sistent with the fact that the 12-coordinate icosahedron is such a favorable coordination polyhedron that it is likely to be nearly impossible to add further ligands to a 12-coordinate system. Even though 12 may be the maximum coordination number for any complex other than a close-packed metallic structure, the following observations based on the information presented in Table II are given below.

a. Coordination Number 13. None of the polyhedra have very high symmetries and all except one have nonzero d- and f-flexibilities.

b. Coordination Number 14. Although several relatively symmetrical polyhedra are found, surprisingly few polyhedra have nonzero f-flexibilities. Furthermore, the only polyhedra with nonzero f-flexibilities have only C_{2v} symmetry.

c. Coordination Number 15. The only polyhedra with nonzero f-flexibilities all have five parallel planes with three ligands each and a threefold rotational axis.

d. Coordination Number 16. Few polyhedra with nonzero f-flexibilities occur. Conspicuous among these few polyhedra are the two D_{4d} polyhedra with at least one staggered pair of four-ligand planes, i.e., a "built-up" version of the square antiprism which is a favorable polyhedron for coordination number eight.

In view of the uncertainty whether molecular complexes with coordination numbers greater than 12 will ever be prepared, it appears inappropriate to attempt to derive any chemical conclusions or predictions at the present time from the above observations concerning possible polyhedra for these very high coordination numbers.

Kinetic Studies of the Racemization of Optically Active (Amino acidato)triethylenetetraminecobalt(III) Complexes. cis-β_2-l-(Phenylalaninato)(triethylenetetramine)cobalt Iodide and cis-β_2-d- and -l-(L-Prolinato)(triethylenetetramine)cobalt Iodides in Aqueous Solutions

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Abstract: Some optically active (L-amino acidato)triethylenetetraminecobalt iodides (abbreviated cis-β_2-[Co(trien)-(L-AA)]I₂) have been prepared, and the loss of optical rotation of aqueous solutions containing these compounds has been studied. Possible structural changes which occur in the overall racemization may include (a) change in relative configuration of the triethylenetetramine ligand about the cobalt atom with respect to the amino acid ligand, (b) racemization of the asymmetric secondary planar amino in the trien group, (c) displacement of various ligands about the Co by water or hydroxyl ions, and (d) racemization of the asymmetric carbon atom in the amino acid. The kinetics of the racemization have been studied by measuring the optical rotation, ellipticity (CD), and absorption spectra as a function of time and by studying the influence on these racemization vs. time curves of pH, charcoal, and the variation of the type of amino acid in the initial reactant. From these measurements a mechanism for racemization is proposed and the relative rates of the various steps in the mechanism are deduced for the various conditions.

The optically active compounds cis-β_2-l-[Co(trien)-(L-phala)]I₂, cis-β_2-l-[Co(trien)(L-prol)]I₂, and cis-β_2-d-[Co(trien)(L-prol)]I₂ have been prepared, and the loss of optical rotation and of ellipticity of aqueous solutions containing these compounds has been studied.[2] One of the features of these complexes is that they have three centers of optical activity, the first due to the arrangement of the quadridentate trien ligand with respect to the other two ligand positions about the cobalt, the second due to the asymmetric carbon of the amino acid, and the third due to the asymmetric secondary planar amine of the trien group. Hence they can go through several types of molecular changes in the process of racemization. In this work we try to delineate the various changes occurring during racemization as well as the relative rates of these changes. Besides yielding information relating structure and chemical activity of these rather complex systems it is hoped that these metal complexes may serve as chemical and optical models for even more complicated enzymatic systems which are potentiated by metal ions.[3]

(1) Address correspondence to this author.
(2) The following abbreviations will be used: trien = triethylenetetramine = NH₂CH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂, phala = phenylalaninato = (C₆H₅)CH₂CH(NH₂)COO⁻, prol = prolinato = NHCH₂CH₂CH₂CHCOO⁻, ala = alinato = CH₃CH(NH₂)COO⁻.
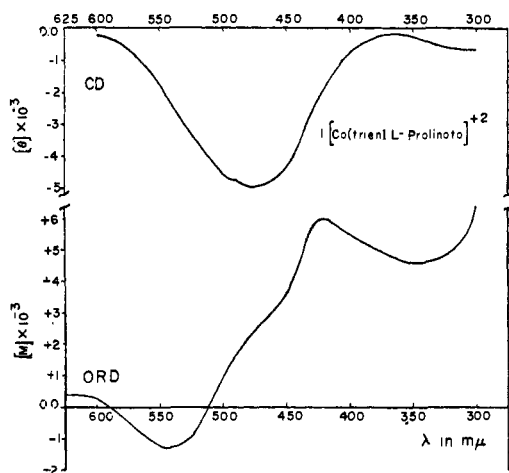(3) (a) J. P. Collman and D. A. Buckingham, J. Amer. Chem. Soc.,

Figure 1. Molar rotatory dispersion and circular dichroism spectra of *l*-[Co(trien)(L-prol)]I₂.

The kinetics of the racemization has been studied by measuring ORD, CD, uv, and visible spectra of solutions which have been heated for various times, and by observing the influence on the above measurements of temperature, pH, and catalytically active charcoal.

Experimental Section

The compounds were prepared using the method of Bryant and coworkers.[4] *cis*-α-[Co(trien)Cl₂]Cl was added to an aqueous solution containing the salt of the amino acid (at 60°) and the product was recrystallized from aqueous sodium iodide. The *l* and *d* isomers of the prolinato complex were separated by fractional crystallization. Eight successive crystallizations were carried out, from which the *l* isomer was obtained as the first cut, the racemate was obtained on the seventh cut, and the *d* isomer was obtained as the eighth cut. It is useful to note that contrary to the results of Saburi, *et al.*,[5] both internal diastereoisomers were recoverable as indicated by Bryant, *et al.*,[4] by fractional crystallization only and in the absence of a resolving agent. There is no evidence of stereospecificity reactions by the prolinato anion in the case of the trien complex, as proposed by Saburi, *et al.*[5] In the case of *cis*-β₂-[Co(trien)-(L-phala)]I₂ the more soluble *d* isomer was not separated from the liquid phase.

Anal. Calcd for *cis*-β₂-[Co(trien)(L-prol)]I₂·H₂O: C, 22.4; N, 11.8; H, 4.7. Found: C, 22.4; N, 11.6; H, 4.9. Calcd for *cis*-β₂-[Co(trien)(L-phala)]I₂·H₂O: C, 28.1; N, 10.9; H, 4.7. Found: C, 28.3; N, 10.6; H, 4.9. Elemental analysis was performed by Galbraith Laboratories, Inc.

Aqueous solutions of the complexes at concentrations of about 10–15 mg/25 ml (unless otherwise specified) were prepared by dissolving the compounds in water or in ammonium hydroxide–ammonium chloride buffer solutions. Table I shows the compositions and the pH of the buffers used. Racemization was effected by heating these solutions at 70–95° in a constant-temperature bath. A cover was placed on the reaction vessel to prevent CO₂ in the

Table I

pH	[NH₄OH], M	[NH₄Cl], M
7.83	0.0514	0.6802
9.33	0.2566	0.0884
9.65	0.2566	0.0842
10.56	2.8486	0.0910
11.18	4.3608	0.0374

85, 3039 (1963); (b) E. L. Smith and R. L. Hill, "The Enzymes," Vol. 4, P. D. Boyer, H. Lardy, and K. Myrback, Ed., Academic Press, New York, N. Y., 1960, p 37.
(4) B. E. Bryant, J. J. Hu, and W. H. Glaze, *Inorg. Chem.*, **5**, 1373 (1966).
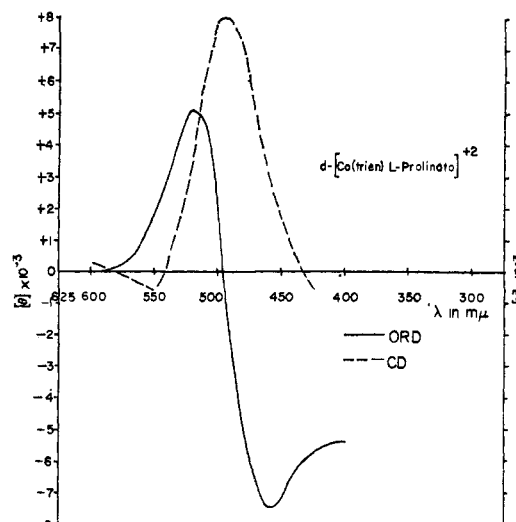(5) M. Saburi, M. Homma, and S. Yoshikawa, *ibid.*, **8**, 367 (1969).

Figure 2. Molar rotary dispersion and circular dichroism spectra of *d*-[Co(trien)(L-prol)]I₂.
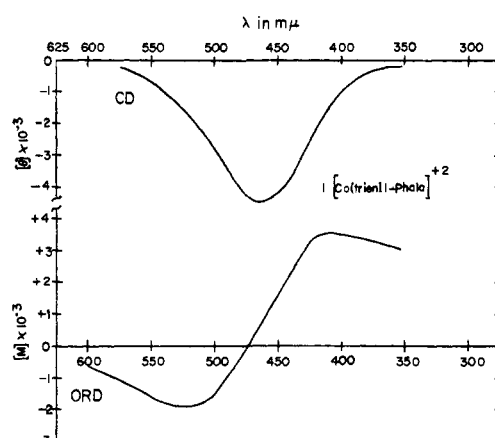

Figure 3. Molar rotatory dispersion and circular dichroism spectra of *l*-[Co(trien)(L-phala)]I₂.

atmosphere from reacting with the solutions. Aliquots were removed from the bath at recorded times and were quenched immediately to temperatures (room temperature or lower) at which racemization was negligible. The loss of rotation was measured by comparing the ellipticity or rotation to that of an unheated portion from the same sample. For studying the effect of charcoal on the reaction, charcoal was added to the reaction flask and filtered out before measurements were made on the solution. The amount of charcoal added was kept at a minimum (5% of the weight of the solid sample) in order to prevent the loss of sample through adsorption of compound on the charcoal surface. The absence of such a loss was indicated by the fact that the absorption spectrum did not decrease during the reaction.

The optical rotations and ellipticities of the solutions were measured using a recording Cary Model 60 spectropolarimeter with a Model 6001 CD attachment. Absorption spectra were correspondingly measured with a Cary 14 spectrophotometer.

In order to further characterize the starting material beyond association with the above spectra, ir and nmr spectra were obtained (for the *l*-prol complex only). The infrared spectrum was recorded on a Beckman-IR5A recording spectrophotometer. Solid samples of the compound in Nujol mulls were examined between potassium bromide plates. For the purpose of obtaining the pmr spectrum, 5.4 mg of the solid sample was dissolved in 0.5 ml of D₂O to which a small amount of 30% DCl was added to improve the solubility. The solution was filtered to remove undissolved crystals, and the spectra of the filtrate was recorded using a Varian HA-220 spectrometer.

Results

The ORD and CD of the starting solutions are shown in Figures 1–3. These spectra compare closely
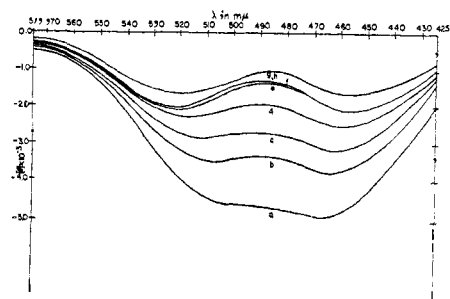
Figure 4. CD spectrum of *l*-[Co(trien)(L-prol)]I₂ in H₂O plus charcoal solution after solution has been held at 95° for various times. Time of heating: (a) 0, (b) 15 min, (c) 35 min, (d) 55 min, (e) 1 hr 40 min, (f) 6 hr 10 min, (g) 18 hr 30 min, (h) 24 hr 30 min.
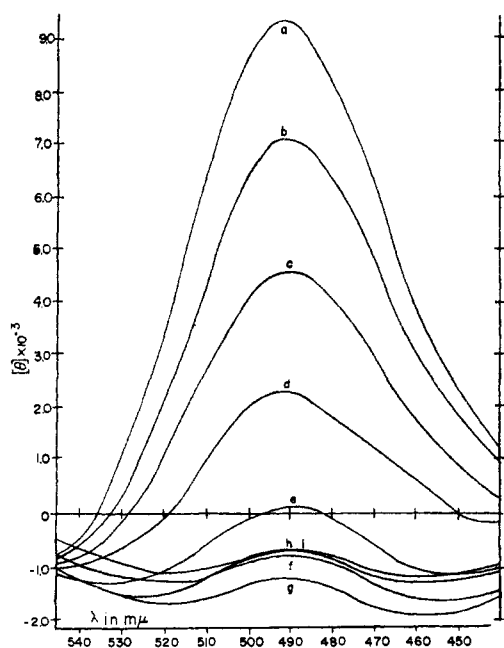

Figure 5. CD spectral changes of *d*-[Co(trien)(L-prol)]I₂ in H₂O plus charcoal solution with time when heated at 95°. Time of heating: (a) 0.0, (b) 10 min, (c) 25 min, (d) 55 min, (e) 1 hr 35 min, (f) 2 hr 35 min, (g) 6 hr, (h) 24 hr, (i) 30 hr 15 min.
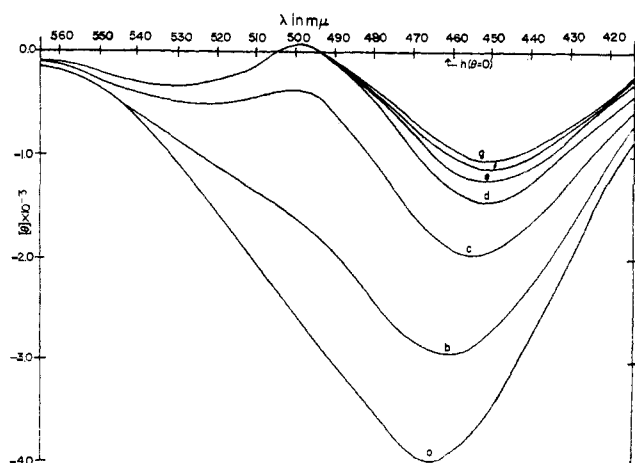

Figure 7. CD spectral changes of *d*-[Co(trien)(L-prol)]I₂ in solution of pH 9.65 when heated at 95°. Time of heating: (a) 0.0, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, (f) 25 min, (g) 30 min, (h) 40 min, (i) 50 min, (j) 60 min, (k) 70 min.

Figure 8. CD spectral changes of *l*-[Co(trien)(L-phala)]I₂ in H₂O *without* charcoal when heated at 95°. Time of heating: (a) 0.0, (b) 30 min, (c) 2 hr, (d) 3 hr 30 min, (e) 5 hr 30 min, (f) 9 hr 30 min, (g) 22 hr 30 min, (h) 26 hr 30 min.

Figure 6. CD spectral changes of *l*-[Co(trien)(L-phala)]I₂ in H₂O plus charcoal solution with time when heated at 95°. Time of heating: (a) 0.0, (b) 5 min, (c) 10 min, (d) 15 min, (e) 25 min, (f) 40 min, (g) 3 hr 55 min, (h) 24 hr.
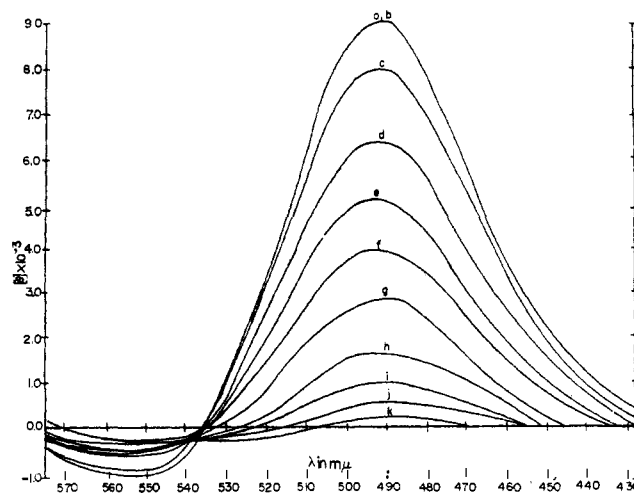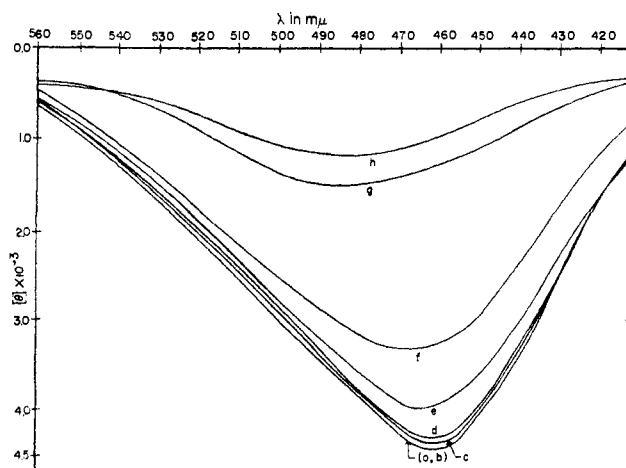
with those obtained by other investigators.[6] When the solutions are heated, the CD and ORD curves decrease in intensity. Since the shapes of the CD curves reveal the types of changes occurring with greater clarity, we shall focus on these curves in this work. In a few cases, however, the rate constants were obtained by both methods and were found to compare favorably.

The general types of changes which occur in the CD spectra as the solutions are continuously heated are shown in Figures 4–8. In charcoal plus water, the CD intensities for all three compounds decrease and the spectra change shape in such a way as to give two peaks on the negative side of zero (*cf.* curve e of Figure 4, curve g of Figure 5, and curve f of Figure 6). The CD then decreases and tends toward zero at all wavelengths. The rate of this latter change for the prol complexes is much slower than for the phala complex. It is to be noted that the *l*- and *d*-prol complexes undergo a change which results in essentially

(6) (a) C. Y. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Lett.*, 4, 15 (1968); (b) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 3, 1356 (1964).
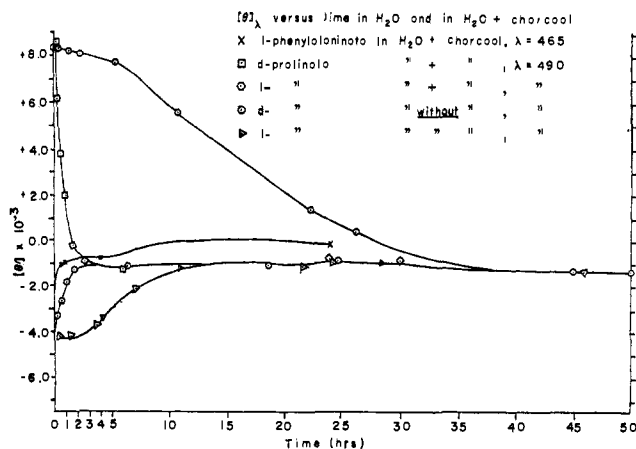
Figure 9. Molar ellipticity *vs.* time for *l*- and *d*-prol and *l*-phala complexes in H_2O and in H_2O plus charcoal at 95°.

Figure 10. Visible spectral changes of *l*-[Co(trien)(L-prol)]I₂ in buffer 9.65 and temperature 95° with respect to time. Time of heating: (a) 15 min, (b) 2 hr 40 min.

identical spectra for both compounds. These spectra are similar to that obtained when equal amounts of cis-β₂-*l*- and cis-β₂-*d*-[Co(trien)(L-prol)]I₂ are mixed together. It is also to be noted that the spectra obtained after the first step in charcoal plus water (*i.e.*, those with two negative bands) are similar to the spectra obtained by Yasui, *et al.*,[7] for [Co(NH₃)₄(L-phala)]²⁺ ions. This indicates that the first step results in a loss of the configurational contribution to the optical activity due to the trien ligand. The uv and visible spectra of the water solutions containing charcoal did not change during racemization.

For neutral water solutions of the prol complexes *not* containing charcoal, the changes in the CD spectra are qualitatively similar to those for water plus charcoal, except that the rates of change are less and there is an initial induction time during which there is little change in optical activity. The comparison of the results in water to those in water containing charcoal is shown in the plot of CD at a given wavelength as a function of time (*cf.* Figure 9).

In basic media the CD for the prol complexes decreases to zero at all wavelengths without a change occurring in the spectral shape. This is shown in Figure 7 for the *d*-prol complex; this type of change also occurs for the *l* complex. Racemization in base is noted to be much faster than that in water. Although the uv spectra remain unchanged with racemization in base, the visible spectra do change, as is noted in Figure 10 for the cis-β₂-*l*-[Co(trien)(L-prol)]I₂ solution.

The spectral changes for cis-β₂-*l*-[Co(trien)(L-phala)]I₂ heated in water and in base are qualitatively similar but differ from those for the prol complexes in any media or for the phala complex in charcoal plus water. This is seen by comparing Figure 8 (the phala complex in water) to Figures 4–7. The intensity of the CD decreases and the CD peak shifts to longer wavelength with racemization, but the prominent splitting of the peak does not occur. In basic media the CD changes occur much more rapidly than in water and also a short induction time is noted. The visible spectrum undergoes a change similar to that noted for the prol complexes.

(7) T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **39**, 2417 (1966).
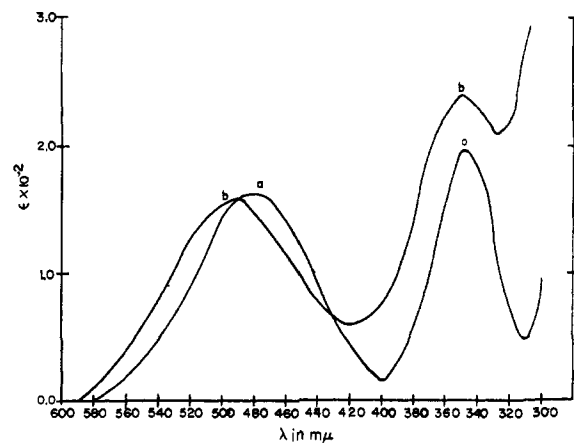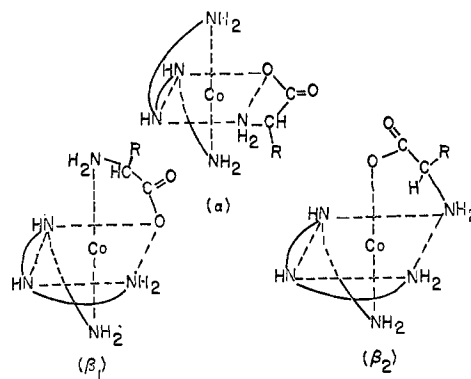

Figure 11. Geometrical configurations of *l*-[Co(trien)(L-AA)]²⁺ ion.

The pH of the water and charcoal plus water solutions did not change with racemization, but when unbuffered basic solutions were used, the pH was found to decrease during the run.

Discussion

Question of Structure of Starting Material. A precise knowledge of the mechanism of racemization of the present compounds is complicated by the existence of the several possible geometrical and optical isomers. The [Co(trien)(L-AA)]²⁺ ion (our starting material) has three geometrical isomers which are depicted in Figure 11, following the notation of Buckingham, *et al.*[8] The α isomer differs from the β isomers in that the trien ligand of the α isomer has a symmetrical configuration, while that of the β isomers does not. Each of the structures shown in Figure 11 has a mirror image structure which is the *d* isomer.

The method of preparation is that of Bryant, *et al.*,[4] who thought because they started with α-[Co(trien)-Cl₂]Cl that they had probably prepared the α isomer. Ir spectra frequently have been used to distinguish between the isomers. There are three regions in the ir spectra[9] which could serve to distinguish between the α and β isomers of [Co(trien)(L-AA)]I₂. The ir spectra we took for our compounds, however, did not enable

(8) D. A. Buckingham, J. P. Collman, D. A. P. Happer, and L. G. Marzilli, *J. Amer. Chem. Soc.*, **89**, 1082 (1967).
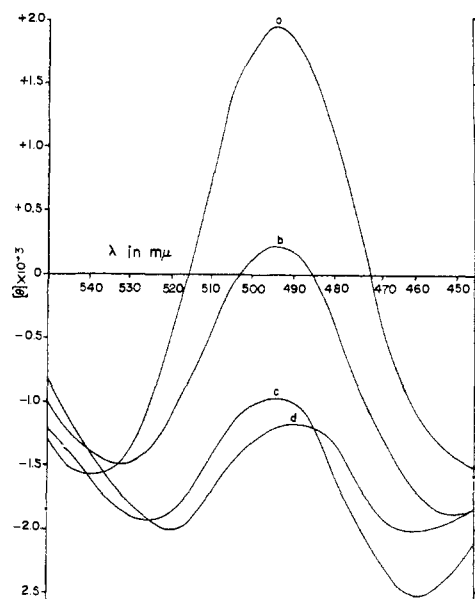(9) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

Figure 12. CD spectra of various mixtures of *d*- and *l*-[Co(trien)(L-prol)]I₂ and of the solution resulting from heating either pure starting material in charcoal plus water until the back-side racemization has occurred. Compositions: (a) *d* complex/*l* complex = 1/1, (b) *d* complex/*l* complex = 2/3, (c) *d* complex/*l* complex = 1/3, (d) curves from Figure 4f and Figure 5g.

us to differentiate between the isomers. Our attempts to identify our compound on the basis of pmr spectra also were not definitive.

Recently Buckingham, *et al.*,[10] reported the crystal structure of the *d* and *l* isomers of the prol complex, which had the same CD spectra observed by Douglas and Lin,[6a] and which agree with our CD spectra (see Figure 1 and 2). Buckingham, *et al.*,[10] on the basis of their X-ray data, identified the structure of their compounds as the most energetically stable *d* and *l* conformers of the cis-β₂ structure for the prol complex. On this basis we conclude that the synthetic procedure of Bryant, *et al.*,[4] yields the most stable *d* and *l* isomers of the cis-β₂ conformer; since the phala complex was prepared in the same manner and exhibits similar spectral properties and kinetic behavior, we conclude that it, too, has the structure of the most stable cis-β₂ conformer.

Proposed Mechanism. In order to account, qualitatively, for the observed spectral changes we propose the following reaction pathway for all the solutions investigated in the present study.

$$A \qquad\qquad A'$$

$$(1)$$
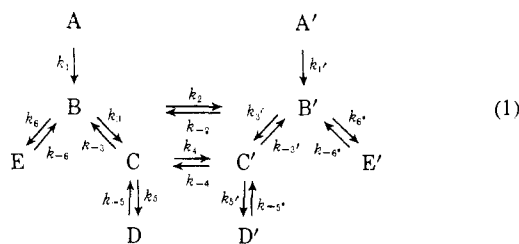
The capital letters represent the following complex ions: A, cis-β₂-*l*-[Co(trien)(L-AA)]²⁺; A′, cis-β₂-*d*-[Co(trien)(L-AA)]²⁺; B, cis-β₂-*l*-[Co(trien)*(L-AA)]²⁺ ᵒʳ ¹⁺; B′, cis-β₂-*d*-[Co(trien)*(L-AA)]²⁺ ᵒʳ ¹⁺; C, cis-β₁-

l-[Co(trien)*(L-AA)]²⁺ ᵒʳ ¹⁺; C′, cis-β₁-*d*-[Co(trien)*(L-AA)]²⁺ ᵒʳ ¹⁺; D, cis-β₁-*l*-[Co(trien)*(D-AA)]²⁺ ᵒʳ ¹⁺; D′, cis-β₁-*d*-[Co(trien)*(D-AA)]²⁺ ᵒʳ ¹⁺; E, cis-β₂-*l*-[Co(trien)*(D-AA)]²⁺ ᵒʳ ¹⁺; E′ cis-β₂-*d*-[Co(trien)*(D-AA)]²⁺ ᵒʳ ¹⁺. States A and A′ are the starting materials in each experiment, where L-AA represents the prol or phala chelate. Species B and B′ are formed from A and A′, respectively, during the initital induction period which is observed in water and basic media (*cf.* Figure 9). Since the CD spectrum changes very little if any during the induction time, species B and B′ are very similar to A and A′. However, the step A → B (or A′ → B′) is necessary in order for any further change to occur (such as B → B′ and B → C). Since conceivable steps in racemization involve detachment of ligands from Co with subsequent rearrangement, we may think of steps A → B (or A′ → B′) as a loosening or detachment of the primary amino group of trien from the Co with perhaps some rearrangement of the carboxyl and (trien)NH₂ groups about the Co. Correspondingly the notation trien* for species B and B′ (and for the remaining species) is used to represent such an activated trien group about the Co. The induction time does not strongly depend on the amino acid, so that this step would not be expected to involve an amino group from the amino acid. With the detachment of an –NH₂ group from the Co, a H₂O molecule or OH⁻ ion may occupy the coordination site left vacant, and we accordingly allow for the complex ion to have a charge of 2+ or 1+. The change of visible spectra (*cf.* Figure 10) in basic solutions is in accordance with the incorporation of an OH⁻ or H₂O into the inner coordination sphere. We believe that the replacement is for an –NH₂ group of the trien ligand and not for the carboxylate group, since the uv band at 220 mμ does not change with racemization. This band is due to an n–π* transition of the chelated carboxylate group,[11,12] whereas the corresponding absorption band for a free amino acid is at approximately 190 mμ and less intense than the observed band.

In terms of the pathway depicted in (1), we can rationalize the racemization results as follows.

Solutions in Charcoal Plus Water. The initial reaction (A → B and A′ → B′) is catalyzed by charcoal to the extent that the induction period is not observed in Figure 9. The first change in CD in Figure 9 is due to the reaction B ⇌ B′ for the prol complexes, and B ⇌ C ⇌ C′ for the phala complex. The conclusion that the phala complex goes to structure C (the β₁ isomers) before the plateau in Figure 9 is reached is rationalized by comparison of our CD spectra at the plateau (see Figures 4f, 5g, and 6f) with those reported by Lin and Douglas.[13] Our CD spectra at the plateau resemble the average CD spectra for the β₁ isomers of the ala complexes reported by these workers, and those of the prol complexes resembles the average CD curve for β₂ isomers. In these comparisons it is assumed that the phala complex exhibits CD spectra similar to those of ala complexes. The steps B ⇌ B′ and B ⇌ C ⇌ C′ can occur by the breaking and remaking of Co–N and Co–O bonds with interchange

(10) D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Chem. Commun.*, 583 (1969).

(11) D. Urry and H. Eyring, *J. Amer. Chem. Soc.*, 86, 4574 (1964).

(12) J. P. Jennings, W. Klyne, and P. M. Scopes, *J. Chem. Soc.*, 294 (1965).

(13) C. Y. Lin and B. E. Douglas, *Inorg. Chem. Acta*, in press.

of the positions of various groups about the cobalt. It is known from racemization studies on trien–cobalt ions that charcoal catalyzes Co–N bond breakage.[14,15] It is to be noted that the CD spectrum at the plateau of Figure 9 for the d and l complexes of proline is *not* identical with (although very similar to) that obtained by mixing the starting d and l compounds in various proportions (see Figure 12). This fact helps substantiate the assumptions that step $A \rightarrow B$ or $A' \rightarrow B'$ occurs and that changes other than the interconversion of cis-β_2-l-[Co(trien)(L-prol)]$^{2+}$ and cis-β_2-d-[Co(trien)-(L-prol)]$^{2+}$ (A $\rightleftarrows$ A') occur.

According to the present mechanism the remaining optical activity of B $\rightleftarrows$ B' (the prol complexes) or B $\rightleftarrows$ C and C $\rightleftarrows$ C' (the phala complex) is lost by the racemization of the L-amino acid in steps C $\rightleftarrows$ D and C' $\rightleftarrows$ D' (for the phala complex) or B $\rightleftarrows$ E and B' $\rightleftarrows$ E' (for the prol complexes). The resulting species which yield zero CD are the equilibrium mixture of B, B', E, and E' (for the prol complexes) or C, C', D, and D' for the phala complex. Although free amino acids do not racemize under the conditions of our experiment, it is possible that the Co(III) ion forms a complex with the amino acid from which the racemization occurs. As an example of such a structure, we might consider the tridentate chelation of the amino acid on the cobalt, such as is shown in eq 2.

l-[Co(trien)(L-AA)]$^{2+}$ activated state l-[Co(trien)(D-AA)]$^{2+}$ (2)
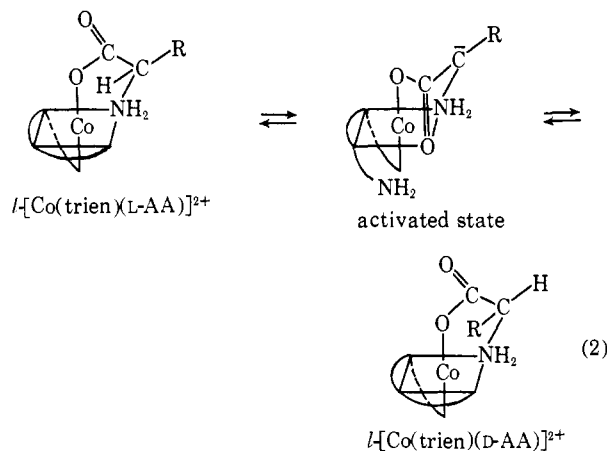
From other studies it has been found that metal ions help to stabilize carbanions.[16] Racemization of the amino acid in the final step is also in accord with the observation that the last step of racemization occurs much more slowly for the prol complex than for the phala complex, which one would expect because of the ring structure of the proline. The inflection in the CD *vs.* time curve (see Figure 9) is brought about by k_2 and k_{-2} (or k_4 and k_{-4}) being much greater than k_6 and k_{-6} (or k_5 and k_{-5}). Thus if one starts with the l complex (compound A in eq 1), the rate of formation of D' is not appreciable until species B' and C' are abundant. Then the concentration of D' increases sharply, and since D' has a positive rotation or ellipticity, the overall CD curve increases positively with the concentration of D'.
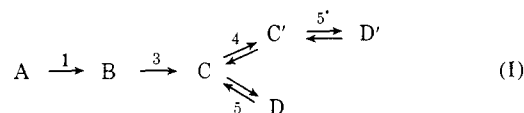
(14) D. Sen and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, **10**, 269 (1959).
(15) B. E. Douglas, *J. Amer. Chem. Soc.*, **76**, 1020 (1954).
(16) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 142–143.

Prol Complexes in Water. The types of changes occurring parallel those in charcoal and water, and we expect the rate-determining steps at each stage to compare accordingly. The large difference in the two cases is the lack of catalysis in water without charcoal, and hence the much slower rates. Observation of the induction time in water is also a case of the lack of catalysis.

Prol Complexes in Base. An induction time is noted in base so that step $A \rightarrow B$ (or $A' \rightarrow B'$) is apparent, although substantially catalyzed by OH$^-$ ions. The fact that the shape of the CD curve does not change while it grows smaller can be explained if the reaction pathway is described by (I), and if step 3 is rate determining after the induction time.

$$A \xrightarrow{1} B \xrightarrow{3} C \underset{5}{\overset{4}{\rightleftarrows}} \begin{matrix} C' \overset{5'}{\rightleftarrows} D' \\ D \end{matrix} \qquad (I)$$

Phala Complexes in Water or Base. In the case of the phala complex, a shift of approximately 20 mμ in λ_{max} is observed as the racemization continues to completion. This can be explained by again assuming that the reaction pathway is described by (I). In this case, the relative rates of steps 3 and 4 are comparable (and are slower than 5 or 5'), such that B and C are both present during the racemization. The shift of λ_{max} to longer wavelength is due to the presence of C (the β_1 isomer). For the ala complex the β_1 isomer has a CD max at 12 mμ longer wavelength than the β_2 isomer,[13] and from a comparison of the spectra of the phala and ala complexes we assume that there is a similar difference in λ_{max} for our case. From ref 13 it is noted that λ_{max} is the same for l-cis-β_2-[Co(trien)-(L-prol)]$^{2+}$ and l-cis-β_1-[Co(trien)(L-prol)]$^{2+}$ so that steps 3 and 4 may both be rate determining in the racemization of the d-prol complex in base. For l-[Co-(trien)(L-prol)]$^{2+}$ the β_2 and β_1 isomers have maxima at different wavelenghts so it is unlikely that there is any significant concentration of species "C" during the initial steps of racemization, since the initial spectrum does not change shape until the CD intensity is much smaller than the initial value. Then, in addition to the main peak at 460 mμ, there appears a peak at 510 mμ, indicating that both the cis-l-β_2 and cis-l-β_1 isomers may be present.

Rate Constants. A general solution of eq 1 is unwieldy, so we shall quantitatively consider only those cases in which a single rate constant may be extracted. If our mechanism is correct, the first few CD spectra in charcoal plus water and also those curves for the prol complexes in water *after* the induction period should correspond to the kinetics for the opposing reactions B $\rightleftarrows$ B' (for the prol complexes) or C $\rightleftarrows$ C' (for the phala complexes). Considering first the prol complexes, we note that the molar ellipticity at any time is related to the relative concentrations of B and B' (C_B and $C_{B'}$) by the equation

$$\theta = \frac{C_B \theta_B}{C_0} + \frac{C_{B'} \theta_{B'}}{C_0} \qquad (3)$$

Here θ_B and $\theta_{B'}$ are the molar ellipticities for pure B and B', respectively, and C_0 is the initial concentration of starting material (B or B'). From the kinetics

Table II. Rate Constants for Various Steps

Compound	Conditions	Temp, °C	Rate constant, sec^{-1}
l-[Co(trien)(L-prol)]I$_2$	H$_2$O + charcoal	95	$k_2 + k_{-2} = 3.9 \times 10^{-4}$
d-[Co(trien)(L-prol)]I$_2$	(0.5 mg charcoal/mg compound) assuming initial curves represent optically pure materials		$k_2 = 0.9 \times 10^{-4}$ $k_{-2} = 3.0 \times 10^{-4}$
d-[Co(trien)(L-prol)]I$_2$	H$_2$O	95	$k_2 + k_{-2} = 3.0 \times 10^{-5}$ $k_2 = 1.09 \times 10^{-5}$ $k_{-2} = 1.91 \times 10^{-5}$
l-[Co(trien)(L-phala)]I$_2$	H$_2$O + charcoal (0.35 mg charcoal/mg compound)	95	$k_4 + k_{-4} = 4.07 \times 10^{-3}$
l-[Co(trien)(L-prol)]I$_2$	Buffer, pH 9.65	95	$k_3 = 2.2 \times 10^{-4}$
l-[Co(trien)(L-prol)]I$_2$	Buffer, pH 10.56	92	$k_3 = 7.9 \times 10^{-4}$
l-[Co(trien)(L-prol)]I$_2$	Buffer, pH 11.3	92	$k_3 = 9.9 \times 10^{-4}$
d-[Co(trien)(L-prol)]I$_2$	Buffer, pH 9.65	95	$k_{3'} = 1 \times 10^{-3}$
l-[Co(trien)(L-phala)]I$_2$	Water	95	$(k_4^* + k_{-4}^*)$ or $k_3 = 1.8 \times 10^{-5}$
l-[Co(trien)(L-phala)]I$_2$	Buffer, pH 9.65	95	$(k_4^* + k_{-4}^*)$ and $k_3 = 4 \times 10^{-4}$

for reversible reactions one readily finds that

$$\theta = \theta_{eq} + (\theta_1 - \theta_{eq})e^{-(k_2 + k_{-2})t} \quad (4)$$

where the molar ellipticity when B and B' have equilibrated (θ_{eq}) is given by

$$\theta_{eq} = \frac{\theta_1 k_{-2} + \theta_2 k_2}{k_2 + k_{-2}} \quad (5)$$

Rearrangement of eq 4 gives

$$\ln \frac{(\theta - \theta_{eq})}{(\theta_B - \theta_{eq})} = -(k_2 + k_{-2})t \quad (6)$$

Equation 6 is derived for prol complex, but by changing subscripts B to C and rate constants k_2 and k_{-2} to k_4 and k_{-4}, respectively, the same equation applies to phala, assuming step 4 to be rate determining in water plus charcoal. The plots corresponding to eq 6 at peak maxima for all the complexes in charcoal plus water and for the prol complexes in water are shown in Figure 13, from which $k_2 + k_{-2}$ and $k_4 + k_{-4}$ are
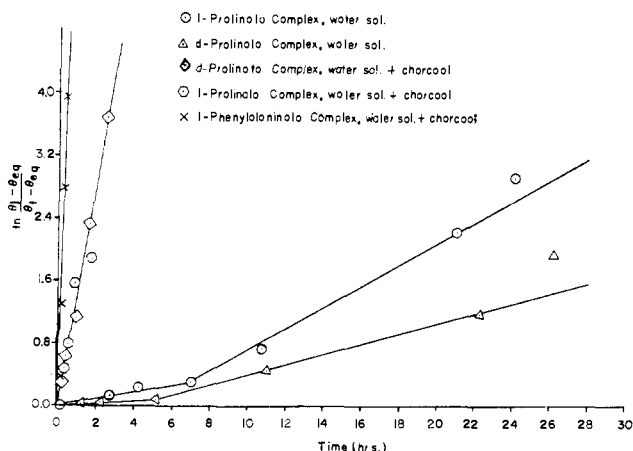

Figure 13. Plot of eq 6 for complexes in water plus charcoal and water at 95°.

obtained from the linear segments and listed in Table II. The numerical value of $k_2 + k_{-2}$ for the water solution was taken as the average of the slopes for the d and l complexes. Assuming that the initial compounds are optically pure, we obtained k_2 and k_{-2} separately from eq 5. These equilibrium values are

obtained from curve f in Figure 4 and curve g in Figure 5 (the latter two curves are very nearly identical). While the rate constants in charcoal likely depend on the activity of the catalyst, which we have not independently measured, the measurements in charcoal proved invaluable in equilibrating the d and l isomers and made possible the separation of k_2 and k_{-2} for the prol complexes. For the phala complex, $\theta_{C'}$ for the d isomer is not known, so k_4 and k_{-4} could not be separated. The plot for the rate constant is based on curve f in Figure 6 as the equilibrium for the steps 4 and -4.

For the prol complex in base the rate constants k_3 and $k_{3'}$ are obtained by the plot of ln θ_i/θ vs. t (θ_i is the initial CD) after the induction period for the prol complexes in base, if the present treatment is correct. The plots are shown in Figure 14 for pH 9.65; the
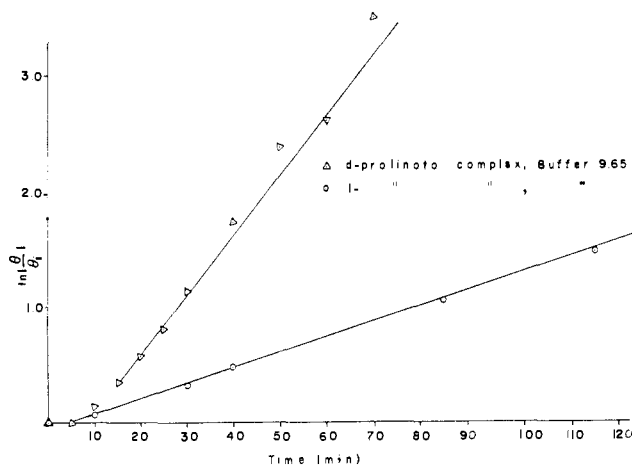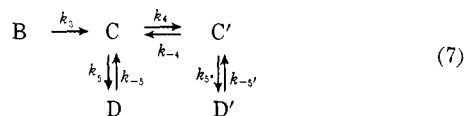

Figure 14. Plot of first-order rate constants for prol complexes in base at 95°.

slopes of the linear segments of this figure are given in Table II. Also shown in Table II are rate constants k_3 for the racemization of cis-β_2-l-[Co(trien)-(L-prol)]$^{2+}$ in basic solutions of higher pH values, for which the racemization curves are not shown in Figure 14. These curves, however, are linear and extrapolate to the origin; i.e., they display no induction times. The induction times are much less in base than in water, which shows the catalytic influence

of OH⁻ ions on the rate constants k_1 and k_1'. Base also catalyzes steps 3 and 3', as seen from the different rate constants, although a quantitative treatment of the effect cannot be given from the sparse data. Also, the concentration of NH_4^+ ions may affect the rate, and this latter concentration varied with the pH for the buffers used.

For cis-β_2-l-[Co(trien)(L-phala)]$^{2+}$ in water and basic solutions, λ_{max} shifts with increasing racemization (see Figure 7). Hence the plot of $\ln \theta_i/\theta$ vs. t does not simply represent the decrease in concentration of one given compound (i.e., steps 3 and 4 are both rate determining). The reaction pathway after the induction time in this case may be explained by the following equation

$$B \xrightarrow{k_3} C \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} C'$$
$$k_5 \updownarrow k_{-5} \quad k_{5'} \updownarrow k_{-5'}$$
$$D \qquad D' \qquad (7)$$

Assuming a rapid equilbrium between C and D, eq 7 can be further simplified to

$$B \xrightarrow{k_3} C^* \underset{k_{-4}/(1+K_{5'})}{\overset{k_4/(1+K_5)}{\rightleftarrows}} C'^* \qquad (8)$$
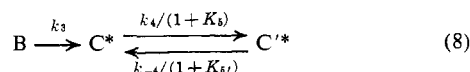
Where $C_{C^*} = C_C + C_D$, $C_{C^{*'}} = C_{C'} + C_{D'}$, $K_5 = k_5/k_{-5}$, and $K_{5'} = k_{5'}/k_{-5'}$. The integral equations and the solutions of eq 8 can be found in the literature.[17,18] The molar ellipticity at any time is given by

$$C_0\theta = C_B\theta_B + C_{C^*}\theta_{C^*} + C_{C^{*'}}\theta_{C^{*'}} \qquad (9)$$

Relating the solutions found in ref 18 to the molar ellipticity by eq 9 and remembering that $\theta_{C^*} = -\theta_{C^{*'}}$, the following equation is obtained

$$\theta = B_0\left\{\theta_B e^{-k_3 t} + \theta_{C^*}\frac{(k_{-4}^* - k_4^*)}{(k_4^* + k_{-4}^*)}[1 - e^{-(k_4^*+k_{-4})t}] + \theta_{C^{*'}}\frac{(k_3 + k_4^* + k_{-4}^*)}{(k_4^* + k_{-4}^* - k_3)}[(e^{-k_3 t} - e^{-(k_4^*+k_{-4})t})]\right\} \qquad (10)$$

where $= k_4^* = k_4/(1 + K_5)$ and $k_{-4}^* = k_{-4}/(1 + K_{5'})$, respectively. If it is assumed that $k_4 = k_{-4}$ and $k_5 = k_{5'}$, respectively, or simply $k_4^* = k_{-4}^*$, eq 10 will take the following form.

$$\theta = B_0\left[\theta_B + \frac{k_3\theta_{C^{*'}}}{2k_4^* - k_3}\right]e^{-k_3 t} - B_0\left[\frac{k_3\theta_{C^{*'}}}{2k_4^* - k_3}\right]e^{-2k_4^* t} \qquad (11)$$

The logarithmic plot of the rate data for this case is

(17) R. A. Alberty and W. G. Miller, J. Chem. Phys., 26, 1231(1957).
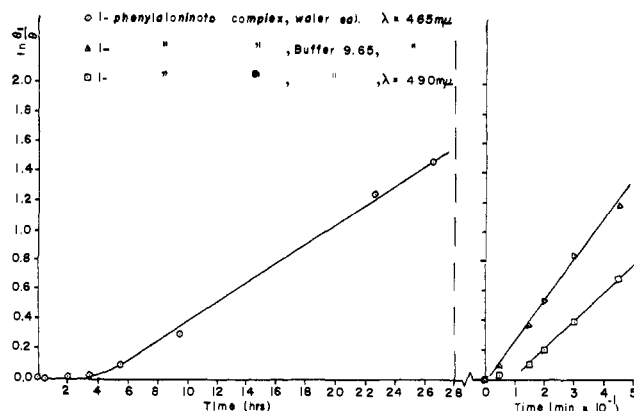(18) A. Rakowski, Z. Phys. Chem., 57, 321 (1907).

Figure 15. Plot of first-order rate constants for phala complexes in base and water, at 465 and 490 mμ, temperature = 95°.

shown in Figure 15. A straight line is obtained from the plot of $\ln \theta_i/\theta$ vs. t at two different wavelengths. Using the approximation that at 490 mμ (λ_{max} for species B), the second term in eq 11 can be neglected (this assumption may be justified because the second term in eq 11 involves only the ellipticity of species C^*, which has its maximum absorption about 20 mμ away from that of species B), the slope of this straight line at 490 mμ will give us k_3. With the same argument k_4^* is obtained from the slope of the straight line at 465 mμ (λ_{max} of species C). These rate data are tabulated in Table II along with the others.

Comparing the results both in Figures 9, 13, 14, and 15 and in Table II, one sees that there is little difference in the induction period for the prol and phala complexes at a given pH. This is in accord with our conclusion that steps A → B or A' → B' involve changes not primarily connected with the amino acid structure. The rate constants k_2 and k_{-2} are greater than k_4 and k_{-4}, as one would expect, considering the greater steric hindrance offered by the prol complex to the attack on its Co–N bond and by the stronger bond formed between the secondary "N" of proline and Co than between the primary "N" of phenylalanine and cobalt.

More work is needed and hence is in progress to further clarify the mechanism of racemization of the present complexes.