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The Reaction of Ethylenediamine with Tetradentate Cobalt(III) Complexes

Laura H. C. Huang

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THE REACTION OF ETHYLENEDIAMINE
WITH TETRADENTATE COBALT(III) COMPLEXES

by

Laura H. C. Huang

A Thesis
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
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Laura H. C. Huang

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TABLE OF CONTENTS

	Page
LIST OF ABBREVIATIONS	vi
LIST OF TABLES	vii
LIST OF FIGURES	viii
I. INTRODUCTION	1
II. EXPERIMENTAL	5
A. Preparation of the Complexes	5
1. Preparation of (-)- <u>trans</u> -ethylenediamine-N, N'-diacetato(ethylenediamine)cobalt(III) nitrate	5
2. Preparation of <u>cis</u> -ethylenediamine-N, N'-diacetato(ethylenediamine)cobalt(III) perchlorate	6
3. Preparation of (+)- <u>trans</u> -N,N'-diethylethyl- enediamine-N,N'-diacetato(1-propylenediamine)- cobalt(III) perchlorate	7
4. Preparation of (-)- <u>trans</u> -ethylenediamine-N, N'-diacetato(1-propylenediamine)cobalt(III) perchlorate	8
5. Preparation of (+)-potassium(ethylenediamine- tetraacetato)cobalt(III)	8
B. Preparation of Ion Exchange SE-Sephadex Column ...	9
C. Reaction of Complexes with Ethylenediamine	9
1. The reaction of (-)- <u>trans</u> -ethylenediamine-N, N'-diacetato(ethylenediamine)cobalt(III) nitrate	9
2. The reaction of (+)- <u>trans</u> -N,N'-diethylethyl- enediamine-N,N'-diacetato(1-propylenediamine) cobalt(III) perchlorate	10
3. The reaction of <u>cis</u> -ethylenediamine-N, N'-diacetato(ethylenediamine)cobalt(III) perchlorate	11

4.	The reaction of (-)- <u>trans</u> -ethylenediamine-N, N'-diacetato(1-propylenediamine)cobalt(III) perchlorate	11
5.	The reaction of (+)-potassium(ethylenediamine- tetraacetato)cobaltate(III)	11
D.	Reaction of Complexes with 10% Ethylenediamine Solution	12
1.	The reaction of <u>trans</u> -tetradentate complexes	12
2.	The reaction of the <u>cis</u> -tetradentate complex	12
E.	Reaction of Complexes with Buffered Ethylenediamine Solution (pH = 9.5)	13
1.	Preparation of buffered ethylenediamine solution	13
2.	The reaction of potassium(ethylenediamine- tetraacetato)cobaltate(III)	13
3.	The reaction of <u>trans</u> -tetradentate complexes	13
4.	The reaction of the <u>cis</u> -tetradentate complex	14
F.	The Reaction of Complexes with Aqueous Sodium Hydroxide	14
1.	The reaction of the <u>trans</u> -tetradentate complex	14
2.	The reaction of the <u>cis</u> -tetradentate complex	14
G.	Equipment	15
III.	RESULTS AND DISCUSSION	16
A.	Preparation and Characterization of D-(+)- <u>trans</u> -N, N'-Diethylethylenediamine-N,N'-diacetato(1-propyl- enediamine)cobalt(III) Perchlorate	16
1.	Visible absorption spectrum	16
2.	Proton magnetic resonance spectrum	18
3.	Optical rotatory dispersion curve	24
B.	Separation of the Reaction Mixture	25
1.	Ion exchange sephadex chromatography	25

2. Thin layer chromatography	25
C. Reaction of Complexes with Ethylenediamine and with Base	27
IV. SUMMARY	37
V. BIBLIOGRAPHY	38
VI. VITA	40

LIST OF ABBREVIATION

DEEDA	N,N'-Diethylethylenediamine-N,N'-diacetate
DSS	2,2-Dimethyl-2-silapentane-5-sulfonate sodium salt
EDDA	Ethylenediamine-N,N'-diacetate
EDTA	Ethylenediaminetetraacetate
en	Ethylenediamine
1-pn	1-Propylenediamine
ord	Optical rotatory dispersion
PDTA	Propylenediaminetetraacetate
pmr	Proton magnetic resonance spectroscopy
tlc	Thin layer chromatography

LIST OF TABLES

Table		Page
I	Acetate ring proton chemical shifts of some tetradentate cobalt(III) complexes	21
II	The reaction of complexes with ethylenediamine	29
III	The reaction of complexes with buffered ethylenediamine and base	34

LIST OF FIGURES

Figure		Page
1	Mechanism for reaction of ethylenediamine with ethylenediaminetetraacetatocobaltate(III)	3
2	Mechanism for reaction of ethylenediamine with propylenediaminetetraacetatocobaltate(III)	4
3	The expected shifts and splittings in tetragonal complexes of cobalt(III)	17
4	The absorption spectra of $\text{trans-}[\text{Co(1-pn)(DEEDDA)}]^+$ and $\text{trans-}[\text{Co(en)(DEEDDA)}]^+$	19
5	The pmr spectrum of (+)- $\text{trans-}[\text{Co(1-pn)(DEEDDA)}]^+$...	20
6	Anisotropic shielding expected for C-N bond	21
7	Absolute configuration for D- $\text{trans-}[\text{Co(1-pn)(EDDA)}]^+$ and D- $\text{trans-}[\text{Co(1-pn)(DEEDDA)}]^+$	23
8	The ord curve of D- $\text{trans-}[\text{Co(en)(EDDA)}]^+$ and D- $\text{trans-}[\text{Co(1-pn)(DEEDDA)}]^+$	26
9	Proposed mechanism for (-)- $\text{trans-}[\text{Co(en)(EDDA)}]^+$ reacted with ethylenediamine	28

I. INTRODUCTION

In recent years several investigators have been involved in the study of reactions of transition metals complexes which result in some stereoselectivity in the formation of products. Dwyer^{1,2} and Bailar³ have studied the reactions of ethylenediamine (en) with several cobalt(III) complexes of ethylenediaminetetraacetic acid (H_4EDTA). They observed that the reaction of anhydrous ethylenediamine with $(-)-K[Co(EDTA)] \cdot 2H_2O$ resulted in the formation of 63% of the isomer $L-(-)-[Co(en)_3]^{3+}$ as product with the remainder being the $D-(+)$ -isomer. Gillard⁴ and Busch⁵ studied the corresponding reaction of en with $(-)-[Co((+)-PDTA)]^-$ and obtained 100% $(+)-[Co(en)_3]^{3+}$ as product.

The stereoselectivity observed in these reactions suggested that reaction must occur by a series of stepwise displacement processes. Busch and Cooke⁶ postulated a mechanism that involves the addition of the first ethylenediamine as the rate-determining step. X-ray studies by Weakliem and Hoard⁷ have shown that the bonds holding the carboxyl groups that are coplanar with the N-C-C-N chelate ring are highly strained. It was postulated that replacement of one of these carboxyl groups by one end of the ethylenediamine was the first step⁶. The inversion of configuration by some two-thirds of the cobalt atoms in the $[Co(EDTA)]^-$ case was explained by the assumption that after the first step the free end of the ethylenediamine has equal probability of replacing each of

the three carboxyl groups that remain coordinated at this stage (Fig. 1). The addition of further ethylenediamine would lead to the products shown.

The retention of configuration for the reaction of $D-[Co-((+)-PDTA)]^-$ arises from a steric effect due to the methyl group^{5,7} which is so oriented that it tends to weaken the two metal carboxyl bonds nearest the carbon atom to which the methyl group is attached, and this then determines the position of entry of ethylenediamine and of its ring closure (Fig. 2).

The purpose of this research was to study the reaction of ethylenediamine with these cobalt(III) complexes in more detail. In this study a series of optically active metal compounds which would approximate intermediates in those proposed mechanisms has been prepared and characterized. These models were chosen such that they were similar to the intermediate expected for planar attack by the ethylenediamine molecule (Fig. 1). Those complexes contained the ligands ethylenediamine-N,N'-diacetate (EDDA) and N, N'-diethylethylenediamine-N,N'-diacetate (DEEDDA) with the coordinated oxygens in a trans configuration and the remaining planar positions occupied by various diamines. The ethylenediamino- and 1-propylenediaminocobalt(III) complexes of EDDA have previously been prepared and resolved^{8,9}. The synthesis of D-(+)-trans- $[Co(1-pn)(DEEDDA)]^{+1}$ and its characterization through visible absorption spectroscopy, optical rotatory dispersion and nuclear magnetic resonance spectroscopy is now reported. The reactions of these complexes with en were studied at various conditions and

in solutions buffered to various pH's.

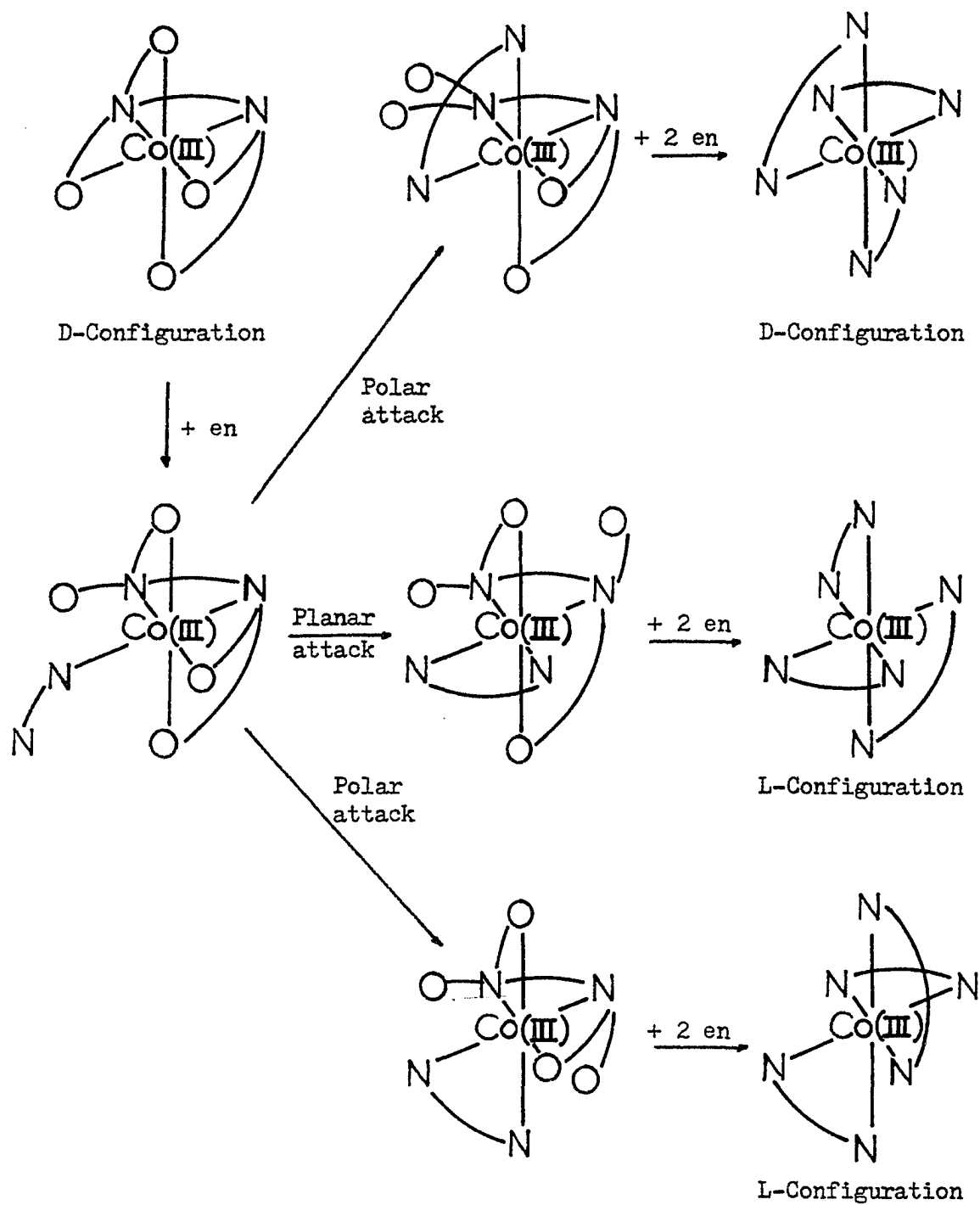


Figure 1. Mechanism for reaction of ethylenediamine with ethylenediaminetetraacetatocobaltate(III)⁶.

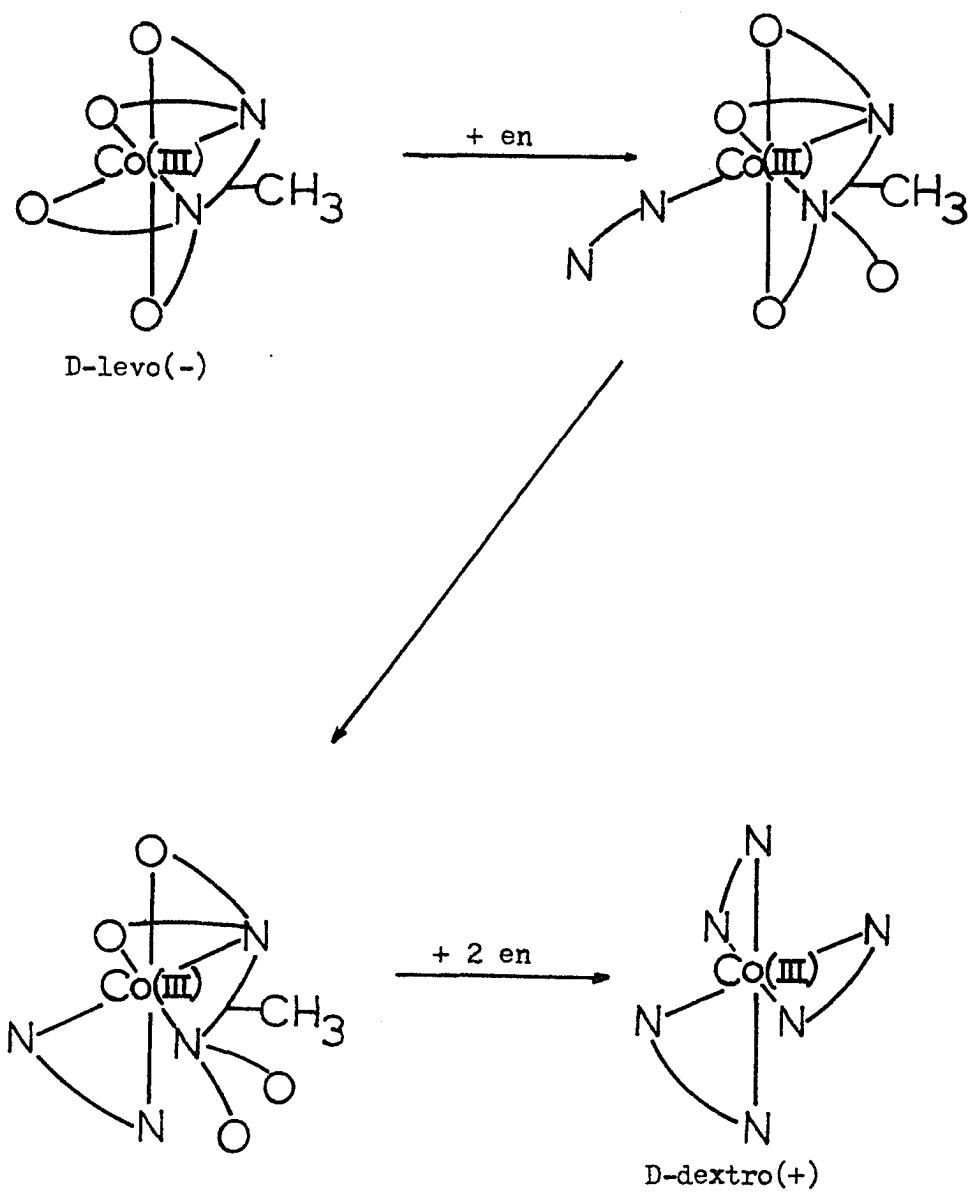


Figure 2. Mechanism for reaction of ethylenediamine with propylenediaminetetraacetatocobaltate(III)⁶

II. EXPERIMENTAL

A. Preparation of the Complexes

1. Preparation of (-)-trans-ethylenediamine-N,N'-diacetato(ethylenediamine)cobalt(III) nitrate

The methods used to prepare and resolve the complex are similar to those described in reference 8 and reference 9. A suspension of 13.1 g (0.1 mole) of cobaltous carbonate and 17.6 g (0.1 mole) of ethylenediamine-N,N'-diacetic acid in 250 ml of water was heated at 60°C with occasional stirring until the carbon dioxide evolution ceased (about 40 min). The pink solution was filtered through a medium fritted glass filter. The precipitate was washed with 15 ml of hot water. To the combined filtrate and washings were added successively 50 ml of 2N nitric acid, 10 g of activated charcoal, and 6.1 g (0.1 mole) of 98% ethylenediamine in 40 ml of water. The oxidation was carried out by the dropwise addition of 11 g of 30% H₂O₂ in 15 ml of H₂O to the stirred solution. After oxidation of the complex and removal of the charcoal, evaporation of the solution on a steam bath to about 50 ml yielded red-violet crystals. These were filtered, washed with three 10-ml portions of water, 50% ethanol, ethanol, and acetone, and air-dried; yield of (+)-trans-[Co(en)(EDDA)] NO₃·H₂O 22.5 g. The compound was identified by its visible absorption spectrum. This compound was then resolved as follows. A solution of 7.464 g (0.02 mole) of trans-[Co(en)(EDDA)] NO₃·H₂O in 160 ml of water was passed through a column (diameter

3 cm), which contained 200 ml of Dowex 1-X8 strong-base anion exchange resin (50-100 mesh) in the chloride form at a rate between 1 and 2 ml/min. The eluted complex was quantitatively collected in a stirred suspension of 3.638 g (0.01 mole) of silver tartrate and 1.501 g (0.01 mole) of tartaric acid in 100 ml of water which was kept shielded from light. The coagulated silver chloride was then filtered, but not washed, and the filtrate was evaporated to about 50 ml on a rotary evaporator. To the stirred solution at 40°C was then added 15 ml of ethanol. Within a few minutes crystallization took place. After stirring 15 minutes, 10 ml of water was added and the mixture stirred an additional 15 minutes. The solid (-)-trans-[Co(en)EDDA]Htart.H₂O was then filtered at 40°C and washed with two 5-ml portions of 60% ethanol, ethanol, and ether. The compound was repeatedly recrystallized from 50% ethanol until the molar rotation was constant. The (-)-diastereomer was converted to the nitrate by passing the solution (1.5 g of (-)-trans-[Co(en)EDDA].Htart.H₂O in 20 ml of water) through a Dowex-1 anion-exchange resin (50-100 mesh) in the nitrate form. Evaporation of the solution on a rotary evaporator to dryness yielded red crystals (-)-trans-[Co(en)EDDA]-NO₃.H₂O, 1 g. Comparison of the visible and ord spectra with the published spectra^{8,9} indicated that the desired compound was obtained.

2. Preparation of cis-ethylenediamine-N,N'-diacetato(ethylene-diamine)cobalt(III) perchlorate

This compound was furnished by D. W. Cooke⁸. Identification was confirmed by comparison of the visible spectrum of the compound

with spectrum previously obtained⁸.

3. Preparation of (+)-trans-N,N'-diethylethylenediamine-N,N'-diacetato(1-propylenediamine)cobalt(III) perchlorate

To a stirred suspension of 18.40 g (0.05 mole) of Ba(DEEDDA) dissolved in 100 ml of water at about 50°C, 14.05 g (0.05 mole) of cobaltous sulfate heptahydrate dissolved in 100 ml of water was added over a period of 30 min. After heating at 60°C for 40 min, the solution was filtered through a layer of Fuller's earth. The precipitate was washed with 20 ml of hot water. To the combined filtrate and washings were added successively 25 ml of 2N HNO₃, 5 g of activated charcoal and 3.7 g (0.05 mole) of 1-propylenediamine. The oxidation was carried out by the dropwise addition of 5.5 g of 30% H₂O₂ in 15 ml of water to the stirred solution. After filtering through a layer of Fuller's earth, the solution was placed on the Dowex 50 cation exchange resin column (Diameter 8.5 cm, length 120 cm). The absorbed band was eluted with 0.3N HCl at 0.5 to 1 ml/min. The red band was collected and evaporated to dryness. The yield of red crystals of (+)-trans-[Co(1-pn)DEEDDA]Cl was 11.17 g. To a 0.72 g of (+)-trans-[Co(1-pn)DEEDDA]Cl dissolved in 50 ml of absolute alcohol, 0.18 g of lithium perchlorate dissolved in 10 ml of absolute alcohol was added. The red precipitate was (+)-trans-[Co(1-pn)DEEDDA]ClO₄·1½H₂O. Yield 0.51 g ([M]₅₈₉ +2617°). Anal. Calcd. for [CoC₁₃H₂₈N₄O₄]ClO₄·1½H₂O: C, 31.89; N, 11.44; H, 6.33. Found: C, 31.98; N, 11.49; H, 6.45.

4. Preparation of (-)-trans-ethylenediamine-N,N'-diacetato(1-propylenediamine)cobalt(III) perchlorate

The procedure for preparation was the same as that described in reference 9. Recrystallization of the (-)-isomer was accomplished by dissolving 1.2 g of product in 100 ml of water at 70°C and then adding 400 ml of absolute ethanol. After the solution had stood for three days, red crystals precipitated out which were filtered, washed with 50% ethanol, ethanol, and ether, and air-dried. The yield of pure (-)-trans-[Co(1-pn)(EDDA)]ClO₄ was 0.8 g ([M]₅₈₉ -5870°; literature value⁹ is -5620°).

5. Preparation of (+)-potassium(ethylenediaminetetraacetato)cobalt(III)

The (+)-isomer was furnished by D. W. Cooke. Recrystallization of the (+)-isomer was accomplished by dissolving 5.28 g of (+)-K-[Co(EDTA)] in 30 ml of water. The solution was cooled to at least 4°C in ice for 10 min. To the cooled solution, ethanol (180 ml) was added. On scratching the sides of the vessel, the dextro isomer crystallized. The yield of violet crystals which were filtered, washed with 50% ethanol, ethanol, and ether, and air-dried was 5.14 g. The ORD curve indicated that the desired compound had been obtained.

B. Preparation of Ion Exchange SE-Sephadex Column

About 15 g ion-exchange SE-Sephadex C-25 (Pharmacia Fine Chemicals Inc., Piscataway, N.J.) in the Na^+ form was stirred with 500 ml of 0.01M NaClO_4 . The ion-exchange Sephadex was allowed to settle for 30 min and the supernatant liquid decanted. After adding 100 ml of 0.01M NaClO_4 , the mixture was rapidly stirred and immediately poured into a column (diameter 2.5 cm, height 25 cm). The ion-exchange Sephadex was allowed to settle and a plug of glass wool was inserted to protect the surface. First 500 ml of 0.01M NaClO_4 and then 4 l of water were passed through the column at full flow rate (4 ml/min) and the column was ready for use.

C. Reaction of Complexes with Ethylenediamine

1. The reaction of (-)-trans-ethylenediamine-N,N'-diacetato(ethylenediamine)cobalt(III) nitrate

Three hundred ml (4.5 mole) of ethylenediamine was added to 0.3062 g (8×10^{-4} mole) of (-)-trans- $[\text{Co}(\text{en})\text{EDDA}]\text{NO}_3 \cdot \text{H}_2\text{O}$ at 25°C . The solution was allowed to stand for 15 hours before 6 l of ether was added to the solution to extract the ethylenediamine. The ether layer was removed and the reaction mixture was placed on a SE-Sephadex column. The absorbed band was eluted with 0.01M NaClO_4 at full flow rate (4 ml/min). After several hours three bands were separated. Numbering from the bottom of the column the first two bands were taken off by eluting with 0.01M NaClO_4 . The third band was absorbed on the top of the column. Using a glass tube attached

to a water aspirator, the resin was removed from the top of the column. The complex was removed from resin using 0.2M NaClO₄. The solutions were evaporated to dryness using a rotary evaporator and the eluting agent removed from the complexes by washing with absolute ethanol. Absorption, ord and pmr spectra of the complexes showed that the first band contained starting material. However the Molar rotation of this complex had decreased. Compared to the pure (-)-trans-[Co(en)EDDA]NO₃·H₂O it retained 44.5% of its optical activity. The second band was identified by visible, pmr and ord spectra to be racemic cis-[Co(en)EDDA]ClO₄. Yield 17.5 mg. The third fraction was racemic [Co(en)₃](ClO₄)₃. Yield 7 mg. The yield of this fraction was determined spectrophotometrically.

2. The reaction of (+)-trans-N,N'-diethylethylenediamine-N,N'-diacetato(1-propylenediamine-cobalt(III) perchlorate

Three ml (5×10^{-2} mole) of ethylenediamine was added to 0.0545 g (1×10^{-4} mole) of (+)-trans-[Co(1-pn)(DEEDDA)]ClO₄ at 25°C. The solution was allowed to stand for 19 hours. Three hundred ml of ether was added to the reaction mixture to extract the ethylenediamine. The ether layer was removed and the solution placed on a SE-Sephadex chromatography column. Two bands were separated in the same manner described for the EDDA complex. Visible absorption spectrum of the first band showed that it contained the unreacted starting material. Visible absorption, nmr and ord spectra, and tlc showed that the second band contained (\pm)-[Co(en)₃](ClO₄)₃.

3. The reaction of cis-ethylenediamine-N,N'-diacetato(ethylenediamine)cobalt(III) perchlorate

Fifty ml (0.75 mole) of ethylenediamine was added to 0.1037 g (3×10^{-4} mole) of cis-[Co(en)EDDA]ClO₄ at 25°C. After 70 hours, ether (4 l) was added to extract the ethylenediamine. The ether layer was removed and the reaction mixture was placed on a SE-Sephadex column. Three bands were separated in the same manner as described for the trans EDDA complex. Visible absorption spectra of the complexes showed that the first band contained trans-[Co(en)EDDA]ClO₄; yield 74.3 mg. The second band contained cis-[Co(en)EDDA]ClO₄; yield 4.5 mg. The third band contained (\pm)-[Co(en)₃](ClO₄)₃; yield 15.1 mg. The concentration was determined spectrophotometrically.

4. The reaction of (-)-trans-ethylenediamine-N,N'-diacetato(1-propylenediamine)cobalt(III) perchlorate

The procedure described for the reaction of (-)-trans-[Co(en)-EDDA]⁺ with ethylenediamine (page 10) was followed. The first fraction was cis-[Co(1-pn)EDDA]ClO₄. The third fraction was (\pm)-[Co(en)₃](ClO₄)₃.

5. The reaction of (+)-potassium(ethylenediaminetetraacetato)-cobaltate(III)

Approximately one-tenth of a gram of the pure optical isomer of (+)-K[Co(EDTA)] was stirred with 50% aqueous ethylenediamine (1.5 ml) at 25°C. After 4 hours, the volume of the solution was adjusted to 25 ml and the rotation measured in a 5-cm tube. The Cotton Effect of the yellow compound indicated that the product is

optically active ($\alpha_{520} +0.30$).

D. Reaction of Complexes with 10% Ethylenediamine Solution

1. The reaction of trans-tetradentate complexes

- a. To each of 0.0942 g of trans-[Co(en)(EDDA)]⁺, trans-[Co(1-pn)(EDDA)]⁺, and trans-[Co(1-pn)(DEEDDA)]⁺, 25 ml (0.04 mole) of 10% ethylenediamine solution was added. After 24 hours the visible absorption spectra were measured (5 ml of reaction mixture diluted to 10 ml). The absorbance at 470 nm showed an increase of approximately 7% over that of the original complex.
- b. To 0.0462 g (1×10^{-4} mole) of (-)-trans-[Co(en)EDDA]NO₃·H₂O 25 ml (0.04 mole) of 10% ethylenediamine solution (pH = 11.7) was added. After 24 hours the Molar rotation of the solution was measured. Compared to the pure (-)-trans-[Co(en)EDDA]NO₃·H₂O the solution had retained 70% of its optical activity. After 48 hours the activity was reduced to 48% of the original activity.

2. The reaction of the cis-tetradentate complex

To 0.1162 g (3×10^{-4} mole) of cis-[Co(en)(EDDA)]ClO₄ twenty five ml (0.04 mole) of 10% ethylenediamine solution was added. After 24 hours the visible absorption spectrum was measured. The peak for the cis-isomer had decreased and a peak at 530 nm formed to give a spectrum which indicated the formation of the equilibrium mixture of

95% trans and 5% cis isomer.

E. Reaction of Complexes with Buffered Ethylenediamine
Solution (pH = 9.5)

1. Preparation of buffered ethylenediamine solution

To a 20% ethylenediamine solution which was cooled in an ice bath, conc. HCl was added dropwise until the pH of the solution was 9.5. This gives a solution which is 0.90 molar in en and 2.43 molar in enH^+ .

2. The reaction of potassium(ethylenediaminetetraacetato)cobaltate-(III)

To 50 mg of $(\pm)\text{-K}[\text{Co}(\text{EDTA})]$ 20 ml of buffered ethylenediamine solution was added. Within 4 hours the violet color of the solution had changed to yellow orange indicating the formation of $\text{Co}(\text{en})_3^{3+}$.

3. The reaction of trans-tetradentate complexes

To 0.0942 g of each of trans- $[\text{Co}(\text{en})(\text{EDDA})]^+$, trans- $[\text{Co}(\text{l-pn})(\text{EDDA})]^+$, and trans- $[\text{Co}(\text{l-pn})(\text{DEEDDA})]^+$, 25 ml of pH9.5 buffered ethylenediamine solution was added. After 24 hours the spectra were measured (5 ml of reaction mixture diluted to 10 ml). The visible and ord spectrum for each of the reaction mixtures was identical with that of the starting material. After 12 days the absorption spectra were obtained again and an increase of 15% in the absorbance at 470 nm was noted.

4. The reaction of the cis-tetradentate complex

To 0.1162 g (3×10^{-4} mole) of cis-[Co(en)(EDDA)]ClO₄ twenty five ml of buffered ethylenediamine solution was added. After one day and again after one week the absorption spectrum was measured (5 ml of reaction mixture diluted to 10 ml) and found to be identical with that of starting material.

F. The Reaction of Complexes with Aqueous Sodium Hydroxide

1. The reaction of the trans-tetradentate complex

To 0.0462 g (1×10^{-4} mole) of (-)-trans-[Co(en)EDDA]NO₃·H₂O 25 ml of aqueous NaOH solution (pH = 11.7) was added. After 24 hours the Molar rotation and visible absorption spectrum of the solution were measured. The compound retained 69% of its optical activity. After 48 hours the complex had retained 46% of its activity. The absorbance at 470 nm after 24 hours showed an increase of approximately 5.3% over that of original complex.

2. The reaction of the cis-tetradentate complex

To 0.0462 g (1×10^{-4} mole) of cis-Co(en)(EDDA)ClO₄ 25 ml of aqueous NaOH solution (pH = 11.7) was added. After one day the absorption spectrum was measured. The peak for the cis-isomer had decreased and a peak at 530 nm formed to give a spectrum which indicated the formation of the equilibrium mixture of 95% trans and 5% cis isomer.

G. Equipment

The visible absorption spectra were obtained using a Cary Model 14 spectrophotometer. The optical rotatory dispersion (ord) spectra were obtained with a Beckman Model-DU spectrophotometer, fitted with a Keston Model D polarimeter attachment (Standard Polarimeter Company, Hackensack, N.J.). The proton magnetic resonance (pmr) spectra were recorded using a Varian Model A-60 spectrometer.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of D-(+)-trans-N,N'-Diethylethylenediamine-N, N'-diacetato(1-propylenediamine)cobalt(III) Perchlorate

The complex trans-[Co(en)(DEEDDA)]⁺ has been prepared by Legg and Cooke⁸ and the trans configuration established by absorption and nmr spectroscopy. The corresponding cis compound was not formed. This suggests that the DEEDDA favors only a trans configuration⁸ because of steric interactions with the en. The similar trans-[Co(1-pn)(DEEDDA)]⁺ was prepared under analogous conditions and again no cis isomer was observed. When the reaction mixture was treated with charcoal to favor the formation of the more stable product the red compound isolated by chromatography exhibited a Cotton Effect in the ord spectrum indicating that the complex is optically active. The fact that the molar rotation was not changed after recrystallization reveals that only one enantiomer was formed. The absorption and pmr spectra established that DEEDDA is in a trans configuration.

1. Visible absorption spectrum

The expected shifts and splittings in tetragonal complexes of Cobalt(III) (Fig. 3) have been discussed theoretically by Ballhausen^{10,11} and Yamatera¹². The splitting of the T_{1g} excited state for trans-MA₄B₂ systems is twice the splitting of a cis complex. Therefore a shoulder is found on the first absorption

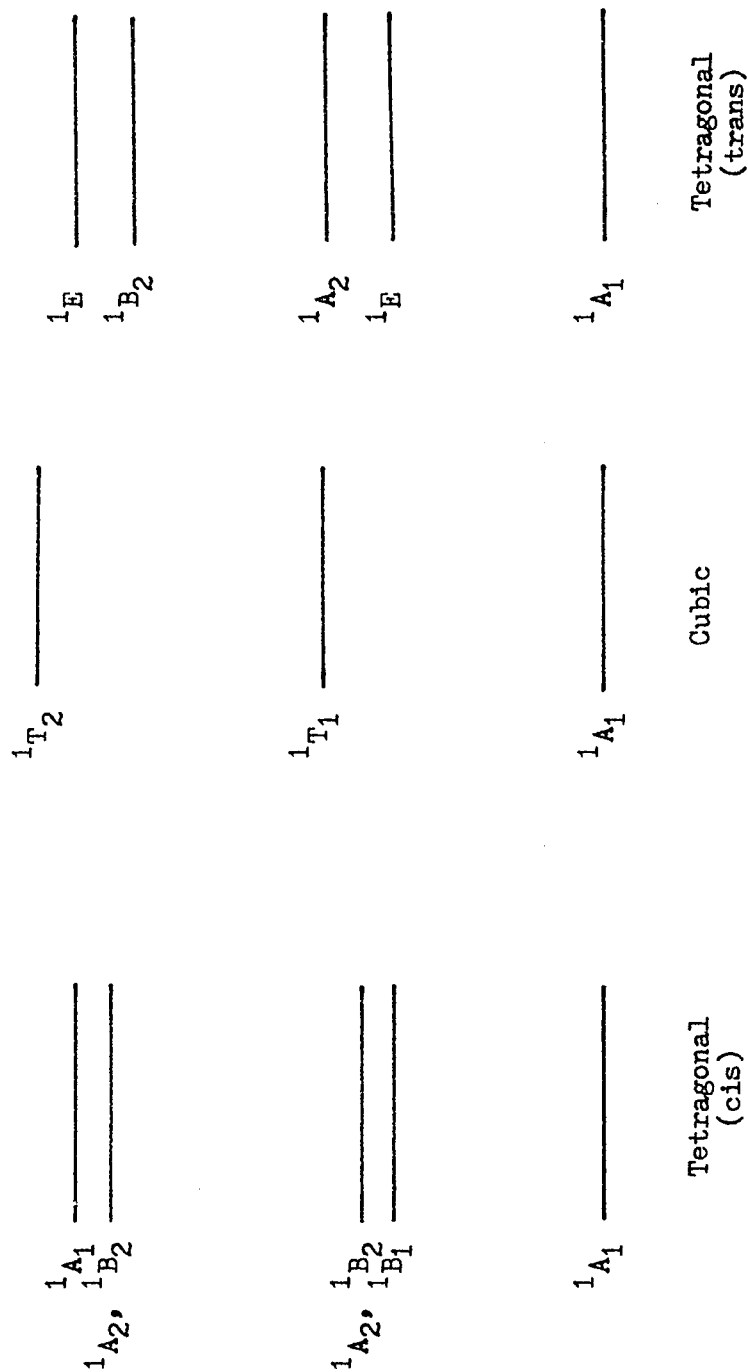


Figure 3. The expected shifts and splittings in tetragonal complexes of Cobalt(III).

band of the trans-MA₄B₂ complex but absent in a cis-MA₄B₂ spectrum because of the small splitting. The absorption spectra^{8,9} of trans-[Co(en)(DEEDDA)]⁺ and similar trans-[Co(L)(EDDA)]⁺, L = en, and 1-pn agree with this theory. The absorption spectrum of [Co(1-pn)-(DEEDDA)]⁺ (Fig. 4) is very similar to that of the ethylenediamine analog. This established that the DEEDA complex was in a trans configuration.

2. Proton magnetic resonance spectrum

The pmr spectrum of [Co(1-pn)(DEEDDA)]⁺ (Fig. 5) has been measured and found to be very similar to those obtained for trans-[Co(en)(DEEDDA)]⁺ and D-(+)-trans-[Co(1-pn)EDDA]⁺. The chemical shifts of the acetate ring protons are given in Table I. The resonance line assignments for trans-[Co(en)(DEEDDA)]⁺ have been reported by Legg and Cooke⁸. The protons associated with the acetate rings of that compound resulted in a symmetrical AB quartet found at relatively lower field (3.5 to 4.3 ppm) due to the combined deshielding effects of the carboxylate and amine groups. Similar results were obtained on compounds with similar acetate rings¹³⁻¹⁶. The chemical shifts of the acetate ring protons has been assigned in terms of the magnetic anisotropy of C-N bonds⁸. According to the anisotropic shielding for C-N bonds (Fig. 6) a proton located in the positive region will be the most shielded and one located in the center of the negative cone will be the most deshielded. A proton located on the edge of the cone which is about 55° to the axis will not be affected.

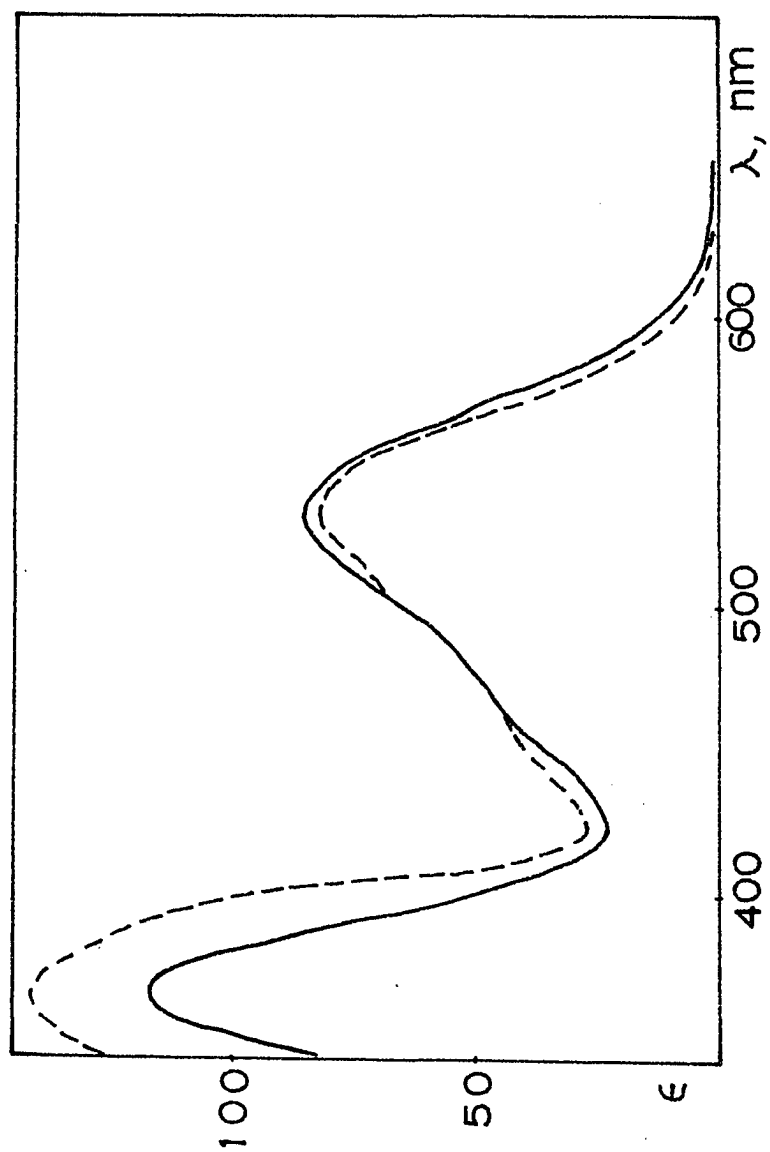


Figure 4. The absorption spectra of $\text{trans-}[\text{Co}(\text{l-pn})(\text{DEDDA})]^+$ (---) and $\text{trans-}[\text{Co}(\text{en})(\text{DEDDA})]^+$ (—).

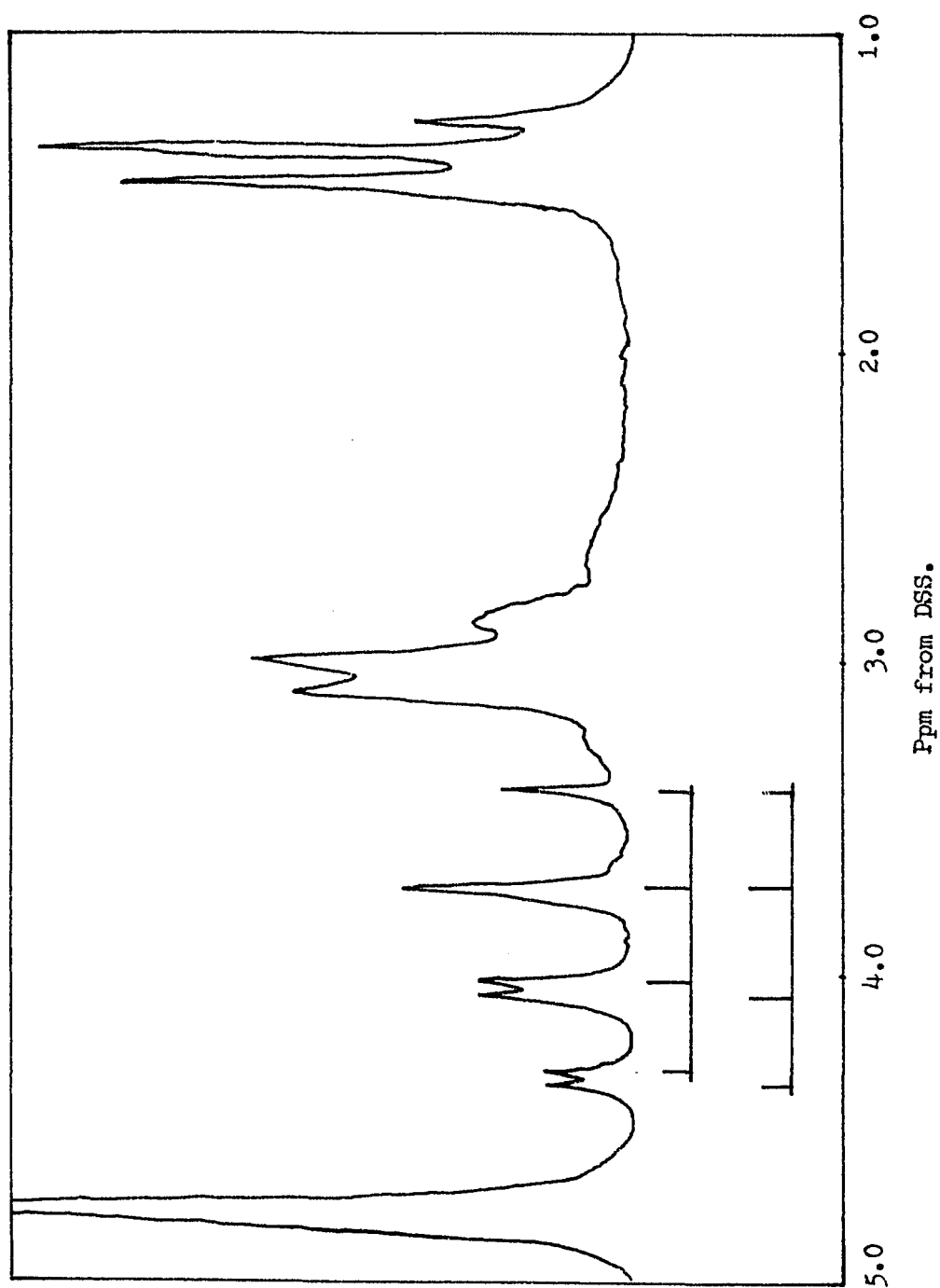


Figure 5. The pmr spectrum of (+)-trans-[Co(1-pn)(DEEDDA)]⁺.

TABLE I

Acetate Ring Proton Chemical Shifts*
of Some Tetradentate Cobalt(III) Complexes

	H _a	H _b
D-(+)- <u>trans</u> -[Co(l-pn)(EDDA)] ⁺ **	4.26 4.23	3.36
D-(+)- <u>trans</u> -[Co(l-pn)(DEEDDA)] ⁺	4.21 4.15	3.61

* Ppm from DSS.

** Reference 9.

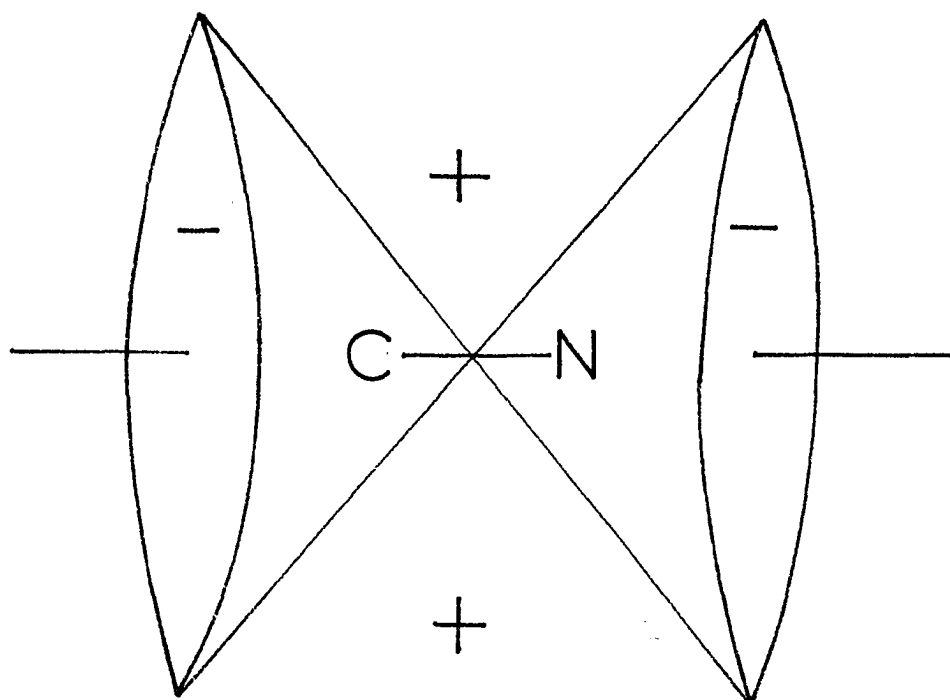


Figure 6. Anisotropic shielding expected for C-N bond.

The absolute configuration of the two complexes which will be confirmed in the subsequent discussion is shown in Fig. 7. In trans- $[\text{Co}(\text{l-pn})(\text{EDDA})]^+$ the proton (H_b) in the acetate ring which is over the ethylenediamine backbone in the region of shielding must be H_b in Table I and the proton (H_a) in the acetate ring which is in the deshielded region away from the ethylenediamine is H_a in Table I. When the proton on the nitrogen is replaced by an ethyl substituent (as in DEEDDA), H_a (the proton which is on the same side of the ring as the alkyl substituent) is placed in a slightly shielded environment compared to the EDDA complex and a shift upfield results from values of 4.26, 4.23 ppm in D-trans- $[\text{Co}(\text{l-pn})(\text{EDDA})]^+$ to 4.21, 4.15 ppm in trans- $[\text{Co}(\text{l-pn})(\text{DEEDDA})]^+$, H_b is in a deshielded environment in the DEEDDA complex and shifts downfield from 3.36 ppm to 3.61 ppm. These observations agree with the results⁸ in trans- $[\text{Co}(\text{en})(\text{EDDA})]^+$ and trans- $[\text{Co}(\text{en})(\text{DEEDDA})]^+$ and complexes with iminodiacetic acid and its N-methyl derivative¹⁷. The absolute configuration of trans- $[\text{Co}(\text{l-pn})(\text{EDDA})]^+$ has been designated⁹ on the basis of the different chemical shift of the H_a protons in the D and L isomers. In the D-isomer, the l-pn and the en backbone of the EDDA are in the k'k' conformation (Fig. 7). In the X-ray determination of trans- $[\text{Co}(\text{l-pn})_2\text{Cl}_2]\text{Cl}$ ¹⁸ in which the l-pn are also in k'k' conformation, the $\text{N}_2\text{-Co}$ bond length was shorter than $\text{N}_1\text{-Co}$ bond length and the $\text{Co-N}_2\text{-C}_2$ bond angle was smaller than $\text{Co-N}_1\text{-C}_1$ bond angle. This meant that the distance between $\text{N}_2\text{-H}$ and one of the H_a 's is different from that between $\text{N}_1\text{-H}$ and another H_a . These two H_a 's in different chemical environments results in two

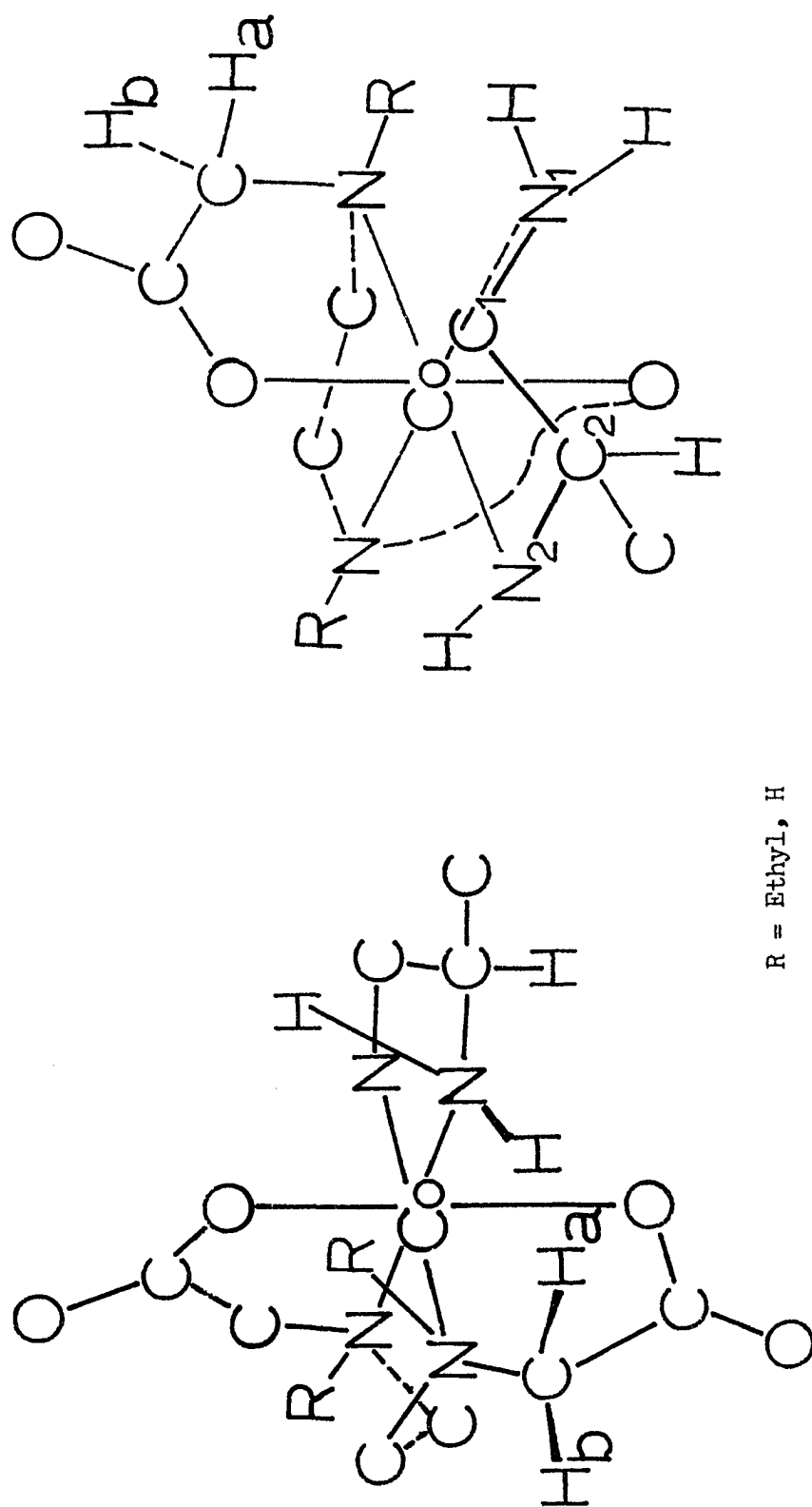


Figure 7. Absolute configuration for $\underline{\text{D-trans}}-\left[\text{Co(1-pn)(EDDA)}\right]^+$ and $\underline{\text{D-trans}}-\left[\text{Co(1-pn)(DEEDDA)}\right]^+$.

sets of AB quartets. In the corresponding L-trans-[Co(1-pn)(EDDA)]⁺ where the rings are in kk' conformation, no such difference in the H_a's exist and only one AB quartet is observed. Thus a doublet for each component of low field proton of the AB spectrum (H_a) region indicates that trans-[Co(1-pn)(DEEDDA)]⁺ is D-isomer. The fact that D-trans-[Co(1-pn)(DEEDDA)]⁺ is the principal isomer obtained from the equilibrium is also consistent with energetic relationships developed by Corey and Bailar¹⁹ that complexes with the k'k' conformation of trans rings are more stable than complexes with the kk' conformation.

3. Optical rotatory dispersion curve

The relationship between the ord curve and absolute configuration has previously been discussed extensively²⁰⁻²⁴. Although rotations of the same sign at particular wavelength do not imply the same relative configuration, similar optical rotatory dispersion curves do imply the same relative configuration if considered relative to corresponding absorption peaks²⁵. It has been pointed out by Sargeson²⁵ that the sign of the Cotton Effect associated with each optically active transition may also be used as a criterion for the configuration of the asymmetric center. He described rotatory dispersion curves of 30 cobalt(III) complexes and assessed the absolute configuration of some of the complexes by relating their rotatory dispersion curves to that of D-(+)-[Co(en)₃]³⁺ ion (The structure of which has been determined by means of X-ray diffraction^{26,27}.). The assessment is supported by kinetic results⁷. The ord curves for (+)-trans-[Co(1-pn)(DEEDDA)]⁺ and D-(+)-trans-[Co(en)-

$(\text{EDDA})]^+$ are given in Fig. 8. By comparison with D-(+)-trans- $[\text{Co}(\text{en})-(\text{EDDA})]^+$, (+)-trans- $[\text{Co}(\text{l-pn})(\text{DEEDDA})]^+$ is identified as the D-isomer.

B. Separation of the Reaction Mixture

1. Ion exchange sephadex chromatography

In order to study the optical activity of a reaction product from an optically active starting complex, a sensitive method had to be developed to separate the product completely from the starting material and additional side products. The selectivity of the ion exchange resin (Dowex 50-X8) has been used to separate cis and trans isomers and compounds with different charges^{8,28}, but the trivalent ions will be absorbed on the resin of the top of the column and be hard to remove. Yoshikawa and Yamasaki²⁹ reported that $[\text{Co}(\text{en})_3]^{3+}$ can be resolved on the ion-exchange Sephadex eluting with 0.15-0.3M sodium-(+)-tartrate. This suggests the trivalent ion can be removed from the Sephadex column by eluting with NaClO_4 solution in various concentrations. The NaClO_4 is chosen as the eluting agent as this compound can be removed easily by washing the dried product with absolute ethanol after the separation. The order of the column elution of the EDDA isomers of first trans and then cis is consistent with the work of Cooke⁸ and Mori and co-workers^{30,31}.

2. Thin layer chromatography

Dwyer and co-workers³² using paper chromatography developed a method for separating the optical isomers $\text{L}-[\text{Co}(\text{l-pn})_3]\text{Cl}_3$,

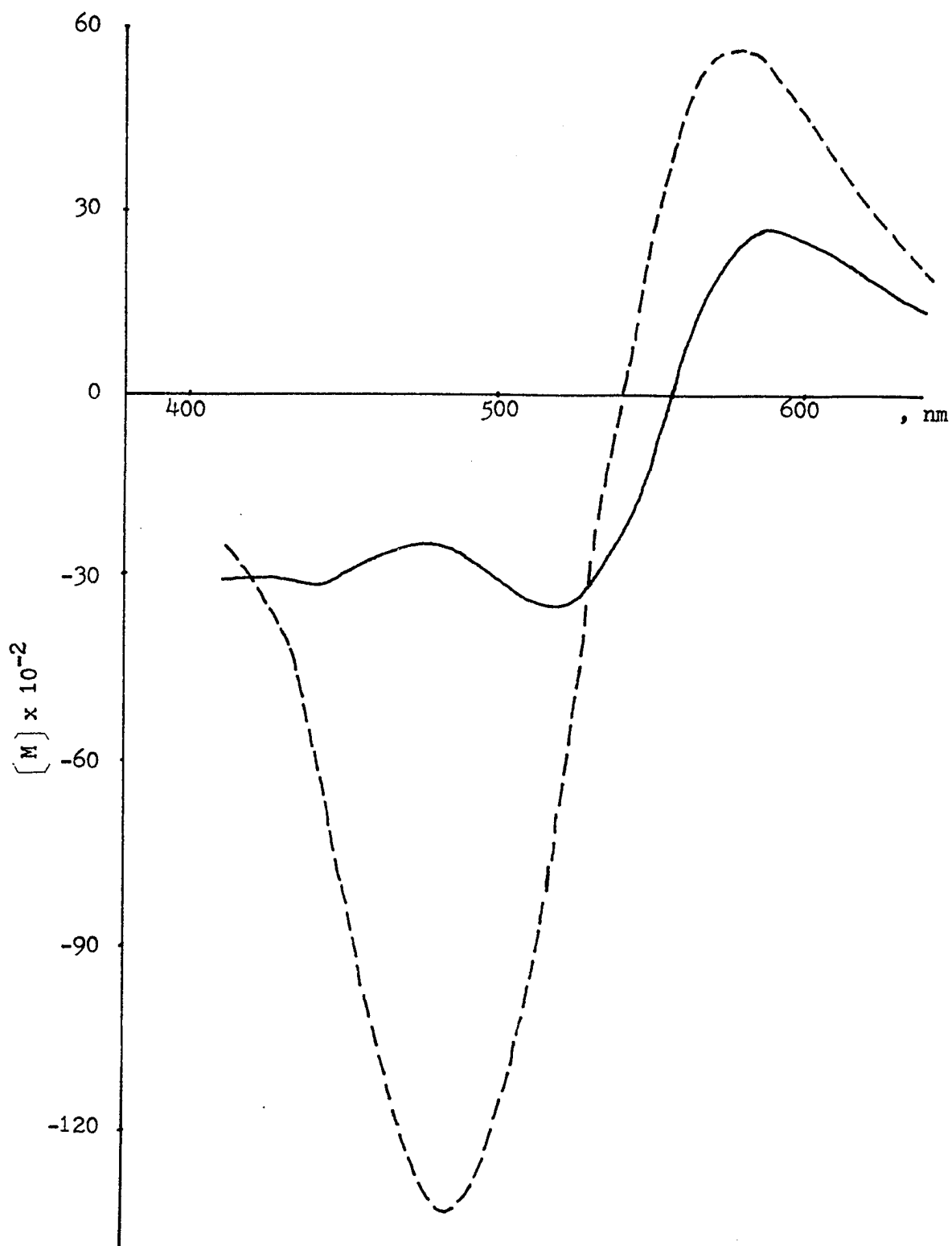


Figure 8. The ord curve of D-trans-[Co(en)(EDDA)]⁺ (- - -) and D-trans-[Co(1-pn)(DEEDDA)]⁺ (—).

$L-[Co(1-pn)_2(en)]Cl_3$, $L-[Co(1-pn)(en)_2]Cl_3$, $D-[Co(1-pn)_3]Cl_3$,
 $D-[Co(1-pn)_2(en)](ClO_4)_3$ and $D-[Co(1-pn)(en)_2](ClO_4)_3$. Because of
 the low yield of the reaction of cobalt(III) complexes with en, thin
 layer chromatography was tried under the same eluting system in order
 to develop a rapid and sensitive separation. The separation was
 completed in five hours. The result is consistent with that reported
 by Dwyer³². When as little as $1 \mu l$ ($1 \mu g/\mu l$) of the sample was
 applied to the plate, the separation still could be detected by
 spraying a NaS buffer solution (5% NaS solution add 3 ml of concen-
 trated aqueous ammonia) to change the cobalt(III) complexes to CoS
 which is black and easily observed.

C. Reaction of Complexes with Ethylenediamine and with Base

The assumed reaction mechanism for the reaction of $L-(-)-K-[Co(EDTA)]$
 with ethylenediamine is given in Fig. 1. Since $L-(-)-$
trans- $[Co(en)(EDDA)]$ is similar to one of the intermediates proposed
 in this mechanism, it seems reasonable to assume that the reaction
 of this complex with ethylenediamine would proceed by a similar
 mechanism (Fig. 9). If the reaction proceeds in a highly stereo-
 specific manner involving a series of stepwise displacements of
 ligands as suggested by the above mechanism then a single enantiomer
 of $[Co(en)_3]^{3+}$ will be expected. The results of the reaction are
 summarized in Table II. The reaction of $L-(-)-$ trans- $[Co(en)(EDDA)]^+$
 with ethylenediamine was slow. $L-(-)-K[Co(EDTA)]$ reacts with
 ethylenediamine under the same condition to give 63% $L-(-)-$
 $[Co(en)_3]^{3+}$ and 37% of $D-(+)-[Co(en)_3]^{3+}$ in less than four hours¹.

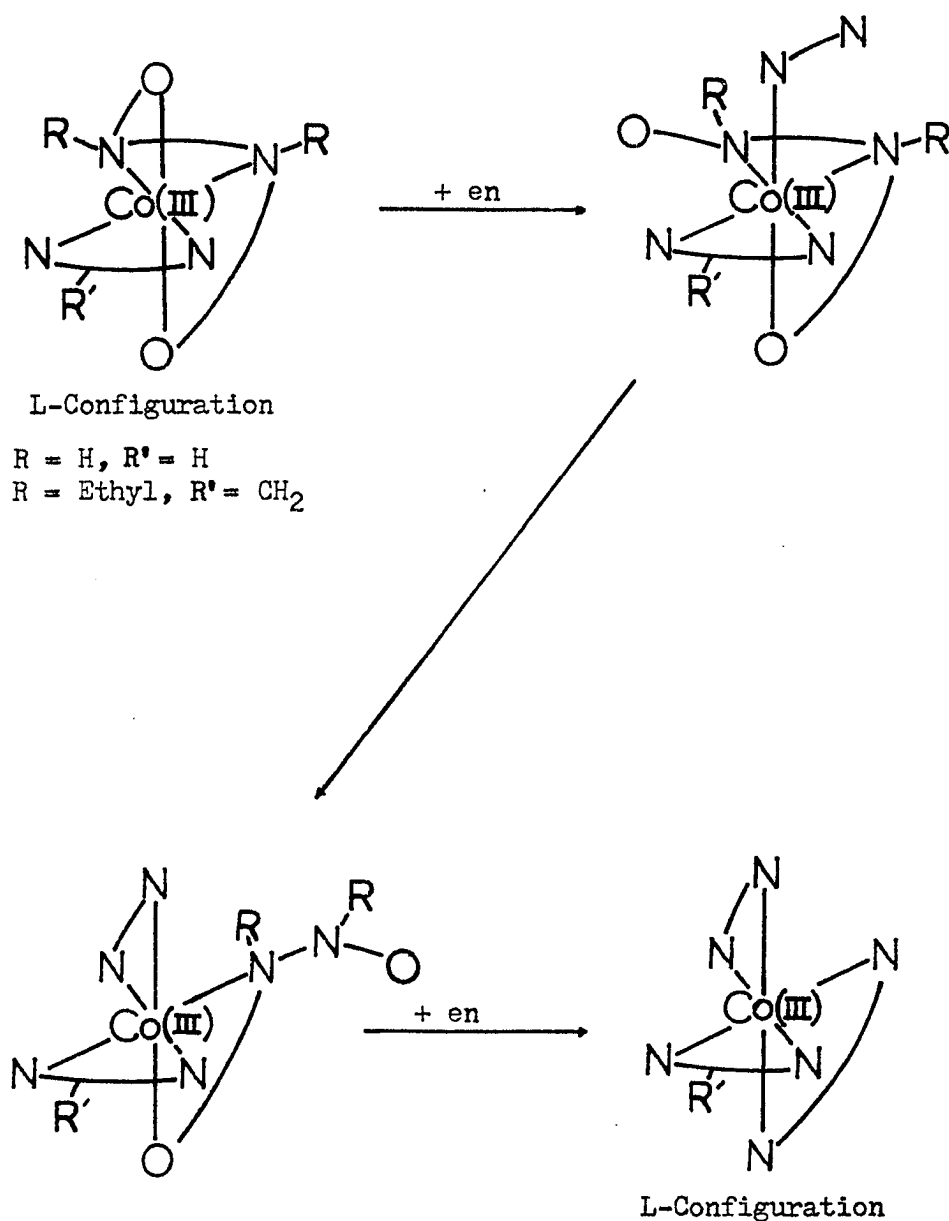


Figure 9. Proposed mechanism for $(-)\text{-trans-}[\text{Co}(\text{en})(\text{EDDA})]^+$ reacted with ethylenediamine.

TABLE II

The Reaction of Complexes with Ethylenediamine

<u>Starting material</u>	<u>Time period</u>	<u>Product mixture</u>
(-)- <u>trans</u> -[Co(en)(EDDA)] ⁺ 0.3026 g (8.1 x 10 ⁻⁴ mole) ethylenediamine (300 ml, 4.5 mole)	15 hours	<u>trans</u> -[Co(en)(EDDA)] ⁺ (44% of activity) (±)- <u>cis</u> -[Co(en)(EDDA)] ⁺ (5.5%, 0.0175 g) (±)-[Co(en) ₃] ³⁺ (3%, 0.0070 g)
(±)- <u>cis</u> -[Co(en)(EDDA)] ⁺ 0.1037 g (2.2 x 10 ⁻⁴ mole) ethylenediamine (50 ml, 0.75 mole)	7) hours	(±)- <u>cis</u> -[Co(en)(EDDA)] ⁺ (4%, 0.00459) (±)- <u>trans</u> -[Co(en)(EDDA)] ⁺ (71%, 0.0743 g) [Co(en) ₃] ³⁺ (15%, 0.0151 g)
(+)- <u>trans</u> -[Co(1-pn)(DEEDDA)] ⁺ 0.0545 g (1.2 x 10 ⁻⁴ mole) ethylenediamine (3 ml, 5 x 10 ⁻² mole)	19 hours	(+)- <u>trans</u> -[Co(1-pn)(DEEDDA)] ⁺ (±)-[Co(en) ₃] ³⁺ (31%, 0.0170 g)
(-)- <u>trans</u> -[Co(1-pn)(EDDA)] ⁺ 0.1051 g (2.5 x 10 ⁻⁴ mole) ethylenediamine (200 ml, 2.5 mole)	15 hours	<u>trans</u> -[Co(1-pn)(EDDA)] ⁺ (47% of activity) (±)- <u>cis</u> -[Co(1-pn)(EDDA)] ⁺ (8%, 0.0084 g) (±)-[Co(en) ₃] ³⁺ (2.5%, 0.0026 g)

After fifteen hours the reaction mixture from the reaction of ethylenediamine with the EDDA complex was separated on Sephadex and gave only 3% $[\text{Co}(\text{en})_3]^{3+}$ which was optically inactive. In addition 5.5% of optically inactive $\text{cis-}[\text{Co}(\text{en})(\text{EDDA})]^+$ was found and the activity of the starting material had decreased to 44% of its original value.

The intermediate postulated in the EDTA reaction corresponding to the EDDA complex had two dangling acetate arms. The steric effects that would exist between these arms and the incoming ethylenediamine might weaken the remaining metal-ligand bonds which should facilitate the displacement of the EDTA ligand. In an attempt to approximate this situation the D-trans complex containing the ligand DEEDDA was prepared with two ethyl groups in place of the dangling acetate arms. The ligand en occupied the fifth and sixth coordination sites. The reaction with ethylenediamine was carried out (Table II) and found to proceed much faster. After 19 hours 31% of the complex had reacted to give product in agreement with the proposed steric interaction. However the reaction is still not nearly as rapid as the reaction with $[\text{Co}(\text{EDTA})]^-$. Perhaps the presence of the dangling acetate groups in this complex beside giving steric interactions also provides a site for hydrogen bonding with the incoming ethylenediamine which makes it easier for the ethylenediamine to react with the complex.

The optical activity of the starting material did not change. If a series of displacement reactions had occurred for this system a single product D-(+)- $[\text{Co}(\text{l-pn})(\text{en})_2]^{3+}$ would have been obtained.

Analysis of the product indicated that it was optically inactive. Thin layer chromatography using authentic compounds indicated that the product was $[\text{Co}(\text{en})_3]^{3+}$. The pmr spectrum of the product gave no methyl signal confirming that there was no l-pn in the product. The same results were obtained in the reaction starting with L-(-)-trans- $[\text{Co}(\text{l-pn})(\text{EDDA})]^{3+}$.

It is apparent from these results that the reactions of ethylenediamine with the EDDA and DEEDDA complexes does not follow the mechanism proposed for the reaction with the EDTA complex. No stereoselectivity was observed in the formation of the products. Furthermore, the absence of l-propylenediamine in the product requires that one step in the mechanism involves the weakening of the cobalt-propylenediamine bonds followed by replacement of this ligand with ethylenediamine in a random fashion.

Further studies of this reaction were completed in an attempt to learn something about the process. One of the products observed in the reaction of the EDDA complex with ethylenediamine was the inactive cis complex. What is the source of this cis complex? Since the cis complex is optically inactive is it possible that the ethylenediamine reacts faster with the cis complex than with the trans which would then lead to inactive product?

The study of this latter possibility was carried out first. Ethylenediamine was reacted with a sample of cis- $[\text{Co}(\text{en})(\text{EDDA})]^+$. This reaction proceeded at a similar rate to the trans isomer. After 70 hours 19% of the complex had been converted to $[\text{Co}(\text{en})_3]^{3+}$. Most of the remaining cis isomer had isomerized to the trans isomer

(only 5.7% of the remaining $[\text{Co(en)(EDDA)}]^+$ was cis). It thus appears that the cis complex is no more reactive than the trans isomer in this reaction.

The observation that the cis complex is no more reactive than the trans complex is consistent with the results found with the DEEDDA complex. When this complex is reacted with ethylenediamine no cis complex is observed in the product mixture. In fact with this ligand no cis complex can be prepared using appropriate synthetic techniques apparently because of steric interactions. Thus if the cis complex was more reactive than the trans it would not be expected that the DEEDDA complex, where no stable cis complex exists, would react at a faster rate than the EDDA complex.

The isomerization of the cis EDDA complex gave a mixture of trans and cis which was identical to that found in the trans EDDA mixture. A similar low proportion of cis was obtained by Legg and Cooke⁸ on the preparation of these complexes under equilibrium conditions. In their reaction mixture the attainment of the equilibrium was assured by the addition of charcoal. Cooke¹⁷ observed that complexes of cobalt(III) with iminodiacetic acid reached equilibrium in basic media.

It is possible that the appearance of the cis EDDA complex in the reaction of the trans complex with ethylenediamine results not from any reaction with ethylenediamine but simply due to the equilibration of these isomers in the basic media. A series of reactions was completed to study this possibility. A solution containing 10% ethylenediamine (pH = 11.9) in water and one

containing 20% ethylenediamine to which hydrochloric acid was added to a pH of 9.5 were prepared. Both solutions have similar amounts of free ethylenediamine but differ in the amount of hydroxide ion. The reactions of the various compounds in these two solutions are summarized in Table III.

The visible spectrum of the cis complex dissolved in the buffered solution was not changed after one week but the reaction in the 10% ethylenediamine solution was changed in 24 hours by the formation of a peak at 530 nm which corresponded to the formation of 95% trans isomer. A less dramatic change was observed in the trans isomer where in the 10% ethylenediamine solution a 7% increase in absorbance was observed in the 470 nm region (the region where the cis complex and $[\text{Co}(\text{en})_3]^{3+}$ absorb) while in the buffered solution it took 2 weeks to develop a 15% increase in the same region. It is apparent that for the formation of an equilibrium mixture the presence of hydroxide ion is more important than the presence of ethylenediamine.

To confirm the fact that a major contributor to this change was the presence of hydroxide ion a series of reactions were carried out in base (pH = 11.7) in the absence of ethylenediamine. The results are tabulated in Table III. After 24 hours the cis complex isomerized to give 95% trans similar to that found in the 10% en solution. After 24 hours the trans complex developed a 5% increase in the absorbance at 470 nm which compares with the 7% increase found after 24 hours reaction with 10% ethylenediamine. The slight increase with the 10% ethylenediamine is due to the formation of

TABLE III

The Reaction of Complexes with Buffered Ethylenediamine and Base

<u>Starting Material</u>	<u>Time Period</u>	<u>% increase of absorbance at 470 nm</u>	<u>Product</u>
<u>trans</u> -[Co(en)EDDA] ⁺)	24 hours in buffer (pH = 9.5)	none	
<u>trans</u> -[Co(1-pn)DEEDA] ⁺)--	12 days in buffer (pH = 9.5)	15%	
<u>trans</u> -[Co(1-pn)EDDA] ⁺)	24 hours in 10% en (pH = 11.7)	7%	
<u>trans</u> -[Co(en)(EDDA)] ⁺	24 hours in base (pH = 11.7)	5.3%	
<u>cis</u> [Co(en)(EDDA)] ⁺	24 hours in buffer (pH = 9.5)		no change
	24 hours in 10% en (pH = 11.7)		95% <u>trans</u>
	24 hours in base (pH = 11.7)		95% <u>trans</u>

$[\text{Co(en)}_3]^{3+}$ product.

If the basic solution can cause isomerization of the complexes it could also cause racemization of those complexes which were optically active. Cooke, Im and Busch³³ observed the racemization of $\text{L-K}[\text{Co(EDTA)}]$ in basic media. The possibility of racemization in these complexes was confirmed by the following reaction. The L-trans complex of EDDA rapidly decomposed in a period of one-half hour in hydroxide solution prepared at $\text{pH} = 14$. The pH of the 10% ethylenediamine solution is 11.7 and the relationship between pH and hydroxide ion concentration may have some meaning in this region. The L-trans isomer did not decompose in $\text{pH} = 11.7$ NaOH solution but did lose optical activity. After a 24-hour period the activity was reduced to 69% of the original value. The data compare with that of L-isomer in 10% en solution. For the same time period, the activity was reduced to 71% of the original value. Thus the loss of activity appears to be due entirely to reaction with hydroxide ion independent of the presence of ethylenediamine.

Loss of activity was also observed in the trans complex isolated from the product mixture in the reaction of $\text{L-(-)-trans-}[\text{Co(1-pn)-(EDDA)}]^+$ with pure ethylenediamine but none was observed in the reaction with the corresponding DEEDDA complex. This is consistent with the results obtained from the preparation of these complexes under equilibrium conditions. The reaction mixture of the 1-pn EDDA complex gave both D and L diastereomers while the mixture of the 1-pn DEEDDA complex gave only the D-isomer. Under equilibrium conditions in base no L isomer of the DEEDDA complex should be

obtained and no loss of activity should be observed.

Knowing that hydroxide ion favors the processes of isomerization and racemization the reaction was studied under conditions of low hydroxide ion concentration. A 20% solution of ethylenediamine in water was prepared and neutralized to pH = 9.5 with hydrochloric acid. $K[Co(EDTA)]$ was found to react readily with ethylenediamine in this solution. After four hours a visible spectrum characteristic of $[Co(en)_3]^{3+}$ was obtained. This was not the case with the EDDA and DEEDDA complexes, however reaction in this solution of D-(-)-trans- $[Co(en)(DEEDDA)]^+$ which had resulted in 20% product in pure ethylenediamine was carried out. Because of the large amount of counter ion in this system no separation on Sephadex was attempted. However in this system no isomerization or racemization is possible for reasons pointed out earlier. Thus any change in the visible spectrum is due to the formation of $[Co(en)_3]^{3+}$. In 10% ethylenediamine solution absorbance after 24 hours increased 7% in the 470 nm region where the $[Co(en)_3]^{3+}$ maximum occurs corresponding to a formation of 7% of product. In the buffer solution no change in the spectrum occurred during the same time period. Similar results were obtained for the EDDA complexes. Thus it appears that for this process the reaction is very slow in much lower concentrations of base.

IV. SUMMARY

From the results of these experiments it is possible to suggest why no stereospecificity exists in the reaction of ethylenediamine with the complexes of EDDA and DEEDDA while stereospecificity does exist in the reactions with EDTA. In the reactions of $K[Co(EDTA)]$ Cooke and Busch⁶ found that the reactions with base and with ethylenediamine were similar. Thus in pure ethylenediamine the reaction with base was insignificant and stereospecificity occurred. In the reactions with EDDA and DEEDDA complexes, however, base plays an important part in the process. In the absence of base the reaction is very slow. The presence of base leads to isomerization and racemization in the reaction and a corresponding loss of stereospecificity. The reaction apparently proceeds by initial attack by base which weakens the cobalt-ligand bonds and results in isomerization and racemization. The fact that these bonds are weakened is consistent with the fact that attack by the ethylenediamine on the 1-propylenediamine complexes resulted in complete removal of the 1-pn in the product mixture.

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VI. VITA

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