isomer of $[Co(tetramine)(aa)]^{2+}$ complexes in good yield(13,14). This means that the trans-dichlorocobalt(III) complexes with chiral tetramines, if obtained selectively, will serve as the starting complex for preparing the β_2-$[Co(N_4)(aa)]^{2+}$ having the fixed absolute configuration. 3(S)8(S)-dimetrien is a unique chiral trien derivative which forms the trans-dichloro complex sterioselectively (4,15). Some amino acidato complexes of this tetramine were obtained and found to take the $-\beta_2$ configuration with good selectivity (16).

Table 2 shows the possible stereoisomers of dianionocobalt(III) complexes of chiral 2,3,2-tet derivatives. It is noteworthy that all of the 2,3,2-tet derivatives have similar geometric structures (Λ-cis-β (RR) and/or Δ-cis-β (SS)) in the cis configuration, despite the fact that these tetramines in the trans form can adopt two diastereomeric ways of coordination due to the different combination of the configuration of coordinated secondary N centers (17-22). Hence, a few chirally substituted 2,3,2-tet will be conveniently employed in the following examination.

2. Asymmetric transformation

In Table 3 are summarized the diastereomeric ratios (Λ-S/Λ-R) of the alaninato, valinato, and N-methyl-alaninato complexes after the epimerization equilibria have been established.

Table 3. Isomeric ratio (Λ-S/Λ-R) of $[Co(N_4)(aa)]^{2+}$

(N_4)	Λ-S /Λ-R		
	ala	val	N-Meala
(en)$_2$	50/50 [a]	39/61 [a]	80/20 [b]
3(S)8(S)-dimetrien	50/50 [c]		85/15 [c]
2(S)10(S)-Me$_2$-2,3,2-tet	66/34 [d]	28/72 [d]	
3(S)9(S)-Me$_2$-2,3,2-tet	61/39		
SS-pyht	18/82 [e]		
trien			60/40 [f]

a) Ref. 1   b) Ref. 25   c) Ref. 16   d) Ref. 24   e) Ref. 29

Sargeson and coworkers have performed the epimerization in 0.01 M NaOH, while the carbonate buffer (pH 10-11) was used in our study in order to minimize the decomposition of the relatively unstable complexes such as Λ-β_2-$[Co(SS-pyht)(ala)]^{2+}$ (SS-pyht=1,7-bis(2(S)-pyrolidyl)-2,6-diazaheptane (23)). It was recently observed that Λ-β_2-[Co(2(S)10(S)-Me$_2$-2,3,2-tet)(S- or R-ala)]$^{2+}$ and Λ-β_2-$[Co(3(S)9(S)-Me_2-2,3,2-tet(S- or R-ala)]^{2+}$ ion, which should be included in the most stable group of $[Co(N_4)(aa)]$, were recovered in ca. 90% yield from the epimerization products in 0.02 M Na$_2$CO$_3$ (pH 11.2 at 40°C, 20h).

The remainder (ca. 10%) was composed of three kinds of cobalt(III) species was probably arose by the decomposition of the initial complexes.

The amino acidato complexes in Table 3 may be classified into three groups with regard to the terminal amino groups of (N_4) and the amino group of (aa); either primary or secondary.

(1) (N_4)-Primary; (aa) - primary. The alaninato complex of 2(S)10(S)-Me$_2$-2,3,2-tet showed a slight preference for the S-ala isomer (Λ-S/Λ-R=66/34, ΔG=-0.40 kcal/mole). However, it is obvious that the Λ-S/Λ-R values of alaninato complexes do not deviate so much from 50/50, even if the (N_4) groups can fix the complex ion in the Λ configuration.

The selectivity for the valinato complexes appeared to be somewhat higher (Λ-S/Λ-R= 4/6— 3/7) than that for alaninato complexes, though only two examples have been studied yet. The valinate ion has the isopropyl group, which is one of the bulkiest substituents in the usual amino acids, and was expected to have the highest degree of selectivity in these systems. The above data therefore implied that the amino acidato complexes having the combination of primary (N_4) and primary (aa) could not achieve a diasteromeric selectivity in the amino acidate moiety exceeding the range of S/R=7/3—3/7.

It is interesting that the predominant configuration of amino acidate alters from alaninate to valinate for two cases((N_4)=(en)$_2$ (1) and 2(S)10(S)-Me$_2$-2,3,2-tet (24)). For both

(N_4), S- and R-enantiomers are favored in the ala and val complexes, respectively the reason for which has not been clarified yet.

(2) (N_4)-Primary; (aa)-secondary. The N-methyl-S- and -R-alaninato complexes of the types $[Co(en)_2(aa)]^{2+}$ and β_2-$[Co(trien)(aa)]^{2+}$ were studied thoroughly by Sargeson and his coworkers from the aspects of preparation, X-ray crystallography, and strain energy minimization. The $[Co(en)_2(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$ ion (N-Me-S-ala=N-methyl-S-alaninate) possesses

three chiral centers: the central metal ion (Λ or Δ), the secondary nitrogen atom ((R) or (S)), and the asymmetric carbon (S or R) of N-meala. The former two are determined simultaneously during complex formation. Then, four combinations, i.e. Λ-(R), Δ-(R), Λ-(S), and Δ-(S), become possible, as shown in Fig. 3.
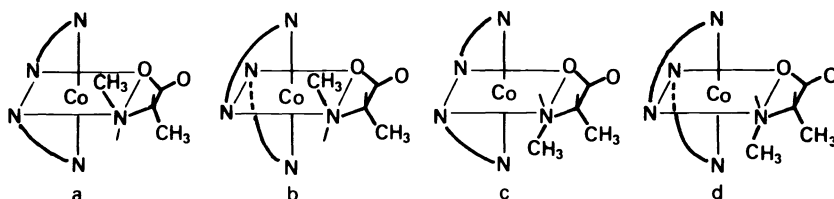
Fig. 3. Diastereomers of $[Co(en)_2(N\text{-}Me\text{-}(\underline{S})\text{-}ala)]^{2+}$ ion;

(a) Λ-(R),   (b) Δ-(R),   (c) Λ-(S),   (d) Δ-(S)

In the Λ-(R) and Δ-(R) structures, the C- and N-methyl groups are situated in the staggered position to each other, while they are eclipsed in the other forms. From the stereochemical point of view, the former arrangement should be much more favorable than the latter. The Λ-(R) and Δ-(R) isomers of $[Co(en)_2(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$ complex were isolated, and the isomer ratio of these two was determined as Λ-(R)/Δ-(R)=80/20 (25).

The epimerization of the Λ-(R)-$[Co(en)_2(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$ (=Λ-(R)-S) isomer was performed in the usual manner. The isomeric ratio of the equilibrated mixture was shown to be Λ-(R)-S/Λ-(S)-R=80/20 as expected (25), since the Λ-(S)-$[Co(en)_2(N\text{-}Me\text{-}R\text{-}ala)]^{2+}$ isomer (abbreviated as Λ-(S)-R) was the optical antipode of the Δ-(R)-$[Co(en)_2(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$, the minor product in the preparative mixture described above.

The strain energy minimization study on the $[Co(en)_2(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$ isomers exhibited a significant steric repulsion between the N-methyl group and the adjacent en chelate in the Δ-(R) isomer (26). It is probable that the observed thermodynamic preference of the Λ-(R) over the Δ-(R) (80:20, ΔG=-0.80 kcal/mole) should be due to the absence of such steric disadvantage.

In order to obtain further information about the asymmetric transformation of N-methylalanine, the 3(S)8(S)-dimetriencobalt(III) complexes of N-Me-S- and -R-alaninate were prepared (16; 3(S)8(S)-dimetrien=3(S)8(S)-3,8-dimethyl-1,4,7,10-tetraazadecane, see Table 1).

The $[Co(3(\underline{S})8(\underline{S})\text{-}dimetrien)(N\text{-}Me\text{-}\underline{S}\text{-}ala)]^{2+}$ ion was found to consist of a single species, which adopted the Λ-β_2-(R)-S configuration (Fig. 4). The N-Me-R-ala complex was composed of two isomers having the configuration Λ-β_2-(R)-R and Λ-β_2-(S)-R as shown in Fig. 4.

These assignments were based on the results of the N-Meala complexes with chiral trien derivatives (27,28). The ratio of Λ-β_2-(R)-R/Λ-β_2-(S)-R at equilibrium (pH 7-8) was estimated as ca. 3/1 from proton NMR data. The composition of the isomer mixture was obtained by comparing the CD (circular dichroism) curve of the equilibrated mixture at pH 12 with the authentic curve of the Λ-β_2-(R)-S and that of the equilibrated mixture (pH 7) of the Λ-β_2-(R)-R and Λ-β_2-(S)-R, as indicated in Fig. 5. The calculated isomer ratio (R)-S:(R)-R:(S)-R was 85 : 11 : 4. From the viewpoint of asymmetric transformation, the Λ-β_2-$[Co(3(\underline{S})8(\underline{S})\text{-}dimetrien)(N\text{-}Meala)]^{2+}$ systems gave Λ-S/Λ-R=85/15 (ΔG=-1.28 kcal/mole). The considerable stereoselectivity should be ascribed to the same reason as that for the Λ-$[Co(en)_2(N\text{-}Meala)]^{2+}$ isomers.

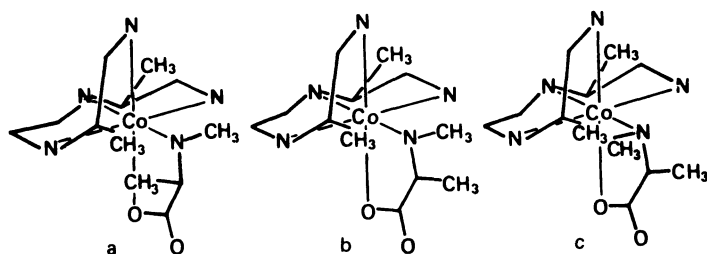Fig. 4. Structures of $\Lambda - \beta_2$[Co(3(S)8(S)-dimetrien)(N-Me-S- and -R-ala)]$^{2+}$;
    (a) $\Lambda - \beta_2$-(R)-R,   (b) $\Lambda - \beta_2$-(S)-R, and (c) $\Lambda - \beta_2$-(R)-S.
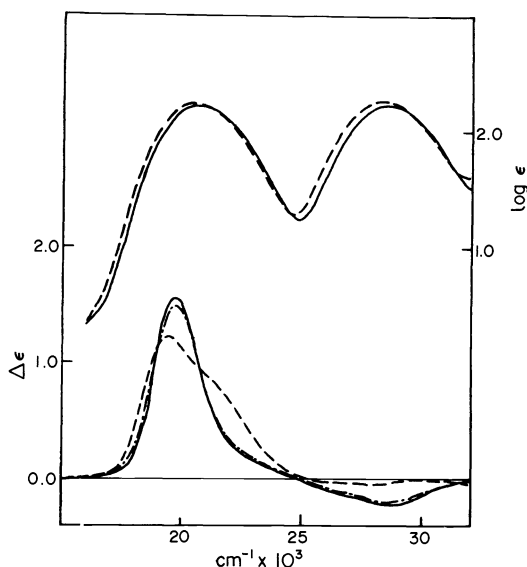
Fig. 5. Visible absorption and CD curves of [Co(3(S)8(S)-dimetrien)(N-Meala)]$^{2+}$:
    $\Lambda - \beta_2$-(R)-S (————), $\Lambda - \beta_2$-(R)-R+$\Lambda - \beta_2$-(S)-R at pH 7 (— — —), and
    the equilibrated mixture at pH 12 (—·—·—)

(3) (N$_4$)-Secondary; (aa)-primary. The striking improvement of the chiral selectivity

in the N-meala complexes, in comparison with that for the α-alanine complexes, impelled
us to examine the effects brought about by substitution at the terminal amino groups of

tetramines. As the first example of such complex, the $\Lambda - \beta_2$-[Co(SS-pyht)(S- or R-ala)]$^{2+}$

ion was investigated (29). It was observed that the CD curve of $\Lambda - \beta_2$-[Co(SS-pyht)-

(R-ala)]$^{2+}$ ion showed little change during the epimerization in carbonate buffer
(pH 10) at 40°C, while the CD of the S-ala complex gradually changed and seemed to
conincide with that of the R-ala complex. Based on this observation, the isomeric ratio
Λ-S/Λ-R was estimated as 10/90 - 5/95. However, it was revealed by the chromatographic
separation of the epimerization product (SP-Sephadex column chromatograpy) that the
reaction was accompanied by considerable decomposition, and that the alaninato complexes
which remained were only 32% (from the S-ala complex) or 40% (from the R-ala complex)
of the amount initially introduced. The main product for the decomposition was the ion

$\Lambda - \beta$-[Co(SS-phyt)CO$_3$]$^+$, the CD curve of which resembles that of $\Lambda - \beta_2$[Co(SS-pyht)(R-ala)]$^{2+}$

unexpectedly. This is the reason for the overestimation of stereoselectivity (Λ-S/Λ-R= 1/9)
mentioned above. The reliable value obtained by recovering the S- and R-ala complex
separately by means of SP-sephadex column chromatography indicated -S/ -R=18/82
(Δ G=0.9 kcal/mole). Preliminary strain energy calculations of SS-pyht complexes of
S-ala and R-ala, based on the X-ray crystallographic analysis of the $\Lambda - \beta_2$-[Co(SS-pyht)-

(R-ala)]$^{2+}$ ion predicted a considerable difference between the stabilities of these
isomers (ca. 0.8 kcal/mole in favor of the R-ala complex) (30). This suggests that

the predominance of the R configuration in the $\varLambda$-β_2-[Co(SS-pyht)(ala)]$^{2+}$ ion was due mostly to less serious strain energy than in the S configuration.
From the view point of asymmetric transformation, N-substitution of the (N$_4$) group, as the pyrrolidine ring of SS-pyht, results in an improvement of the stereoselectivity as above. On the other hand, it accelerates some unfavorable side reactions. It seems rather hard to overcome these two conflicting demands for (N$_4$), selectivity and stability, but attempts directed to reduce the steric congestion about the secondary nitrogens of SS-pyht are now in progress.

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