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STEREOCHEMISTRY OF COBALT(III) COMPLEXES OF

TRANS-1,2-CYCLOPENTANEDIAMINE

A THESIS

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STEREOCHEMISTRY OF COBALT(III) COMPLEXES OF

TRANS-1,2-CYCLOPENTANEDIAMINE

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

The subject of this investigation is the stereochemistry trans-1,2-cyclopentanediaminecobalt(III) complexes. Jaeger and Blumendal made one of the most significant investigations of the stereochemical behavior of complex ions containing asymmetric ligands when they studied the cobalt (III) and rhodium(III) complexes of trans-1,2-cyclopentanediamine (cptdin). The cptdin molecule, having no plane of symmetry, is capable of being resolved into enantimorphs. Jaeger assumed that cptdin functions as a bidentate ligand. If so the complex ion, $Co(cptdin)_3^{3+}$, should exhibit eight optical isomers. However, he was able to isolate only two of the eight isomers, viz., $D-Co(l-cptdin)_3^{3+}$ and $L-Co(d-cptdin)_3^{3+}$ and in no case could he isolate the mixed complexes of the type $D-Co(l-cptdin)(d-cptdin)_2^{3+}$.

On the basis of these findings and previous investigations by other workers of propylenediamine (also asymmetric) complexes, Jaeger attributed the drastic reduction in the number of complexes to a preferred diasymmetrical configuration. The complex tends to generate the most symmetrical possible diastereisomer.

A consideration of the geometry of the cyclopentanediamine ring and the requirements for chelate formation show that it is unlikely that the diamine molecule functions as a bidentate ligand. In an unstrained configuration, the nitrogen-nitrogen distance is 3.5 angstrom units and the most favorable nitrogen-cobalt-nitrogen bond angle is 18 degrees. These values are to be compared to optimum values of bidentate cobalt:

a nitrogen-nitrogen bond distance of 2.5 A and a nitrogen-cobalt-nitrogen

bond angle of 90 degrees. This, in conjunction with the comparatively

rigid cyclopentane ring, makes the formation of chelate rings unlikely.

Reinvestigation of the complex, alleged by Jaeger to be $Co(cptdin)_3^{3+}$,

shows that the complex is, in fact, $Co_2(cptdin)_7(H_2O)_2^{6+}$. The cptdin

molecules are not bidentate but rather three of them bridge the two

cobalt atoms while the remaining four are singly coordinated to the

cobalt. The remaining coordination positions are occupied by the two

water molecules, one on each cobalt. The amine molecules in the complexes

are found to possess the same configuration, i.e., all dextro or all levo.

A closer consideration of the structure of $Co_2(cptdin)_7(H_2O)_2^{6+}$

shows that there should be three geometrical isomers, differing only in

position of one water molecule in relation to the other. Three such com-

pounds are isolated from the crude $Co_2(cptdin)_7(H_2O)_2^{6+}$ by column chro-

matography. The visible and infrared spectra of the three are identical

but the optical rotatory dispersion curves shows some minor differences.

During this investigation two experimental techniques have been

developed. Consideration of the empirical formula of $Co_2(cptdin)_7(H_2O)_2^{6+}$

indicates, first, the complex is not a monomer and, second, some of the

NH_2 groups are not coordinated to the cobalt. In order to elucidate

the structure of the complex cations, the degree of polymerization of

the cations and the number of uncoordinated NH_2 groups have been deter-

mined.

A modification of the van Slyke nitrogen determination allows

the uncoordinated NH_2 groups to be replaced and their number determined.

While most primary amines react rapidly with nitrous acid, the NH_2 groups

ix

of the complex are replaced only after 14 hours.

There are relatively few good methods of determining the charge on highly charged cations in aqueous solution. The method developed consists of calculating the approach parameter, $\underline{a}$, of the Debye-Huckel equation for solutions of the complex in large excesses of potassium nitrate, when various allowed values of the cationic charge are assumed, and comparing these calculated values of $\underline{a}$ to the value of $\underline{a}$ for pure potassium nitrate.

CHAPTER I

INTRODUCTION

Coordination compounds of the type $M(AA)_3$ and $\underline{cis}$-$M(AA)_2X_2$, where AA is an optically inactive bidentate ligand, are capable of showing optical activity. For example, enantimorphs of trisethylene-diaminecobalt(III) chloride and $\underline{cis}$-dichlorobisethylenediaminecobalt(III) chloride have long been known.

Introduction of an optically active ligand greatly increases the number of isomers possible. $\underline{Trans}$-1,2-cyclopentanediamine(cptdin) has no plane of symmetry and thus is capable of being resolved into optical isomers. Should this ligand act as a bidentate ligand, coordination compounds of the type cis-$M(cptdin)_2X_2$ should exhibit six optical isomers:

$D\text{-}llX_2$	$L\text{-}llX_2$
$D\text{-}ldX_2$	$L\text{-}ldX_2$
$D\text{-}ddX_2$	$L\text{-}ddX_2$

where D or L represents the sign of the rotation of the complex at the sodium D line and $\underline{d}$ or $\underline{l}$ represents the sign of the rotation of the free ligand at the sodium D line. In the case of octahedral complex ions of the type $M(AA)_3$ there are eight isomers possible:

D-ddd	L-lll
D-ddl	l-ddl
D-dll	L-dll
D-lll	L-ddd

Since propylenediamine(pn) is unsymmetrical, it introduces further complications as a result of the increase in the number of geometric isomers resulting from the relative position of the methyl groups. In one of the few cases in which these geometric, that is alpha, beta isomers, were isolated, Werner (23) was able to characterize all ten isomers of the complex $[Co(en)(pn)(NO_2)_2]^+$. There are two _trans_ isomers but since propylenediamine may be dextro or levo rotatory there are eight _cis_ isomers possible, viz., αDd, βDl, βLd, αLl, αLd, βLl, αDl, and βDd.

In most of the early investigations of coordination compounds with optically active ligands very few of the many possible isomers were isolated. In one of the earliest investigations Tschugaeff and Sokoloff (22), using optically active propylenediamine, were able to obtain only two tris-propylenediaminecobalt(III) salts. The D-$[Co(d-pn)_3]Br_3 \cdot 2H_2O$ was obtained from the _d_ base while the _l_ base yielded L-$[Co(l-pn)_3]Br_3 \cdot 2H_2O$. No evidence was found of alpha-beta isomers.

Smirnoff (21) using active base confirmed the results of Tschugaeff and Sokoloff by isolating only two salts, viz., D-$[Co(d-pn)_3]Br_3 \cdot 2H_2O$ from the _d_ base and L-$[Co(l-pn)_3]Br_3 \cdot 2H_2O$ from the _l_ base.

In the same publication Smirnoff observed that reacting $H_2(PtCl_6)$ with racemic base followed by resolution yielded only two salts, designated as D-$[Pt(l-pn)_3]Cl_4$ and the enantiomorph L-$[Pt(d-pn)_3]Cl_4$. Reacting hydrogen hexachloroplatinate (21) with either _d_ or _l_ base yielded but one salt, which, when converted to the bromide salt, had a specific rotation of ±140. The value was unchanged when the bromide was converted to the tartrate salt, recrystallized and the bromide salt regenerated.

In one of the most important investigations of this nature Jaeger and Blumendal (10) used trans-1,2-cyclopentanediamine and cobalt(III) and rhodium(III) to investigate the stereochemistry of these ions. Treatment of a mixture of cobalt(III) and an excess of racemic base with hydrogen peroxide yielded a pink salt given the formula $[Co(cptdin)_3]Cl_3 \cdot 4H_2O$. Conversion of this salt to the mixed chlorotartrate salt, resolution and regeneration of the chloride salt yielded but two isomers $L-[Co(d-cptdin)_3]Cl_3 \cdot 4H_2O$ and $D-[Co(l-cptdin)_3]Cl_3 \cdot 4H_2O$. Treatment of cobalt(III) chloride and either $\underline{d}$ or $\underline{l}$ base with hydrogen peroxide yielded but one salt. In no case could a salt containing both $\underline{d}$ and $\underline{l}$-cyclopentanediamine be isolated.

The resistance to formation of complexes containing both $\underline{d}$ and $\underline{l}$-cyclopentanediamine was demonstrated by the reaction:

$$3l - cptdin + 3D-[Co(d-cptdin)_2Cl_2]Cl \longrightarrow \begin{array}{c} 2L-[Co(d-cptdin)_3]^3Cl_3 \\ D-[Co(l-cptdin)_3]^3Cl_3 \end{array}$$
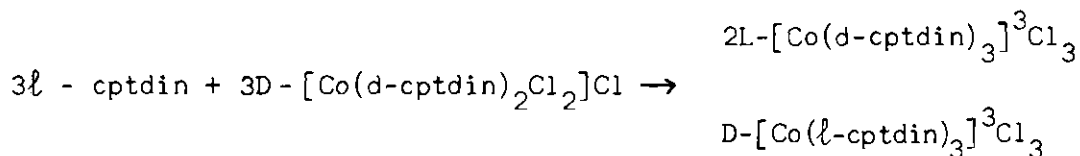
While complexes containing $\underline{d}$ and $\underline{l}$ ligands may be formed initially, Jaeger reasoned that they disproportionate in the following fashion (10):

$$3D-[Co(ddl)]^{3+} \longrightarrow 2L-[Co(ddd)]^{3+} + D-[Co(lll)]^{3+}$$
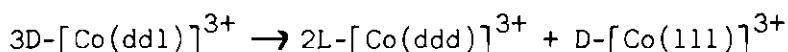
This reaction of necessity requires the disproportionation and reformation of the fragments. While cobalt(III) complexes are quite inert, equilibria can easily be obtained through cobalt(II) intermediates via electron transfer. No such mechanism exists for the equally inert rhodium(III), however (5).

Jaeger commented on the unusual pink color of the complex but did not consider it significant.

Based on these findings and previous findings concerning propylene-diamine and cobalt(III) and platium(IV), Jaeger attributed the drastic reduction in the number of isolated complexes to a preferred dissymetrical configuration. The complex tends to generate the most symmetrical possible diastereoisomer.

One exception to this stereochemical reduction is noted. Lifschitz (12) was able to isolate three of the possible four tris-d-alaninecobalt(III) complexes by reacting d-alamine with cobalt(III) hydroxide. He called these α, α', and β and showed that the rotatory dispersion curves of these complexes were quite different. While he was unable to resolve the β isomer into its enantiomonphs, nevertheless it is one of the few cases of authentic, α, β isomerism.

Jaeger attributed the isolation of the three d-alanine complexes to a greater strength in the alanine chelate ring. Dwyer (5) in question-ing Jaeger's proposal believes the free energy difference between the L-dd and D-dd alanine isomers is greater then in the tris-(propylenediamine) complexes.

In a series of papers Dwyer and coworkers (5, 6, 7, 8,9) question the findings of the Tschugaeff (22) and Smirnoff (19). In addition to describing the preparation of optically pure d and l-propylenediamine, Dwyer isolated two salts formulated as D-$[Co(d-pn)_3]I_3 \cdot H_2O$ and L-$[Co(d-pn)_3]I_3 \cdot H_2O$ having respectively $\alpha]_D$ + 24 and -214 degrees. The more stable salt could be isomerized with charcoal at 20 degrees in 0.5 hours to yield an equilibrium mixture in which the L-ddd isomer is present

to the extent of 14.8 percent. This corresponds to a free energy dif-

ference of 1.02 Kcal/mole. Furthermore another isomer believed to be of

the type L-11d was isolated.

Using Smirnoff's method of preparation, two optical isomers of

$\underline{tris}$-d-propylenediamineplatinum(IV) chloride and a significant amount

(40 percent) of $\underline{bis}$-d-propylenediamineplatinum(II) chloride were isolated.

Repeated recrystallization of the chloride salt yielded L-$[Pt(d-pn)_3]Cl_4$

having a specific rotation at the sodium $\underline{d}$ line of -212 degrees. This is

in contrast to Smirnoff's value of -178 degrees. By fractional crystal-

lization of the oxalate salt followed by regeneration of the chloride salt

another isomer D-$[Pt(d-pn)_3]Cl_4$ was isolated. In another paper (8) Dwyer

and coworkers described the preparation of the salts L-$[Pt(1-pn)(d-pn)_2]Cl_4$

and D-$[Pt(1-pn)(d-pn)_2]Cl_4$ by reaction of 1-propylenediaminetetrachloro-

platinum(IV) with d-propylenediamine followed by resolution of the tar-

trate salt and regeneration of the chloride salt. The L-$[Pt(d-pn)_2(1-pn)]Cl_4$

had a specific rotation of -71 degrees and dextro isomer had a specific

rotation of +83 degrees.

Thus Dwyer has conclusively shown that many of the results derived

from previous investigation of propylenediamine coordination compounds are

in error. While there may be a stereospecific interaction of one propyl-

enediamine ligand with another in a coordination complex, it is not nearly

so pronounced as was previously thought.

Furthermore no recourse need be taken to the idea (10) that the

complexes tend to generate the most symmetric isomer to the exclusion of

all others. Corey and Bailar (2) have shown that an isolated nonrigid

five membered chelate ring may adopt one of two conformations, designated

k and k', which are enantiomers but energetically equivalent. In the case of <u>tris</u>-ethylenediamine complexes four conformations are possible, viz., kkk, kkk', kk'k', and k'k'k'. Evaluation of hydrogen-hydrogen interactions lead to a free energy difference of 1.8 Kcal/mole between the most extreme forms. The carbon-carbon bonds in the more stable conformer, designated as kkk, are approximately parallel to the short trigonal axis of the complex, while the carbon-carbon bonds are oblique to the short trigonal axis in the less stable k'k'k' conformer. Thus the kkk conformer is known as the "lel" form while the k'k'k' is known as the "ob" form.

The interpretation of Dwyer's findings are relatively straightforward. The most stable cobalt(III) complexes of propylenediamine are $D-[Co(d-pn)_3]^{3+}$ and $L-[Co(l-pn)_3]^{3+}$. Propylenediamine may, in principle, form both k and k' chelate rings. The methyl groups must be axial in one ring and equatorial in the other (Figure 1). The energy difference in the two rings, due primarily to steric repulsion of the axial methyl groups, is sufficient to insure the formation of only type of ring in the complex: k (say) for the dextro propylenediamine and k' for the levo propylenediamine. As the most stable configuration of octahedral complexes is the lel form, all the propylenediamine molecules will be levo in one configuration and dextro in the other. Because the formation of complexes of the type $[Co(d-pn)_2(l-pn)]^{3+}$ necessitates that one methyl group be axial and the remaining two equatorial, an equilibrium mixture of cobalt(III) and racemic propylenediamine can be expected to contain relatively minor amounts of such "mixed" complexes.

Interpretation of Jaeger's stereospecific results are also rationalized on this basis by Corey and Bailar. Because of the almost flat
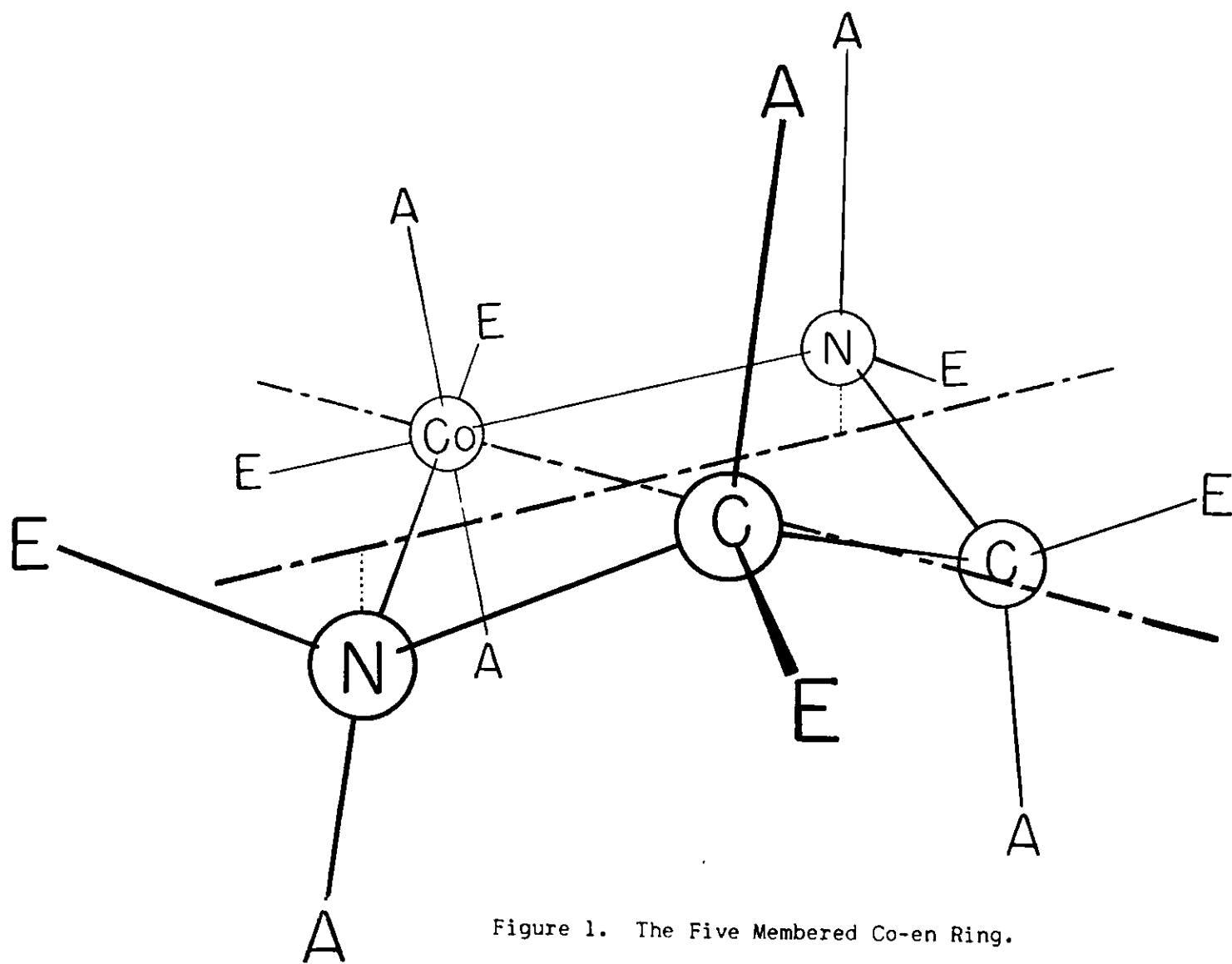
Figure 1.   The Five Membered Co-en Ring.

rigid cyclopentane ring, the N-C-C-N chain possesses a fixed gauche con-
figuration. Assuming the formation of enantiomorphs to be equilibrium
controlled, the dextrorotatory isomer may be designated D-[M(kkk)] and
the levoratatory L-[M(k'k'k')]. Both will assume the thermodynamically
stable lel conformation to the exclusion of the less stable of conforma-
tion. Because of the fixed gauche configuration imposed by the cyclo-
pentane ring, steric repulsion between cyclopentanediamine ligands in
complexes of the type M(kkk') is very great.

With the publication of Dwyer's results of propylenediamine
complexes there remained but one authentic instance where the number of
optical isomers was drastically reduced, viz., Jaeger's, presumably
because of the stereochemical reasons outlined by Corey and Bailar.
Implicit in all of the conclusions drawn from Jaeger's investigation
of cyclopentanediamine complexes is the assumption that trans-1,2-cyclo-
pentanediamine functions as a bidentate ligand. Indeed this idea is so
firmly rooted that it had never been questioned until recently.

Consideration of the geometry of the cyclopentanediamine ring and
the requirements for chelate formation show that it is unlikely that the
diamine molecule functions as a bidentate ligand. In an unstrained con-
figuration the nitrogen-nitrogen distance in the free diamine molecule is
3.5 A and the most favorable nitrogen-cobalt-nitrogen bond angle is about
1& degrees. These values are to be compared with optimum values of
bidentate coordination cobalt(III) compounds: a nitrogen-nitrogen bond
distance of 2.75 A and a nitrogen-cobalt-nitrogen bond angle of 90 degrees.
This, in conjunction with the comparative rigidity of the cyclopentanedia-
mine ring, makes the formation of a chelate ring seem unlikely.

The angle formed between the projection of the two carbon-nitrogen bonds in the strain-free chelate ring when viewed down the carbon-carbon axis in 48.8 degrees (Figure 2). The analogous angle is the cyclopentane ring is 109 degrees (Figure 3). Therefore severe angle strain is introduced by the trans fusion of the two five membered rings (18).

For reasons outlined above, the assumption that cyclopentanediamine functions as a bidentate ligand is probably incorrect and thus Jaeger's results and conclusions are subject to considerable uncertainty. Because much of the theories and ideas concerning stereochemical interactions of optically active ligands in complex ions are derived from Jaeger's investigation of cobalt(III) and rhodium(III) cyclopentanediamine complexes, it was felt that Jaeger's work should be reinvestigated to determine the exact nature of the cyclopentanediamine complexes.

109°
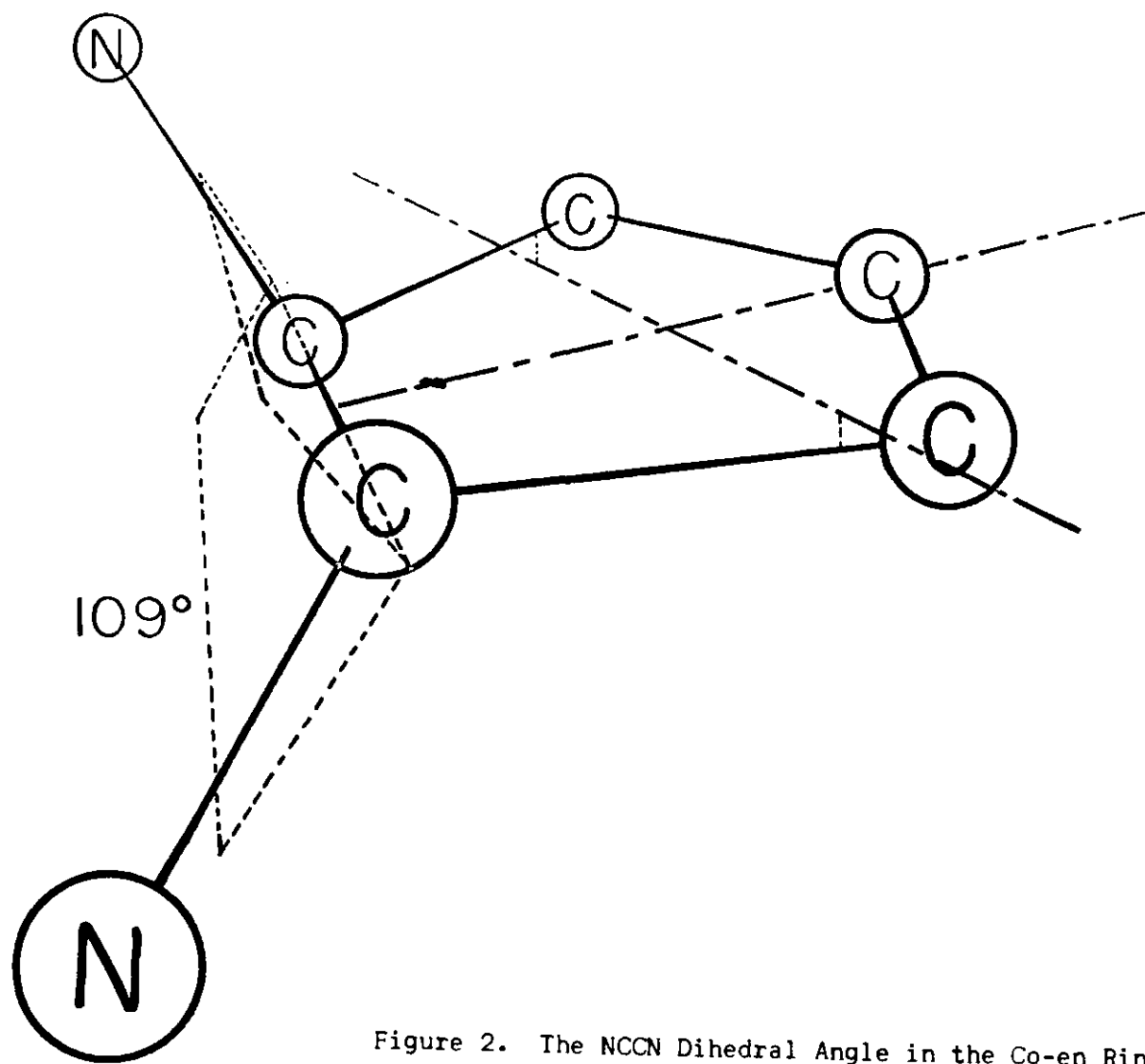
Figure 2. The NCCN Dihedral Angle in the Co-en Ring.
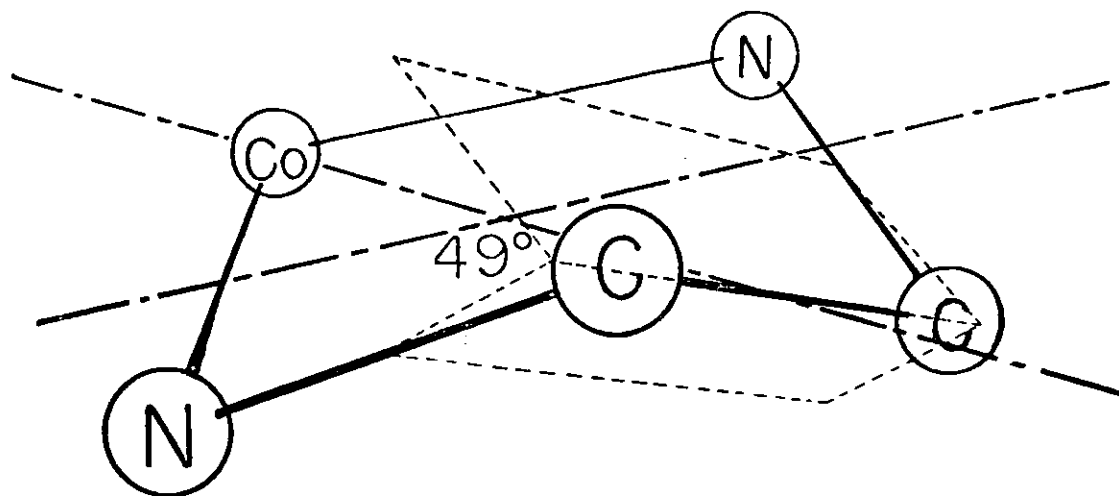
Figure 3.   The Minimum NCCN Dihedral Angle in the Free
            trans-1,2-cyclopentanediamine Molecule.

CHAPTER II

PREPARATION AND CHARACTERIZATION OF
1,2-CYCLOPENTANEDIAMINE

Preparation of Starting Material

Starting material for the preparation of <u>trans</u>-1,2-cyclopentane-diamine was adipic acid. Fisher esterification of the adipic acid yielded diethyl adipate. Dieckmann ring closure of this ester produced 2-car-bethoxypentanone. Reaction of 2-carbethoxypentanone with sodium nitrite followed by acidification with 6.0 N sulphuric acid and then by the addition of hydroxylamine yielded 1,2-cyclopentanedioxime. Hydrogenation of this oxime yielded a mixture of secondary amines in addition to the desired <u>trans</u>-1,2-cyclopentanediamine. The dioxime was reduced in fair yield to the desired amine with sodium in ethanol.

Preparation of Diethyl Adipate

Diethyl adipate was prepared by Fisher esterification of adipic acid with ethanol. Five hundred grams of adipic acid was heated under reflux with two liters of absolute ethanol and five ml of concentrated sul-phuric acid in a three liter flask for 24 hours. The reaction mixture was cooled and 100 grams of sodium hydroxide dissolved in approximately 1500 ml of water was added, causing two layers to separate. The entire mix-ture was extracted with three 300 ml portions of diethyl ether. The water layer was saved for recovery of adipic acid and monoethyl adipate.

The ether extract was washed with 25 ml of saturated sodium chlor-ide solution; then dried over magnesium sulphate. After standing for 24

hours the magnesium sulphate was filtered off and washed with diethyl

ether, with the washings being combined with the ether extract. The

ether and unreacted alcohol were distilled off at atmospheric pressure then

the diethyl adipate was distilled under reduced pressure (130-138/16mm).

The unreacted adipic acid and monoethyl adipate were recovered by

adding enough concentrated hydrochloric acid to the water extract to reduce

the pH to one or two. Usually two layers separated at this point. The

entire mixture was extracted with three 300 ml portions of diethyl ether,

then the ether phase washed with 25 ml of saturated sodium chloride solu-

tion. The extract was dried over magnesium sulphate for 24 hours.

The ether was distillled off at atmospheric pressure, then the

monoester was distilled under reduced pressure (125-135/7mm). Any

unreacted acid remaining in the still pot was recrystallized once from

ethanol and both monoester and acid were reesterified. The yield, based

on the adipic acid used, was about 85 percent.

Preparation of 2-Carbethoxypentanone

The 2-carbethoxypentanone was prepared by the method of P. S.

Pinkney (17). Fifty grams of sodium, cut in small pieces, was added to

a three liter flask which contained 1,250 ml of dry benzene. To this 303

g of diethyl adipate and three ml of absolute ethanol were added. The

flask was fitted with a reflux condenser and heated for 24 hours. During

the course of the reaction a white solid formed around the sodium; this

was broken up by vigorous shaking.

The reaction mixture was cooled in ice and the unreacted sodium

was decomposed by slowly adding ice and 12 N hydrochloric acid with

vigorous stirring. When the sodium had decomposed the water and benzene

layers were separated and the water extracted once with 300 ml of fresh benzene. This benzene extract was combined with the original benzene layer and washed with 300 ml of five percent sodium carbonate solution followed by 300 ml of water and finally by 25 ml of saturated sodium chloride solution. The benzene was dried for 24 hours over magnesium sulphate.

The magnesium sulphate was filtered off and washed with 100 ml of benzene. The washings were added to the extract and the benzene distilled off at atmospheric pressure. The 2-carbethoxypentanone was distilled off under reduced pressure (115-119/16mm) followed by unreacted diethyl adipate (130-138/16mm). The reaction was run numerous times and the average yield based on diethyl adipate used was 83 percent.

Preparation of 1,2-cyclopentanedioxime

The 1,2-cyclopentanedioxime was prepared by the method of Cope, et al., (3). To a one liter three neck flask, 63 grams of 2-carbethoxypentanone was added, followed by 27.8 grams of sodium nitrite dissolved in 320 ml of water. A white precipitate formed immediately. Nitrogen was passed over the mixture while it was stirred. Stirring was continued until all the solid dissolved, usually 48 hours.

At the end of this time the mixture was cooled to zero degrees and 120 ml of 6.0 $\underline{N}$ sulphuric acid slowly added, care being taken that the temperature did not rise above ten degrees. After the acid was added, the yellow mixture was continuously extracted for 36 to 48 hours with diethyl ether. During the extraction the mixture turned black.

The ether extract was reduced to 100 ml volume and an aqueous solution of 27.8 g of hydroxylamine hydrochloride and 16 g of sodium hydroxide was added. Almost immediately a brown precipitate of 1,2-cyclopentanedioxime

formed with a considerable evolution of heat. The mixture was stored at 10 degrees overnight; then filtered and washed once with 50 ml of cold water. The average yield of 13 runs was 38.4 g (73 percent of theoretical).

Hydrogenation of 1,2-cyclopentanedioxime

Thirty grams of 1,2-cyclopentanedioxime was placed in a 250 ml heavy-walled flask. To this 150 ml of freshly distilled absolute alcohol and three grams of a five percent palladium on charcoal catalyst was added. The mixture was hydrogenated under an initial pressure of 50 psi at room temperature. The reaction quickly took up hydrogen and the reaction was complete in 90 minutes. The calculated pressure drop was 80 psi, but only a 53 psi drop was observed.

The charcoal was filtered off and half the mixture was mixed with ten grams of fresh catalyst and rehydrogenated. A pressure drop of only 1.5 psi was observed. The ten grams of catalyst was filtered off and the two alcohol solutions combined and stored in a dessicator which contained sodium hydroxide. In spite of this, the solution, originally orange, turned black in three hours.

The procedure was repeated with a second 30 grams of dioxime but after 15 hours of hydrogenation a pressure drop of only 44 psi was observed. The catalyst was removed by filtration and the orange solution combined with the first run. In both runs the odor of ammonia was present.

The alcohol was stripped off under vacuum and an unsuccessful attempt was made to distill the product on a steam bath at two mm pressure.

The black liquid would not distill.

Preparation of Benzoyl Adduct of Hydrogenation Products

The crude amine described above was added to a one liter flask followed by 250 ml of an aqueous solution of five percent sodium hydroxide aqueous solution and 150 ml of chloroform. The flask was equipped with a dropping funnel, stirrer and reflux condenser. One hundred and fifty ml of benzoyl chloride was slowly added to the mixture through the dropping funnel. When all the benzoyl chloride was added the mixture was stirred for two hours and then allowed to stand overnight.

As the reaction mixture was slightly acidic, 20 grams of solid sodium hydroxide was dissolved in it. The chloroform layer was separated from the water layer and the latter washed with 150 ml of chloroform. The chloroform was stripped off under vacuum leaving a black tar-like residue.

The residue was filtered by suction leaving a black crystalline solid. The solid was dissolved in 100 ml of hot carbon tetrachloride and partially decolorized with five grams of charcoal. The charcoal was filtered off and the carbon tetrachloride evaporated off to leave a brown solid. The solid was fractionally crystallized three times yielding five fractions. The melting points of the first four fractions in order of increasing solubility were 114-115, 110-113, 98-110, and 84-85. The fifth fraction could not be crystallized.

Chromatographic Elution of the Benzoyl Derivatives of the Hydrogenation

Two-tenths of a gram of the most insoluble fraction was dissolved in one ml of chloroform and added to the top of a silicic acid chromatographic

contained about four grams and the fourth 0.5 gram. A fifth band was eluted considerably later than the first four and contained about two grams of solid. There remained on the column a black residue which could only be eluted with pure methanol.

In view of the considerable number of bands and the strong odor of ammonia in the original hydrogenated solution it was thought that most if not all of the cyclopentanedioxime was converted to a variety of secondary amines rather than the desired amine.

Hydrolysis of the Benzoyl Derivative of
the Hydrogenation Products of 1,2-cyclopentanedioxime

Three and one half grams of the most insoluble fraction of the recrystallized derivative of the hydrogenated cyclopentanedioxime was added to a 100 ml flask followed by 50 ml of distilled water. The solid was not wet by the water; therefore, to increase its solubility, one ml of absolute ethanol was added to the mixture. Thirty-six ml of concentrated hydrochloric acid was then added and the mixture heated under reflux overnight. In the course of heating the mixture turned black.

The black solution was cooled and made strongly basic with 100 ml of saturated sodium hydroxide solution and extracted with diethyl ether for 18 hours.

The ether extract was filtered; then dry hydrogen chloride passed into it for 1.5 hours. Pale yellow crystals separated and were filtered off. They were placed in a dessicator and pumped for three minutes. The solid, which weighed 1.39 grams, was later used in an unsuccessful attempt to prepare a cobalt(III) complex.

Reduction of Cyclopentanedioxime with Sodium in Alcohol

The cyclopentanedioxime was reduced by the method of Jaeger (10) and Cope (3). Ten grams of cyclopentanedioxime and two liters of absolute ethanol were added to a three liter flask. To this solution 180 grams of sodium, cut in small pieces, was slowly added. During the course of the addition, the solution turned black, then yellow. The solution was heated under reflux until all the sodium reacted with the alcohol: generally about twelve hours.

When the reaction was complete, the alcohol was steam distilled away and the remaining amine-water mixture cooled and then continuously extracted with diethyl ether for 48 hours. The ether was then stripped off and the amine distilled through a column having about five plates and stored in a sealed glass vial. The above procedure was repeated numerous times.

When sufficient amine had been accumulated it was washed into a 300 ml flask with ethyl alcohol. The flask was fitted with a capillary and dry nitrogen was bubbled very slowly into the flask to prevent bumping. Most of the alcohol was distilled off at 120 mm and 45 degrees. The pressure was then reduced to 60 mm and the amine distillation begun. The distilling column, one cm wide and 90 cm long, was packed with glass helices. The reflux ratio was kept above forty by means of a still head timer. Typical distillation data are found in Table 1.

The last fraction was taken off at 10 mm pressure when the pot temperature began to rise too high. The first four fractions were saved, as they contained considerable amounts of cis-1,2-cyclopentanediamine. The latter fractions included the last were used to prepare cobalt(III) complexes.

Table 1. Distillation Data of Cyclopentanediamine

Pot Temperature	Head Temperature	Sample Volume
100-103	42- 65	one ml
103-103	65- 95	one ml
103-103	95- 99	five ml
103-103	99-100	ten ml
103-107	100-102	seven ml
107-107	102-102	ten ml
107-107	102-102	ten ml
107-110	102-103	ten ml
110-110	103-104	eight ml
110-115	104-104	five ml
115-160	104-	fifteen ml

The infrared spectrum of the first fraction is almost identical with the spectrum of latter fractions. The only significant difference is in the region of 6.2 microns. In the first several fractions a small peak of variable intensity occurs at 6.2 microns but is absent in the latter fractions. This peak is thought to be caused by ammonia which absorbs in this region (14) and is often present as a decomposition product of the amine.

Several distillations of the amine were made and the first few fractions, now rich in cis-1,2-cyclopentanediamine, were combined and distilled at 60 mm pressure through a Ray distilling column (23). The

still head, column and pot were completely jacketed. The head temper-
ature was measured with an iron-constantan thermocouple and the take off
rate was controlled by a capillary. The infrared spectrum of the first
few fractions, presumably cis-1,2-cyclopentanediamine, contained no
absorption maximum at 6.2 microns, but the chemical shifts of the pro-
ton nuclear magnetic resonance spectrum were different from authentic
trans-1,2-cyclopentanediamine. The NMR spectra of cis and trans-1,2-cyclo-
pentanediamine in 50 percent deuterium oxide are shown in Figure 4.

Preparation of Trans-1,2-cyclopentanediaminedihydrochloride

Approximately four ml of distilled trans-1,2-cyclopentanediamine
was added to 100 ml of absolute alcohol and dry hydrogen chloride passed
through the solution for two hours. The white cyclopentanediaminedihydro-
chloride was filtered by suction and dried in air. Calculated for
$C_5H_{14}N_2Cl_2$; N, 16.2%; C, 34.7%; H, 8.0%. Found N, 16.4%; C, 34.8%; H,
8.5%.

Attempted Resolution of Trans-1,2-cyclopentanediamine

Twenty-four grams of d-10-camphorsulphonic acid was slowly added
to five grams of trans-1,2-cyclopentanediamine dissolved in 100 ml of
absolute ethanol. The solution was evaporated to dryness in a vacuum
dessicator and the salt fractionally crystallized from isopropyl alcohol
by dissolving the salt in boiling alcohol and cooling in ice for one to
two hours. The crystals were filtered off by suction and washed twice
with ten ml of cold isopropyl alcohol. Portions of the salt were reserved
for amine recovery.

The amine was recovered by dissolving the camphorsulphonic salt
in three ml of a saturated sodium hydroxide solution and continuously
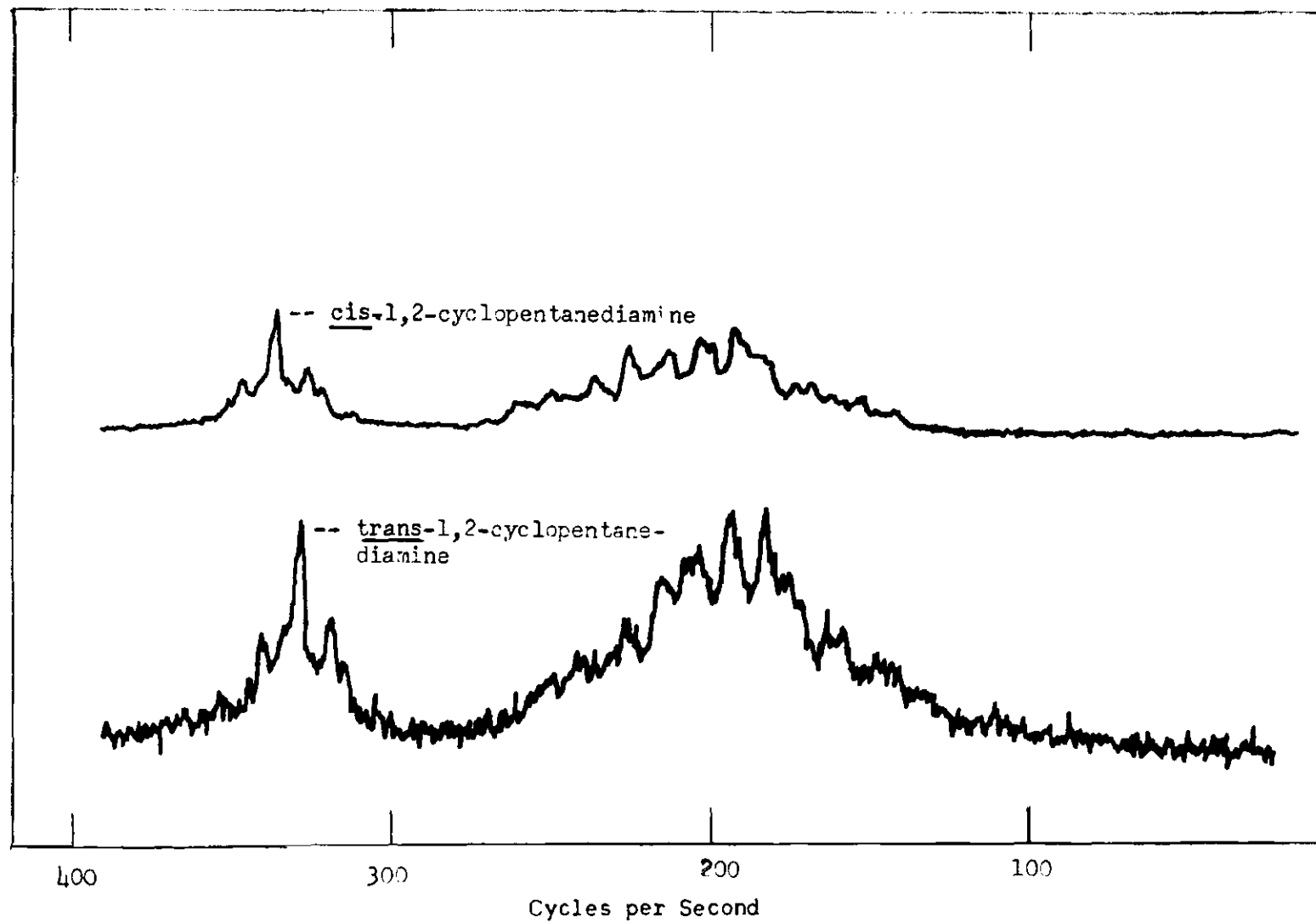
Figure 4. Proton NMR Spectra of Diamines

22

extracting the mixture with benzene for 24 hours. The benzene extract was dried over potassium hydroxide (five grams) for twenty-four hours then the rotation measured in a four decimeter tube. The concentration of the amine in the benzene was determined by adding an aliquot of the benzene extract to twenty ml of water and titrating the mixture with hydrochloric acid to the methyl orange end point.

The specific rotation of the amine after four recrystallizations was 11.3 degrees. After six crystallizations it increased to 18.1 degrees and after nine recrystallizations it was 18.8 degrees. Crystallization was discontinued because it was evident that there was very little difference in solubility between the two diastereomers. It will be shown in Chapter IV the specific rotation of the amine is at least 41 degrees and, therefore, many more recrystallizations of the camphorsulphonic acid salt would be required to effect a complete resolution of the amine.

Another unsuccessful attempt to resolve the trans-1,2-cyclopentanediamine, this time with d-tartaric acid was made. After ten recrystallizations of the tartrate salts from an ethanol-water solvent the specific rotation was only -21 degrees in dry benzene.

CHAPTER III

PREPARATION OF COBALT(III) COMPLEXES

Sodium triscarbonatocobaltate(III) trihydrate was prepared by hydrogen peroxide oxidation of cobalt(II) nitrate in the presence of sodium bicarbonate. The cyclopentanediamine complexes were then prepared by adding the sodium triscarbonatocobaltate(II) trihydrate to a solution of cyclopentanediamine dihydrochloride.

Preparation of Sodium Triscarbonatocobaltate(III) Trihydrate

The sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Dinkard (1). Fifty ml of water was added to a 500 ml flask containing 46 grams of sodium bicarbonate. The flask was fitted with a stirrer and immersed in an ice bath.

A solution of 29.1 grams of cobalt(II) nitrate hexahydrate and ten ml of 30 percent hydrogen peroxide in 50 ml of water was slowly added to the sodium bicarbonate solution. Stirring was continued for 30 minutes after the cobalt(II) nitrate solution had been added.

The green precipitate was filtered by suction, washed with water three times, followed by alcohol, and then ether. The yield was 24 grams, 66 percent of theoretical. The green filtrate doubtless contained much more product but no effort was made to recover it. The sodium triscarbonatocobaltate(III) was prepared as needed, as its shelf life in about two weeks.

Preparation of 1,2-cyclopentanediaminecobalt(III) Complexes

Attempted Preparation of Tris-trans-1,2-cyclopentanediamine Cobalt(III)

Chloride

One and four-tenth grams of sodium triscarbonatocobaltate(III) tri-
hydrate was slurried with 20 ml of water and 1.39 grams of what was thought

to be 1,2-cyclopentanediaminedihydrochloride was added to the slurry.

The amine hydrochloride was derived from the hydrogenation products of

1,2-cyclopentanedioximine (page 18). Frothing occurred immediately. The

slurry was heated on a water bath for 30 minutes and a brown precipitate

formed. This was filtered, recrystallized and found to be white. On

drying it turned green but when a small portion of it was burned it left

no residue, indicating that it contained no cobalt.

The pink filtrate, on addition of hydrochloric acid, turned green.

No precipitate formed however when the volume of the filtrate was reduced

to four ml, indicating that the filtrate contained only cobalt(II).

Preparation of $Co(cptdin)_2(CO_3)C.1-1/2 H_2O$

Seven and six-tenth grams (0.044 mole) of racemic trans-1,2-cyclo-

pentanediaminedihydrochloride (cptdin.2HCl) was added to a slurry of 5.2

grams (0.014 mole) of sodium triscarbonatocobaltate(III) trihydrate and

warmed on a water bath for 30 minutes. Considerable frothing occurred

with the green mixture gradually turning deep red. The cptdin.2HCl used

in this preparation and all those following was prepared from amine ob-

tained by the sodium reduction of cyclopentanedioxime.

The red mixture was cooled and several ml of alcohol added to

precipitate the complex. The complex was filtered by suction, washed with

alcohol and ether; then recrystallized from water. Analysis for

Co(cptdin)$_2$(CO$_3$)Cl.1-1/2 H$_2$0; calculated: C, 34.6%; N, 14.7%; H, 7.0%;
Co, 15.5%; ionic chloride, 9.29%;, covalent chloride none. Found; C,
35.07%; N, 13.98%; H, 7.24%; Co, 14.7%; covalent chloride, none; ionic
chloride 9.71%.

Preparation of $[Co_2(C_5H_{12}N_2)_7(H_2O)_2]Cl_6 \cdot 2H_2O$

Seven and two-tenth grams of cyclopentanediaminedihydrochloride
(.041 mole) was dissolved in two ml of water. To this 1.4 grams of sodium
triscarbonatocobaltate(III) trihydrate(.0039 mole) was added. The mixture
was heated on a steam bath for 30 minutes then cooled. Five ml of abso-
lute alcohol was added to the now red mixture and the resulting precipitate
filtered by suction. The pink precipitate was washed with alcohol then
ether and recrystallized once from water. The yield was 0.7 grams, 33
percent of theoretical. Calculated for $[Co_2(C_5H_{12}N_2)_7(H_2O)_2]Cl_6 \cdot 2H_2O$; C,
38.1%; N, 17.6%; H, 8.34%; Co, 10.68%; ionic chloride 19.3% covalent chlor-
ide, none. Found: C, 37.15%; N, 17.5%; H, 7.00%; Co, 10.54; ionic chlor-
ide, 20.8%; covalent chloride, none. Recrystallization of the complex
reduced the percentage of ionic chloride to 19.6 percent.

The preparation was repeated numerous times except that the ratio
of cyclopentanediaminedihydrochloride(cptdin·2HCl) to triscarbonatocobal-
tate(III) trihydrate was six rather than ten, as above. The yield varied
from practically zero to 80 percent with the average about 50 percent.

Preparation of Prasecobaltic Chloride and Violeocobaltic Chloride

A bright green precipitate was isolated by adding one ml of con-
centrated hydrochloric acid to five grams of $[Co(cptdin)_2(CO_3)]Cl \cdot 1$-1/2 H$_2$0
dissolved in five ml of water. On washing the bright green precipitate
with absolute alcohol the crystals crumbled and their color changed to

dull green. By dissolving either green solid in water and slowly evaporating the resulting solution to dryness on a water bath a violet solid could be isolated. No attempt to analyze these salts was made. However the conversion of the green salts to the violet salt is analogous to the behavior of <u>trans</u>-bisethylenediaminedichlorocobalt(III) chloride (green) and <u>cis</u>-bisethylenediaminedichlorocobalt(III) chloride (violet). Undoubtedly the bright green precipitate contains hydrogen chloride of crystallization which is washed out with the ethanol.

Heating 0.5 grams of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ with 0.5 grams of bone charcoal at 50 degrees for 12 hours followed by filtration of the charcoal yielded a violet colored solution. Addition of three ml of concentrated hydrochloric acid caused a green solid to precipitate out of solution over a period of two weeks. No attempt to analyze this salt was made.

Preparation of $[Co(cptdin)_4]Cl_3 \cdot 8H_2O$

Four and six-tenth grams (2.7×10^{-2} mole) of cptdin·2HCl was added to a slurry of 3.3 grams ($.91 \times 10^{-2}$ mole) of sodium triscarbonatocobaltate(III) trihydrate and the mixture was warmed on a water bath for 30 minutes. Carbon dioxide was slowly liberated, with the black solution slowly turning deep red.

After cooling the mixture, approximately five ml of absolute ethanol was added to the mixture, causing a pale pink solid to precipitate. The solid was filtered off and, when redissolved in water, appeared to effervesce. The water solution was evaporated almost to dryness. Dark red crystals formed which, when recrystallized, appeared to be $[Co(cptdin)_2(CO_3)]$ Cl· 1-1/2 H_2O.

The filtrate which yielded the pink solid was further evaporated on a steam bath. On cooling, ten ml of alcohol was added, causing a brown-pink solid to precipitate. The solid was dissolved in water with no evolution of carbon dioxide. Three drops of concentrated hydrochloric acid were added and the mixture was allowed to stand overnight. A blue-violet solid precipitated. When the solid was dissolved in water and acidified with concentrated hydrochloric acid, a green solid slowly precipitated. The green and violet precipitates appear to be the same as the praseocobaltic chloride and violeocobaltic chloride described previously.

On further evaporation of the original filtrate, followed by addition of ethanol, a brown solid precipitated. On recrystallization a pink salt was obtained which appeared to be identical to $[Co_2(cptdin)_7 (H_2O)_2] Cl_6 \cdot 2H_2O$. However, elemental analysis best agrees with $[Co(cptdin)_4] Cl_3 \cdot 8 H_2O$. Calculated for $[Co(cptdin)_4] Cl_3 \cdot 8H_2O$: ionic chloride, 15.4%; Co, 8.53%; C, 34.8%; N, 16.5%; H, 8.97%; covalent chloride, none. Found: ionic chloride; 14.9%; Co, 8.41%; C, 35.1%; N, 17.02%; H, 7.49%; covalent chloride, none.

Several attempts were made to prepare more $[Co(cptdin)_4] Cl_3 \cdot 8 H_2O$ but $[Co(cptdin)_2(CO_3)] Cl \cdot 2H_2O$, praseocobaltic chloride, and violeocobaltic chloride were the only salts isolated.

Methods of Analysis

Ionic chloride was determined by potentiometrically titrating the complex using silver and calomel electrodes. Approximately 0.05 g of the complex was dissolved in 20 ml of water and titrated with silver nitrate.

Because the covalent chlorine is bound strongly to the cobalt in the complex, the covalent chloride could be determined only by destroying the complex. The complex was dissolved in two ml of water containing 0.2 grams of sodium hydroxide. The solution was heated to dryness, cooled, and the black residue taken up with two ml of concentrated perchloric acid. The solution was diluted to 20 ml and titrated with silver nitrate. The chloride thus determined was the ionic chloride plus covalent chloride. The covalent chloride was determined by subtracting the ionic chloride from the total chloride.

Cobalt was determined by titration with ethylenediaminetetraacetic acid. The complex was pretreated by dissolving it in two ml of water and adding 0.2 grams of sodium hydroxide then heating to dryness. After cooling, the black residue was taken up with two ml of concentrated hydrochloric acid. About ten ml of distilled water, 0.2 grams of sodium acetate and a small amount of murexide indicator were added to the green solution. Concentrated ammonia was then added until the color of the solution was yellow. If too much ammonia was added cobalt(II) hydroxide precipitated, but a few drops of concentrated hydrochloric acid took it back into solution. Occasionally the solution was turbid with silica. If so, the silica was filtered off, washed and discarded. The clear solution was then titrated with ethylenediaminetetraaceticacid(EDTA).

The EDTA was standardized against a magnesium solution. Magnesium metal was weighed into a volumetric flask and dissolved in a few ml of concentrated hydrochloric acid; then made up to the mark. The magnesium was titrated hot with EDTA using erico T indicator. The color change was from light green to dark violet.

The carbon, nitrogen and hydrogen analyses were made by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

Preparation of Tris-cis-1,2-cyclopentanediaminecobalt(III) Chloride

The first fraction of amine from the Ray distilling column was converted to the dihydrochloride salt by dissolving the amine in dry ether and passing dry hydrogen chloride through the solution for 90 minutes. The white solid was filtered off and allowed to dry in air.

An 0.828 gram sample of the cis-1,2-cyclopentanediamine dihydrochloride(0.00479 mole) was dissolved in two ml of water then 0.289 grams (0.000798 mole) sodium triscarbonatocobalt(III) trihydrate added. The mixture was heated on a water bath for 10 minutes then allowed to stand overnight.

Ten ml of absolute alcohol was added to the solution and the resulting precipitate was filtered, washed with alcohol and dried. The product, contaminated with sodium chloride, was dissolved in about 50 ml of water and precipitated by adding excess sodium iodide. The iodide salt was filtered off, washed with a little water and converted to the chloride salt by grinding the precipitate with freshly precipitated silver chloride. The silver halides were filtered off and the filtrate concentrated. The visible spectrum of the filtrate showed absorption maxima at 348 and 485 millimicrons. On evaporating the filtrate to dryness the solid was found to contain 31.7 percent ionic chloride and 5.01 percent cobalt and therefore was greatly contaminated with sodium chloride. There was not enough sample to purify it by recrystallization but the visible spectrum indicates that it was not $[Co_2(cptdin)_7(H_2O)_4]Cl_6$ and therefore it probably was $Co(cpcdin)_3Cl_3$.

The visible spectrum of the filtrate showed two absorption maxima, one about 340 millimicrons and the other about 475 millimicrons. The exact positions of the maxima were difficult to determine because of interference from amine decomposition products.

An attempt was made to purify the filtrate by absorbing it on a chromatographic column of IRC-50 resin and eluting it with 0.01 $\underline{M}$ hydrochloric acid. A complex containing cobalt(III), as shown by the visible spectrum, was eluted from the resin but it rapidly decomposed on concentrating and could not be isolated.

CHAPTER IV

CHARACTERIZATION OF $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$

Separation and Resolution of $[Co_2(cptdin)_7(H_2O)_2 Cl_6 \cdot 2H_2O$

By Fractional Crystallization

A 4.6 gram sample of $[Co_2(cptdin)_7(H_2O)_2]$ $Cl_6 \cdot 2H_2O$ was dissolved
in 380 ml of boiling methanol-water solution (70 percent methanol). The
red solution was cooled to 35 degrees and 30 ml of diethyl ether was added,
causing a pink solid to precipitate. The mixture was heated for 15 min-
utes, then cooled in ice for thirty minutes, filtered, washed with 10
ml of methanol, then ether and dried. The weight of the precipitate was
2.4 grams.

The 2.4 grams was dissolved in 200 ml of boiling 70 percent methanol
and cooled to 35 degrees. One hundred ml of diethyl ether was added and
the mixture cooled in ice for 30 minutes. The pink precipitate was fil-
tered, washed once with 10 ml of methanol and then with ether. One and
five-tenth grams was recovered. Calculated for $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$;
19.3 percent ionic chloride and found 19.3 percent ionic chloride.

The filtrate from the first recrystallization was reduced in vol-
ume until most of the pink solid precipitated from solution. The solid
was redissolved in 70 percent methanol, heated to boiling, cooled, and
precipitated with ether. The resulting filtrate was evaporated to dryness
yielding 1.7 grams. Calculated for $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$; 19.3
percent ionic chloride and found 19.5 percent ionic chloride.

The 1.7 grams (0.00155 mole) of $[Co_2(cptdin)_7(H_2O)_2] Cl_6 \cdot 2H_2O$ from the soluble fraction was dissolved in 100 ml of water and 1.12 grams (0.00309 mole) of silver $\underline{d}$-tartrate added. The mixture was stirred for 15 minutes and the silver chloride filtered off. The filtrate was evaporated to dryness and the resulting solid was recrystallized from 70 percent methanol. Four fractional crystallizations yielded a solid with a specific rotation of -356 degrees. A fifth crystallization yielded a salt whose rotation was -358 degrees. This salt was thought to be resolved but it will be shown that this was not the case.

The insoluble fraction of $[Co_2(cptdin)_7(H_2O)_2] Cl_6 \cdot 2H_2O$ was partially resolved by dissolving 1.2 grams of the complex (0.00109 mole) in 100 ml of water and warming it for ten minutes with 0.820 grams (0.00225 mole) of silver $\underline{d}$-tartrate and filtering while hot to remove the silver chloride. The filtrate was evaporated to dryness, then fractionally crystallized twice to yield a solid of specific rotation -850 degrees. A further recrystallization yielded a solid of specific rotation of -958 degrees. There was insufficient sample for further recrystallization. For reasons unknown, this experiment could not be repeated. Repeated fractional crystallization of one sample, both as chloride salt and the tartrate salt was attempted from both water and the water-methanol solution. Fractional crystallization of a second sample as the nitrate salt was attempted. Conversion of both samples to the tartrate salt yielded a tartrate salt whose specific rotation was only -490 ± 10 degrees. It will be shown that there are, in fact, three geometrical isomers of the cation $Co_2(cptdin)_7(H_2O)_2^{+6}$. The tartrate salt which had the specific

rotation of -490 degrees is undoubtedly a mixture of all three isomers.

Determination of the Degree of Polymerization of $Co_2(cptdin)_7(H_2O)_2^{+6}$

Because the ratio of amine to cobalt in the complex $[Co_2(cptdin)_7$ $(H_2O)_2]$ $Cl_6 \cdot 2H_2O$ is 3.5 the complex must be a dimer at the minimum and may be a tetramer or even contain six cobalt atoms per cation. As the complex is soluble in water, higher polymers can probably be ruled out. Several methods of determining the degree of polymerization were considered but thought to be inapplicable.

In theory, conductance measurements of dilute solutions should yield the charge on the cation. However the Onsager limiting slope for either a cation of charge six or twelve would be so great that it would be very difficult to distinguish between the two slopes.

Likewise molecular weight measurements based on colligative properties were considered. These methods yield the mean molecular weight. In the case of $[Co_2(cptdin)_7(H_2O)_2]$ Cl_6 whose minimum molecular weight is 1067, the mean molecular weight of the dimer is 152 while the mean molecular weight of the tetramer is only 172. In order for a measurable vapor pressure increase, melting point decrease, etc., to occur the solution must be rather concentrated. But because of the large size and high charge of the cation the activity coefficient of the cation is probably quite different from unity causing marked deviation from ideality and making the results subject to uncertainty.

Therefore it was thought that the best method for determining the degree of polymerization would be one which corrected for activity changes

or kept them to a minimum by using dilute solutions. One such method would be to measure the Ksp of the complex at constant ionic strength.

Two attempts were made to measure the charge on the cation by measuring the solubility product of the complex at constant ionic strength while the anion concentration was changed by adding a salt with an anion in common with the complex.

The solubility product (Ksp) of the compound containing the complex and a uninegative anion is given by the following expression,

$$Ksp = (complex)(anion)^n \tag{1}$$

where n is the charge on the cation of the complex. The anion concentration and the amount of salt added which contained the common anion are given by the following expression:

$$Ksp = [complex] [n(complex) + (added\ anion)]^n \tag{2}$$

In practice the anion concentration derived from the complex is quite small compared to the added anion, (A), even when n is as high as twelve. Equation two then becomes:

$$Ksp = (complex)(A)^n \tag{3}$$

Taking the logarithm of both sides of equation (3)

$$log\ Ksp = log(complex) + n\ log(A) = constant \tag{4}$$

Rearranging equation (4):

$$log\ (complex) = -n\ log\ (A) + constant \tag{5}$$

This is the equation of a straight line where n is the slope and "constant" the intercept. By plotting log (complex) against log (A) it should be possible to determine the slope of the line, hence the charge on the complex cation.

Experimental

Approximately 0.5 grams of $[Co_2(cptdin)_7(H_2O)_2] Cl_6 \cdot 2H_2O$ was dissolved in 24 ml of warm water. To the warm solution one gram of sodium iodide dissolved in hot water was slowly added. The yellow complex which precipitated immediately was digested on a water bath for 15 minutes, cooled, filtered, washed with cold water twice followed by alcohol then ether.

An excess of the iodide salt was added to nine sodium iodide solutions of different concentration, each shaken for 36 hours at room temperature and the absorbance of each solution measured at 490 millimicrons in ten cm cells. The sodium iodide solutions had been made to constant ionic strength with sodium chloride. The specific absorbance of the salt at 490 millimicrons is 81.5 per mole of cobalt. The concentration of the cobalt was determined by use of the Beer-Lambert Law. The value of the cobalt and iodide concentrations are found in Table 2.

The logarithm of the cobalt concentration versus the logarithm of the iodide concentration was plotted and the best straight line drawn through the locus of points. At higher sodium chloride concentrations (lower sodium iodide concentration) there is considerable curvature in the locus of points. The slope of the best straight line is 1.4 and it decreases with increasing chloride concentration. As the minimum value of n must be six this plot indicates that the composition of the solid

Table 2. Sodium Iodide and Iodide Complex Concentrations

Iodide Concentration	Absorbance	Corrected Absorbance	Complex Concentration	log (complex)	log (iodide)
0.010 M	0.0503	0.0485	0.000697	-3.157	-2.000
0.020 M	0.0473	0.0455	0.000558	-3.245	-1.699
0.030 M	0.0511	0.0493	0.000607	-3.217	-1.523
0.040 M	0.0391	0.0375	0.000460	-3.337	-1.398
0.050 M	0.0348	0.0330	0.000406	-3.392	-1.301
0.060 M	0.0246	0.0228	0.000280	-3.553	-1.222
0.080 M	0.0192	0.0174	0.000213	-3.672	-1.097
0.090 M	0.0158	0.0140	0.000172	-3.765	-1.046
0.100 M	0.0116	0.0098	0.000120	-3.931	-1.000

complex is variable and that it is dependent on the sodium chloride con-

centration.

A similar attempt was made to determine the charge on the cation

by measuring the solubility product of $[Co_2(cptdin)_7(H_2O)_2]$ $(NO_3)_6$ at

constant ionic strength. An excess of the nitrate salt was added to

nine solutions of sodium nitrate, each shaken for 36 hours and the

absorbance of each solution measured at 490 millimicrons in ten cm cells.

The sodium nitrate solutions were made to constant ionic strength with

sodium chloride. The values of the cobalt and nitrate concentrations are

found in Table 3. The data was treated in the same way as it was with

the measurements on the iodide salt. The best straight line through the

points has a slope of 0.38 indicating that the composition of the complex

Table 3. Sodium Nitrate and Nitrate Complex Concentration

Nitrate Concentration	Absorbance	Corrected Absorbance	Complex Concentration	log (complex)	log (nitrate)
0.0100 M	0.0306	0.0288	0.000353	-3.454	-2.000
0.0200 M	0.0364	0.0346	0.000424	-3.372	-1.699
0.0300 M	0.0323	0.0305	0.000374	-3.417	-1.523
0.0400 M	0.0298	0.0280	0.000343	-3.467	-1.398
0.0500 M	0.0300	0.0282	0.000345	-3.468	-1.301
0.0600 M	0.0252	0.0234	0.000287	-3.542	-1.222
0.0700 M	0.0270	0.0252	0.000309	-3.510	-1.155
0.0800 M	0.0272	0.0254	0.000311	-3.508	-1.097
0.0900 M	0.0282	0.0190	0.000233	-3.632	-1.046

is very dependent on the sodium chloride concentration.

The results of both experiments indicate that the composition of the solid compound which is in equilibrium with the solution, is indefinite and in the case of the iodide salt, changes quite markedly with the iodide concentration.

Determination of the Degree of Polymerization of $Co_2(cptdin)_7(H_2O)_2Cl_6$ Using the Debye-Hückel Equation

The solubility product experiments indicate that the composition of the complex was markedly dependent on the concentration and nature of the electrolyte used to maintain the solution at constant ionic strength. By use of the Debye-Hückel equation a rather novel method of determining

the degree of polymerization is possible which makes no recourse to constant ionic strength solutions.

One common form of the Debye-Hückel equation valid for solutions of ionic strength less than 0.1, is the following:

$$\log f \pm = \frac{-A\ Z_+ Z_-\ \sqrt{I}}{1 + Ba\ \sqrt{I}} \qquad (6)$$

where $\underline{A}$ and $\underline{B}$ are constants, Z_+ and Z_- are the cation and anion charge, I the ionic strength and using mole fractions, f± the mean ionic activity coefficient of the salt and $\underline{a}$ the approach parameter. The values of $\underline{A}$ and $\underline{B}$ for aqueous solutions at 25° C are; 0.5115 and 0.3291 Angstrom respectively.

Consider the following equilibrium reaction of a sparingly soluble complex where v_+ and v_- are the number of cations and anions formed.

$$A_{v+} B_{v-} = v_+\ A^{v-} + v_- B^{v+} \qquad (7)$$

The following is the expression for the solubility product:

$$Ksp = C_+^{v+}\ f_+^{v+}\ C_-^{v-}\ f_-^{v-} \qquad (8)$$

where C represents the molar concentration and f the molar activity coefficient of the ions in question. Taking logarithms of both sides of the equation the following is obtained

$$\log Ksp = \log C_+^{v+}\ C_-^{v-} + \log f_+^{v+}\ f_-^{v-} \qquad (9)$$

Taking $f_\pm^{v} = f_+^{v+}\ f_-^{v-}$ and $v = v_+ + v_-$ the following expression is found.

$$\log K_{sp} = \log IP + (v_+ + v_-) \log f_\pm^v \qquad (10)$$

where IP is the ion product, i.e., $C_+^{v+} C_-^{v-}$.

Solving for $f_\pm$ in equation (10) the following expression is obtained:

$$\log f_\pm = (1/(v_+ + v_-))(\log K_{sp} - \log IP) \qquad (11)$$

This value of $\log f_\pm$ is equated to its value in equation (6) and the resulting equation rearranged to give the general expression.

$$\text{Log } K_{sp} = \log IP - \frac{(v_+ + v_-) A|Z_+Z_-|\sqrt{I}}{1 + Ba\sqrt{I}} \qquad (12)$$

The low rotation chloride complex was converted to the nitrate salt by adding excess potassium nitrate to a solution of the chloride salt. The pink precipitate was filtered off and washed twice with water then stirred with a fresh potassium nitrate solution overnight. The pink solid was filtered, washed twice with a little cold water, followed by alcohol then ether.

An excess of this nitrate salt was then shaken for 48 hours with thirteen potassium nitrate solutions at 25 degrees and the absorbance of each solution measured at 490 millimicrons in ten cm cells. The data are found in Table 4. The specific absorbance of the complex is 81.5 per cobalt.

The high rotation chloride complex was similarly converted to the nitrate salt. An excess of this salt was shaken for 48 hours at 25 degrees with nine solutions of potassium nitrate and the absorbance of

Table 4. Absorbance of High Rotation Complex

Potassium Nitrate Concentration	Corrected Absorbance of Complex
0.0759	0.0452
0.1012	0.0354
0.1263	0.0273
0.1520	0.0245
0.1771	0.0267
0.202	0.0211
0.226	0.0210
0.253	0.0202
0.278	0.0177
0.304	0.0166

each solution measured at 490 millimicrons in ten cm cells. The data

are found in Table 5.

If the charge on the anion is unity, equation (12) reduces to:

$$\log Ksp = \log IP - \frac{(Z_+ + 1)(Z_+)A \sqrt{I}}{1 + Ba \sqrt{I}} \qquad (13)$$

For any given experimental solution, $\log IP$ and $\sqrt{I}$ may be

calculated from the known concentrations leaving $\log Ksp$, Z_+, and $\underline{a}$ as

undetermined quantities. Thus for $\underline{n}$ solutions of different concentra-

tions a series of $\underline{n}$ simultaneous equations in three unknowns arises.

Since these equations are nonlinear, the general calculation of

the best values for the unknowns (in the least squares sense) presents

Table 5.   Absorbance of Low Rotation Complex

Potassium Nitrate Concentration	Absorbance of Complex
0.0759	0.0883
0.1012	0.0588
0.1267	0.0364
0.1520	0.0439
0.1771	0.0428
0.202	0.0339
0.226	0.0270
0.253	0.0264
0.1129	0.0567
0.1401	0.0317
0.201	0.0472
0.157	0.0430
0.176	0.0381

computational difficulties. Therefore, the data was treated in the fol-
lowing way. Since Z_+ must be some multiple of six and is probably not
greater than 18, Z_+ was arbitrarily assigned a value and the best least
squares value of log Ksp and $\underline{a}$ assuming that arbitrary Z_+ were calculated
in the following fashion.

If the sum of the squares of the deviations are defined in the
following way:

$$\sum_{1}^{N} \left[\log Ksp - \log IP + \frac{((Z_+ + 1)(Z_+)A\sqrt{I})}{1 + Ba\sqrt{I}} \right]^2 = D^2 \qquad (14)$$

Taking the partial derivative of D^2 with respect to $\underline{a}$ and equating to zero one obtains:

$$\sum_{1}^{N} 2\left[(\log Ksp - \log IP + \frac{(Z_+ + 1)(Z_+)A\sqrt{I}}{1 + Ba\sqrt{I}} \right]\left[- \frac{(Z_+ + 1)(Z_+)(AB\sqrt{I})}{(1 + Ba\sqrt{I})^2} \right] = 0 \quad (15)$$

Since the quantity in the right bracket is never zero,

$$\sum_{1}^{N} \left[\log Ksp - \log IP + \frac{(Z_+ + 1)(Z_+)A\sqrt{I}}{1 + Ba\sqrt{I}} \right] = 0 \qquad (16)$$

Thus the best value of log Ksp for a given value of $\underline{a}$ is:

$$\log Ksp = \frac{1}{N} \sum_{1}^{N} \left[\log IP - \frac{(Z_+ + 1)(Z_+)(A\sqrt{I})}{1 + Ba\sqrt{I}} \right] \qquad (17)$$

$\underline{a}$ was varied in a trial and error fashion until the minimum value of D^2 was found. The process was then repeated for other possible values of Z_+ and in this way values of $\underline{a}$, log Ksp and D^2 were found for all of the possible values of Z_+. Then an examination of $\underline{a}$ and D^2 enabled one to choose the best value of Z_+. The calculated values of $\underline{a}$, log Ksp and D^2 when Z_+ is assumed six and twelve are found in Table 6. The parameter, $\underline{a}$ is of the order of 2.8 angstrom unites (4) for potassium nitrate. The ratio of complex to potassium nitrate in solution was at most 1:20 and most solutions were even more dilute in complex. Therefore the expected

Table 6. Results of Debye-Hückel Experiment

	Low Rotation Dimer	High Rotation Dimer	Low Rotation Dimer	High Rotation Dimer
$\underline{a}$	2.9	2.9	5.7	5.7
pKsp	$14.65 \pm .02$	$14.86 \pm .04$	$31.98 \pm .04$	$32.16 \pm .06$
D^2	.00139	.00484	.00365	.00808

value of $\underline{a}$ for the solutions should be near 2.8 angstrom units. Two calculations were made on the soluble complex and two on the insoluble complex; four in all. The complex in question was first assumed to be a dimer then a tetramer and the assumption which yielded the value of $\underline{a}$ closest to 2.8 angstrom unites was thought to be the correct one.

Chromatographic Separation of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$

In an effort to separate the various geometrical isomers of the complex $[Co_2(cptdin)_7(H_2O)_2] \, Cl_6(H_2O)_2$ ions exchange chromatography was resorted to. Attempts were made to separate the isomers of the complex using 100-200 mesh Dowex 50 X2 sulphonic acid resin with perchloric acid as the elutant. Approximately 0.25 grams of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ was added to a chromatographic column one cm wide and 15 cm deep. One molar perchloric acid failed to move the complex while five molar perchloric acid moved the complex only slowly. Ten molar perchloric acid, which was finally used, eluted the complex in ten days.

Some slight separation occurred as shown by the optical density of the effluent. To remove the perchloric acid from the complex, potassium

hydroxide was slowly added to the effluent neutralizing the acid and precipitating potassium perchlorate, which was filtered off. The large volume of effluent was concentrated over sulphuric acid in a vacuum dessicator. Potassium perchlorate, as it accumulated, was filtered off. But when the volume of the solution was reduced to about 30 ml, the perchlorate salt of the complex precipitated from solution and it was found impractical to free the complex from potassium perchlorate. Because of the difficulty of separating the potassium perchlorate from the complex and because of the danger in using concentrated perchloric acid in contact with the organic resin this experiment was not repeated.

Another attempt to separate the geometric isomers of the complex, using 100-200 mesh Dowex 50 X2 sulphonic acid resin and calcium chloride as the elutant, was made. Approximately 0.5 grams of crude $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$, contaminated with cobalt(II) chloride and $[Co(cptdin)_2(CO_3)]Cl$ was added to the top of a resin bed three cm wide and thirty cm long then eluted with five molar calcium chloride. The $[Co(cptdin)_2(CO_3)]Cl$ elated first followed by cobalt(II) chloride then $[Co(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$. The three compounds were cleanly separated from one another but there was no separation of $[Co_2(cptdin)_2(H_2O)_2]Cl_6$ into its geometric isomers. Therefore the experiment was not repeated.

Separation of the geometric isomers of the complex was attempted using IRC-50 carboxylic acid resin and dilute hydrochloric acid as the eluent. Approximately 0.25 grams of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ was added to the top of a column three cm wide and 25 cm long, washed with 100

ml of water and eluted with 0.01 M hydrochloric acid at a rate of five

ml per minute. Fractions of 25 ml were collected and their optical

density measured at 490 millimicrons.

Some evidence of separation was found since the curve obtained

by plotting optical density versus effluent volume was broad with a

shoulder at the leading edge of the curve. Because the separation of

$[Co_2(cptdin)_7(H_2O)_2]$ $Cl_6 \cdot 2H_2O$ into its geometrical isomers was so slight

the IRC-50 resin was not used for this purpose.

Amberlite CG-50 of 400-600 mesh was then used to separate the

complex into its geometrical isomers. The resin was slurried with

water and left to settle overnight. The fines which had not settled

out were discarded and the procedure repeated. Enough resin, slurried

in water, was poured into a column three cm wide to form a resin bed 70

cm deep. The column was washed with water until the pH of the effluent

was above four. Then approximately 0.25 grams of $[Co_2(cptdin)_7(H_2O)_2]$

$Cl_6 \cdot 2H_2O$ dissolved in a little water was added to the column, and eluted

with hydrochloric acid solution of pH 2.1. Using a flow rate of 0.3 ml

per minute, fractions of forty ml were collected and their optical

densities measured at 490 millimicrons. A plot of the optical density

versus effluent, Figure 5, clearly shows three components, one almost

completely separated and the other two partially separated. The spectrum

of each of the three bands from 300 millimicrons to 600 millimicrons is

almost identical. Two maxima, one at 352 and the other at 490 occurs.

The visible spectra of a mixture of the three complexes is shown in Figure

6.

A similar experiment was performed using partially resolved com-

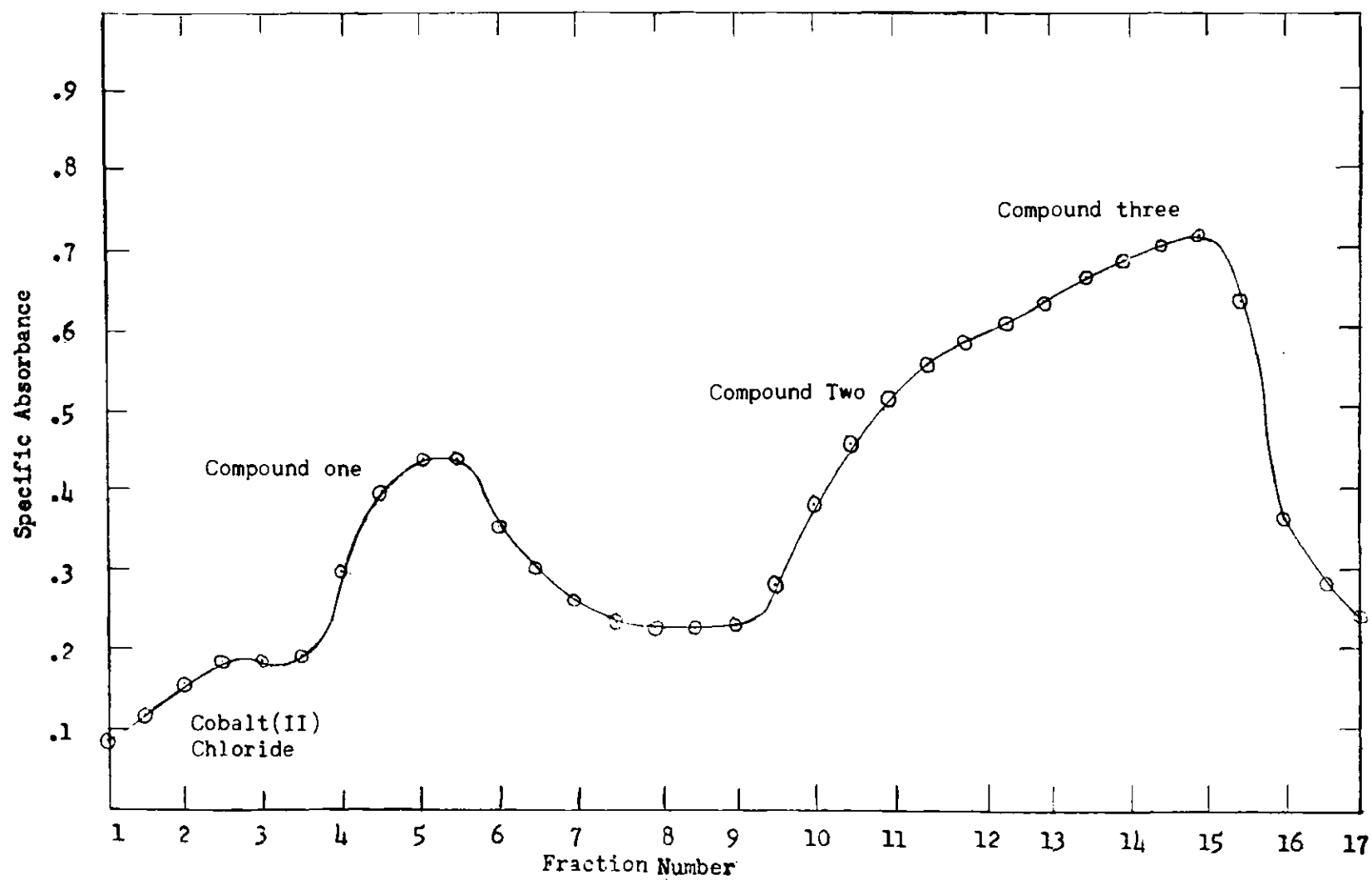plex. The ratio of the observed rotation to optical density was almost

Figure 5.   Chromatographic Elution of $Co_2(cptdin)_7(H_2O)_4Cl_6$.
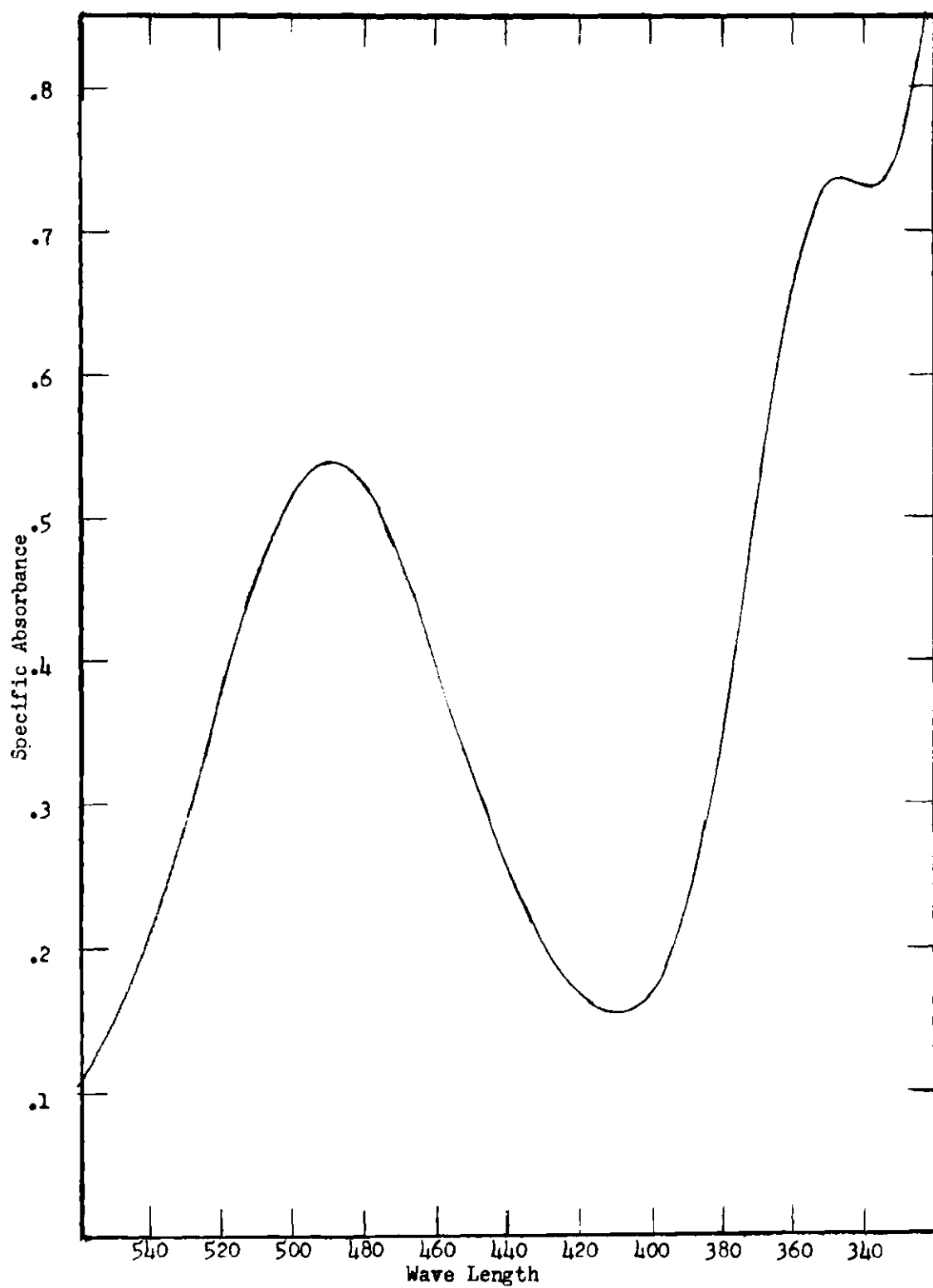
Figure 6. Visible Spectra of $Co_2(eptdin)_7(H_2O)_4Cl_6$

zero for the first component, rising to about 2.8 degrees per absorbancy unit for the second component and 3.7 degrees per absorbancy unit for the third component. Several runs were made and when enough of each compound was collected each was resolved.

Resolution of the Third Component from the Chromatographic Column

Eight-tenth grams of the third component from the chromatographic column was stirred with 0.526 grams of silver d-tartrate in 500 ml of water for one hour. The silver chloride was filtered off and the pink solution evaporated in a vacuum dessicator over sulphuric acid. As it accumulated the solid which formed on the sides of the evaporating dish was scraped into the solution. When the liquid had evaporated to 25 ml, the red crystals were filtered off, washed with a little cold water followed by ethanol and finally ether. The specific rotation of the crystals was -490 degrees. The solid was dissolved in water and allowed to evaporate overnight. The crystals were filtered, washed with water, ethanol and then ether and found to have a specific rotation of -426 degrees. On recrystallizing the solid again the specific rotation dropped to -419. A further fractional crystallization yielded crystals whose specific rotation was -418 degrees. As the small change in rotation was insignificant, the salt was considered resolved. A decrease in specific rotation on fractional crystallization is rather unusual but it is evident that the starting material was contaminated with the complex in band two. The optical rotatory dispersion curve of band three is shown in Figure 7.

Resolution of the Second Component from the Chromatography Column

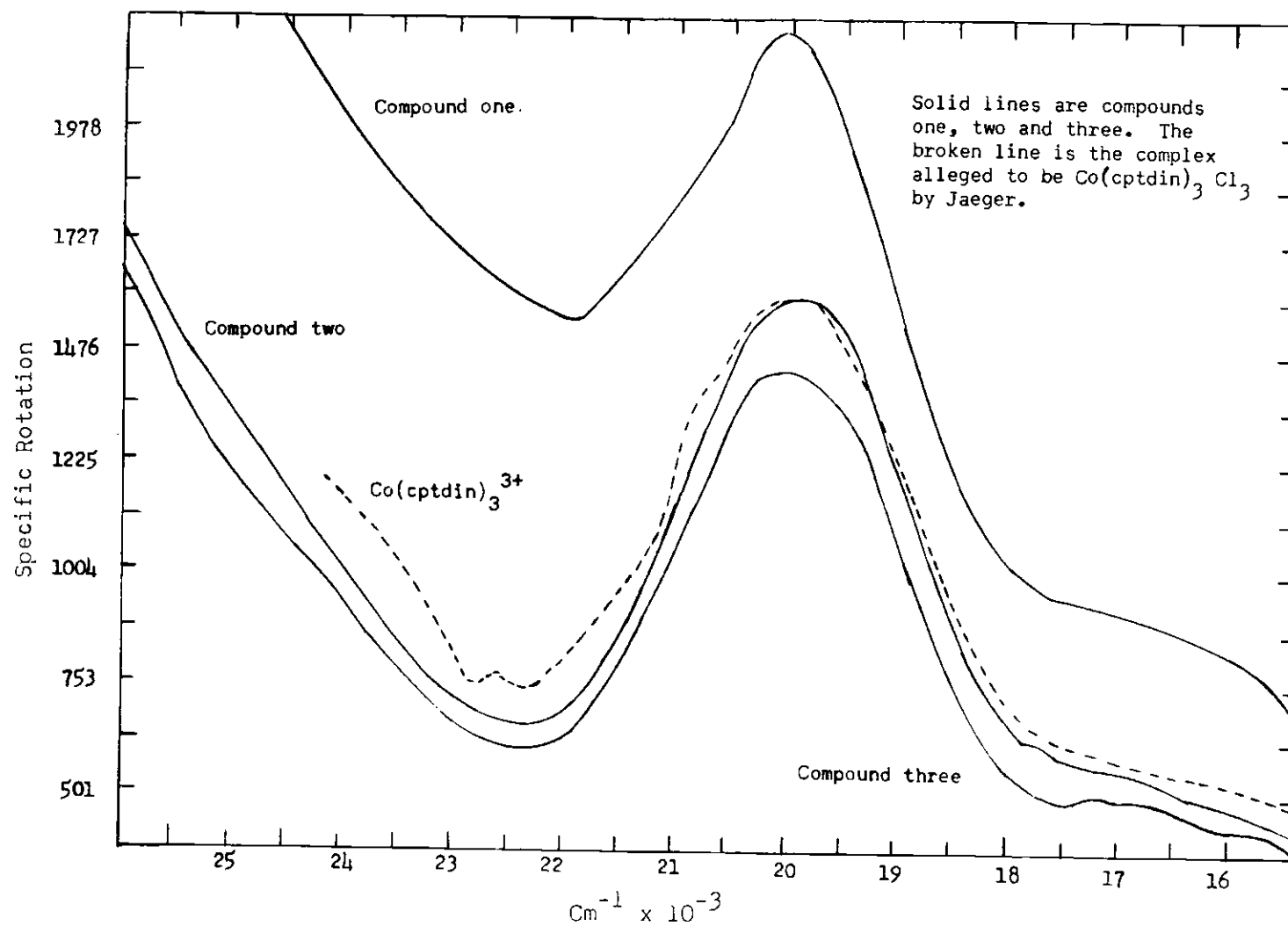To 40 ml of water, 0.356 grams of the second component from the

Figure 7. Optical Rotatory Dispersion Curves

chromatography column was added. This solution was stirred with 0.234 grams of silver d-tartrate for one hour then the silver chloride was filtered off. The pink solution was allowed to evaporate to 20 ml and the pink crystals were filtered off, washed with a little cold water followed by ethanol then ether. The specific rotation of the crystals was -478. With a second fractional crystallization the specific rotation of the solid dropped to -476 and a third recrystallization yielded crystals whose specific rotation was -484 degrees. Because these changes in specific rotation are small and random, the salt was considered resolved. The optical rotatory dispersion curve of this compound is shown in Figure 7.

Resolution of the First Component from the Chromatography Column

Because the specific rotation of compounds two and three were considerably less than -958 degrees it was believed that the first compound from the chromatographic column corresponded to the salt whose specific rotation was -958 degrees and a mixture of the second two compounds from the column corresponded to the salt whose specific rotation was -358 degrees. In order to ascertain if this supposition was correct a quantity of compound one was collected and partially resolved.

To 22 ml of water, 0.0646 grams of compound one was dissolved. This solution was stirred with 0.0422 grams of silver d-tartrate for one hour then the silver chloride filtered off. The pink solution was evaporated in a dessicator until pink crystals formed. These crystals were filtered off, washed with a little water followed by alcohol then ether. Their specific rotation was -213. These crystals were again recrystallized by dissolving them in water and evaporating the solution in a dessicator.

The pink crystals which were filtered off were found to have a specific rotation of -600 degrees. There was insufficient sample for a further recrystallization but the specific rotation of this sample was considerably greater than the totally resolved compounds two and three. Therefore compound one must correspond to the high rotation salt and compounds two and three correspond to the low rotation salt.

Resolution of a Mixture of Compounds One and Two

Because there was insufficient sample to totally resolve compound one, a mixture of compound one and two was resolved by converting the chloride salt to the chlorotartrate salt. To 50 ml of water 0.654 grams of the mixture of compounds one and two was added. To this 0.429 grams of silver d-tartrate was added then the mixture stirred for one hour. The silver chloride was filtered off and the pink solution allowed to evaporate in a dessicator. As it accumulated the pink solid which formed on the sides of the evaporating dish was scraped into the solution. The pink crystals which formed in the solution were filtered off and found to have a specific rotation of -252 degrees.

The filtrate was allowed to evaporate further and a second crop of crystals filtered off which had a specific rotation of -483 degrees. The first and second crops of crystals were combined then dissolved in water and evaporated in a dessicator until crystals formed. The pink salt which formed was filtered off and found to have a specific rotation of -625 degrees. On further recrystallization the specific rotation dropped to -608 degrees. As this change in rotation was not significant the salt was considered resolved. The optical rotatory dispersion curve of this salt is shown in Figure 7.

Recovery of Cyclopentanediamine from Small Amounts
of Cobalt(III) Complexes

The complex was dissolved in five ml of nearly saturated sodium
hydroxide solution followed by 0.5 gram of sodium sulfide. The mixture
was heated for ten minutes to decompose the complex then continuously
extracted for eight hours with benzene. The benzene extract was filtered
and stored over potassium hydroxide (five grams) for 24 hours and the
rotation measured. The concentration of amine in benzene was found by
adding the benzene to 20 ml of distilled water and titrating the mixture
with hydrochloric acid to the methyl orange end point.

Specific Rotation of cptdin from Band Three

The Specific rotation of the third component from the chromatog-
raphy column was -478 degrees. About 0.15 grams of this complex was
treated in the manner described above except that no sodium sulfide was
used. The observed rotation in a four decimeter tube was 0.232 degrees.
The concentration of amine in benzene was 0.00140 grams per ml of ben-
zene. This corresponds to a specific rotation of 41.5 ± 1.8 degrees
for the recovered amine.

Specific Rotation of cptdin from Band Two

The specific rotation of the second component from the chromatog-
raphy column was -418. About 0.1 grams of this complex was treated in
the manner described above. The observed rotation in a two decimeter
tube was 0.169 degrees. The concentration of amine in benzene was 0.00201
grams per ml of benzene. This corresponds to a specific rotation of 42.1
degrees ±1.0 degrees.

Specific Rotation of cptdin from the Mixture of Band One and Two

The specific rotation of the mixture of components one and two was

-625. About 0.1 gram of this salt was treated in the manner described above. The observed rotation in a two decimeter tube was 0.140 degrees. The concentration of amine in benzene was 0.00158 grams per ml of benzene. This corresponds to a specific rotation of 44.3 degrees.

Determination of the Specific Rotation of the Totally Resolved cptdin

In order to determine the configuration of the amine molecules in the complex the specific rotation of the recovered amine should be compared to the specific rotation of the amine which was resolved with an optically active acid. Thus should the complex contain six dextro and one levo amine molecule, a specific rotation of +42 degrees for the recovered amine corresponds to +59 degrees for the totally resolved amine.

As previously noted it was impractical to totally resolve this amine with d-tartaric acid or d-camphorsulphonic acid because the specific rotation of the amine recovered from the optically active salt of the acid was 19 degrees after nine recrystallizations. But because some resolution occurred there is a difference in solubility between the two diastereomers. In order to determine if the amine recovered from the complex is optically pure it was converted to the camphor sulphonic salt, recrystallized, and the specific rotation of the amine recovered from this salt determined. Because the dextro amine which is present in greatest amount forms the less soluble diastereomer and because only a small portion of this diastereomer was precipitated it is believed that changes in specific rotation could be detected if the amine was optically impure.

To 0.0707 grams of trans-1,2-cyclopentanediamine dissolved in 100 ml of benzene, 0.2 grams of d-camphor sulphonic acid was added. 100 ml of 2-propanol were added and the solution boiled down to dryness. The

solid was dissolved in 25 ml of hot isopropyl alcohol and evaporated to 5 ml, then cooled in ice. The crystals were filtered, washed with a little cold isopropyl alcohol and dried.

These crystals about .08 grams in weight were dissolved in five ml of nearly saturated sodium hydroxide solution and extracted overnight. The benzene was filtered on to potassium hydroxide (five grams), stored for 24 hours to dry it, then the rotation of the benzene solution measured in a two decimeter tube. The observed rotation was 0.116 degrees which corresponds to a specific rotation of 41.1 degrees. Because there was no change in specific rotation the amine was considered optically pure.

Determination of Uncoordinated Amine Groups in
$Co_2(cptdin)_7Cl_6 \cdot 4H_2O$
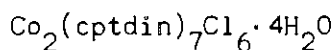
Consideration of the formula $[Co_2(cptdin)_7(H_2O)_4] \cdot Cl_6$ shows there are fourteen $-NH_2$ groups present but only twelve positions available for coordination. Because the number of coordinated $-NH_2$ groups plus coordinated water molecules equals twelve, knowledge of the number of uncoordinated $-NH_2$ groups allows one to determine the number of coordinated water molecules.

Nonaqueous Titration of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$

Several attempts were made to titrate various salts of the $[Co_2(cptdin)_7(H_2O)_2^{6+}]$ cation in glacial acetic acid and acetonitrile. Because there was little of the separated complex available a mixture of the geometric isomers was used in initial experiments. In glacial acetic acid the complex was titrated with 0.1 $\underline{N}$ perchloric acid in

glacial acetic acid while in acetonitrile the complex was potentiometrically titrated with 0.1 $\underline{N}$ perchloric acid in dioxane.

1. Titration of the Perchlorate Salt. Excess 70 percent perchloric acid was added to a nearly saturated solution of $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$. The red precipitate was filtered, washed with cold water followed by absolute alcohol then ether. The perchlorate salt was only slightly soluble in glacial acetic acid and acetonitrile and no break in the titration curve was observed.

2. Titration of the Nitrate Salt. The nitrate salt of the complex cation was prepared by adding an excess of sodium nitrate to a nearly saturated solution of the chloride salt of the complex. The resulting pink precipitate was filtered, washed with cold water followed by ethyl alcohol then ether. Like the perchlorate salt, the nitrate salt was only slightly soluble in acetic acid and acetonitrile and therefore no break was obtained in the potentometric titration curves.

3. Attempted Titration of the Chloride Salt. The chloride salt of the complex cation was only slightly soluble in acetonitrile and acetic acid. When the complex was titrated in either of these solvents no break was observed in the titration curve.

4. Titration of the Tetraphenylborate Salt. Excess sodium tetraphenylborate was added to a nearly saturated solution of the chloride salt. The pale yellow salt which precipitated almost quantitatively was washed with cold water and dried in air. Because the salt is very soluble in absolute alcohol and ether, neither of these were not used to dry the salt.

The tetraphenylborate salt of the complex would not dissolve in

either acetonitrile or dry acetic acid. However the salt could be
dissolved in acetic acid when a drop or two of water was added to this
solvent. Potentiometric titration with perchloric acid in acetic acid
produced a small point of inflection in the titration curve. It was
found that the point of inflection did not depend on the amount of com-
plex added but was dependent on the amount of water added.

Van Slyke Nitrogen Determination

The van Slyke method has long been used to determine nitrogen
in primary amines and amino acids. Nitrous acid reacts with primary
amines liberating nitrogen by the following reaction:

$$HNO_2 + RNH_2 \longrightarrow ROH + N_2 + H_2O$$
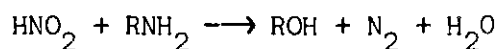
While nitrous acid also reacts with secondary amines, nitrogen
is not one of the products. Nitrous acid does not react with tertiary
amines. The basis for the van Slyke nitrogen determination is the liber-
ation of one mole of nitrogen per mole of primary amine group. Associated
with the liberation of nitrogen is a vast amount of nitric oxide formed
from the decomposition of nitrous acid. This nitric oxide is generally
removed with potassium permanganate or ferrous sulphate.

Coordinated amine groups are essentially secondary rather than
primary and therefore would not show the customary nitrous acid reaction
of primary amines. But uncoordinated amine groups, being primary, might
be expected to liberate nitrogen. Therefore the van Slyke method might
be suitable for distinguishing between coordinated and uncoordinated
amine groups.

The apparatus shown in Figure 8 was designed to remove the nitric oxide from the reaction mixture and allow the volume of liberated nitrogen to be determined. Nitrous acid was generated by adding one ml of glacial acetic acid to a sodium nitrite solution. The nitrite solution was made by dissolving 800 grams of sodium nitrite in one liter of water.

In a typical run three ml of dilute complex solution was added to the right burette and washed in with five ml of distilled water. The solution was degassed by closing the three way stop cock and lowering the leveling bulb thereby reducing the pressure. The small amount of gas was expelled, care being taken that no solution is lost.

Five ml of sodium nitrite solution was added to the burette followed by one ml of distilled water. One ml of glacial acetic acid was then added to the burette and its contents mixed by forcing mercury over from the left burette. Copious amounts of nitric oxide were liberated immediately. After ten minutes most of the gas was forced from the left burette to the right burette and the three way stop cock closed. The pressure was reduced in the right burette below atmospheric pressure and twelve ml of ferrous sulphate slowly allowed to trickle into the burette from the cup. The pale green ferrous solution immediately turned dark brown. When all the ferrous solution was added the ferrous solution was washed out of the capillary with one or two ml of distilled water.

The gas remaining in the right burette was forced back into the left burette and the spent ferrous sulphate expelled into the cup. Generally the process was repeated several times in the first two hours then the reaction left to run overnight. While most van Slyke reactions are relatively rapid, at least 14 hours were required to displace the nitrogen from the complex.

Figure 8.   van Slyke Apparatus.

On standing overnight the gas in the left burette was forced into the right burette, the stop cock closed and the remaining reaction mixture expelled into the cup. The pressure in the left burette was reduced below atmospheric and ferrous sulphate allowed to enter the left burette. The gas and ferrous solution were mixed by forcing both back and forth from one burette to the other several times. The remaining gas was forced into the left burette and the spent ferrous sulphate expelled and several ml of distilled water admitted. This was mixed with the remaining ferrous solution then most of the mixture expelled. The process was repeated once more to remove almost all the ferrous solution.

The remaining nitrogen was forced into the right burette which was calibrated, and the pressures inside and outside were equalized by moving the mercury leveling bulb to the same height as the mercury column inside the burette and the reading noted on the burette. Each graduation on the burette corresponded to 0.0509 ml while the dead space at the top of the burette had a volume of 0.197 ml.

A blank was run with trisethylenediaminecobalt(III) chloride and the amount of gas converted to moles of nitrogen. This amount of gas was subtracted from the amount of liberated nitrogen from the cyclopentane-diamine complex. The blank was about ten percent of the total amount of nitrogen liberated. The number of moles of liberated nitrogen was divided by the number of moles of complex used. Two runs on the low rotation complex obtained by recrystallization of the chloride salt yielded a value of 4.03 and 3.63 moles of nitrogen per mole of complex used. The average was 3.86 ± 0.18 uncoordinated amine group per molecule. Two runs

made on a mixture of compound one and two yielded a value of 4.13 and

3.86 moles of nitrogen per mole of complex used. The averages are in

good agreement with four, especially when it is considered that the small

amount of nitrogen is accompanied by vast amounts of nitric oxide. The

low rotation complex is a mixture of compounds two and three. There-

fore all three compounds from the chromatographic column contained four

uncoordinated amine groups per mole of complex.

CHAPTER V

DISCUSSION AND CONCLUSION

The investigation of trans-1,2-cyclopentanediamine complexes of cobalt(III) and rhodium(III) by Jaeger and Blumendall was one of the most significant investigations of the stereospecific nature of metal complexes containing asymmetric ligands. But for reasons noted in Chapter I, consideration of the geometry of the chelated trans-1,2-cyclopentanediamine molecule make it unlikely that the trans-1,2-cyclopentanediamine molecule functions as a bidentate ligand. Because the conclusions and theories concerning coordination compounds of asymmetric ligands (15, 13, 2) depend in large part on the original investigation of Jaeger, and because the exact nature and even composition of several of the compounds reported is uncertain (10) it was thought desirable to reinvestigate the cyclopentanediaminecobalt(III) complexes using pure base and determine the exact composition of some of these complexes.

The trans-amine was prepared in much the same manner as described by Jaeger. But contrary to his report, the amine was not pure. On careful fractional distillation two fractions were isolated, boiling about four degrees apart, with the lower boiling fraction comprising about five to ten percent of the total mixture. The proton NMR spectra of the two fractions shown in Figure 4, are quite similar but the chemical shifts are slightly different.

The infrared spectra of the two fractions were identical save for a single peak at 6.2 microns which was present in the lower boiling

fractions. This single peak was variable in intensity and may be due to ammonia which often occurs as a decomposition product of the amine and also absorbs at 6.2 microns (14). The infrared spectra of the two fractions were otherwise identical; because of this similarity in spectra the lower boiling fraction was thought to be cis-1,2-cyclopentanediamine.

There is no reason to doubt that the amine used by Jaeger contained cis-1,2-cyclopentanediamine. He used hydrogen peroxide to oxidize the cobalt(II) but the yield of cobalt(III) complex from hydrogen peroxide oxidization of cobalt(II) in the presence of excess ligand is very low. Because the cis-1,2-cyclopentanediamine has a configuration more suitable for chelate formation and because the amine is in considerable excess over cobalt(II) during the oxidation, the complexes obtained by Jaeger may have contained considerable amounts of cis-1,2-cyclopentanediamine in addition to the expected trans isomer.

The pink complex described by Jaeger as $[Co(cptdin)_3]Cl_3 \cdot 4H_2O$ was of particular interest for two reasons. Its composition and chemistry, should it indeed have the composition ascribed to it by Jaeger would be comparatively simple compared to dichlorobis-trans-1,2-cyclopentane-diaminecobalt(III) chloride or some of the "mixed" ethylenediamine cyclopentanediamine complexes. The properties of the pink complex could be compared to the analogous trisethylenediaminecobalt(III) chloride complex whose structure is well known (11). The optical rotatory dispersion curve of the alleged $[Co(cptdin)_3] Cl_3 \cdot 4H_2O$, shown in Figure 8, was also given by Jaeger.

The color of the alleged tris-trans-1,2-cyclopentanediamine-cobalt(III) chloride is most peculiar because, with this one exception, all known trisdiaminecobalt(III) chloride complexes as well as hexaammine-

cobalt(III) chloride are yellow. Pink cobalt(III) complexes generally contain five coordinated amine groups with the sixth coordination position occupied by water or a halogen.

Due to the sensitivity of the base to oxygen, the yield of complex using the conventional air oxidization method (24) as well as hydrogen peroxide oxidization is very low. The method described by Bauer and Drinkard (1) was used and good yields of complex were obtained. By using a six to one excess of amine to sodium triscarbonatocobaltate(III) trihydrate a pink complex having the empirical formula $Co_2(cptdin)_7(H_2O)_4Cl_6$ was easily isolated.
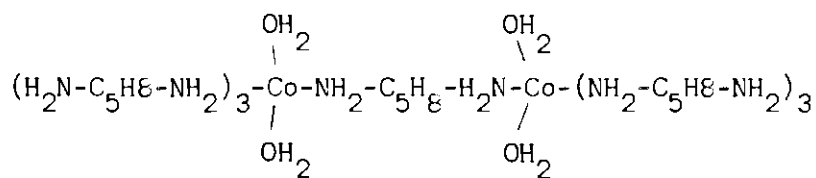
Fractional crystallization of the chloride salt of the complex followed by conversion to the tartrate salt and fractional crystallization yielded two fractions whose specific rotations were -358 and -958 degrees with the former present in considerable excess over the latter. Neither of these fractions was completely resolved. Column chromatography of the crude complex mixture showed that there were three isomers present. The specific rotation of the second and third compounds from the column were -478 and -418 degrees respectively. The specific rotation of the first compound eluted from the column was at least -600 degrees. Because the specific rotation of the first compound from the chromatography column was at least -600 degrees while the specific rotations of the second and third compounds were only -478 and -418 degrees respectively, the first compound from the chromatography column must correspond to the fraction whose specific rotation was -958 degrees while the second two compounds correspond to the fraction whose specific rotation was -358 degrees. This second fraction evidently is an incompletely resolved mixture of the latter
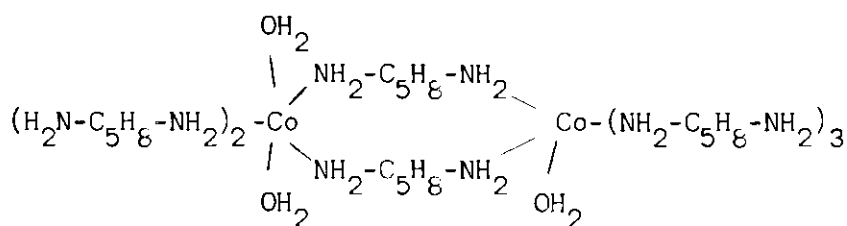
two compounds from the chromatography column.

The degree of polymerization of the two fractions having a specific rotation of -958 and -358 degrees was shown to be two. As noted, the fraction having a specific rotation of -358 degrees is believed to be a mixture of two complexes. Because the three geometrical isomers can be separated only with great difficulty several experiments were performed with a mixture of two of the three geometrical isomers. However the properties measured are of such a nature that the results obtained are still definitive and unambiguous. For example the degree of polymerization of the salt with the specific rotation of -358 is two, i.e., both isomers comprising the mixture are dimers. Similarly other experiments, i.e., the van Slyke reaction and amine recovery were sometimes performed with mixtures but again the results obtained were unambiguous.

At this point it was possible to consider some likely structures for the pink complex. Several of the more likely structures are shown in Figure 9. Structures containing more than three bridging cyclopentanediamine molecules are severely hindered and therefore unlikely. Likewise structures containing a bridging amine molecule and a bridging water molecule are ruled out because they are severely strained, while structures containing only bridging water molecules are also ruled out because they would be expected to be quite acid. No such acidity was observed.
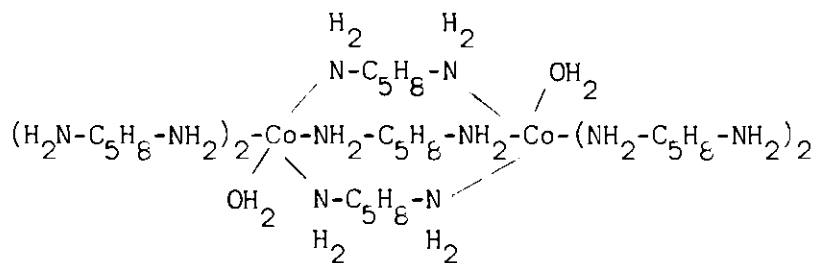
The four structures shown in Figure 9 contain six, five and four uncoordinated NH_2 groups respectively. Structure IV contains two types of cobalt; one with no coordinated water molecules and the other with two coordinated water molecules. The long wave length maxima of the analogous complexes $Co(NH_3)_4(H_2O)_2^{+3}$ and $Co(NH_3)_6^{+6}$ occurs at 498 and 478

66

OH$_2$ OH$_2$

(H$_2$N-C$_5$H$_8$-NH$_2$)$_3$-Co-NH$_2$-C$_5$H$_8$-H$_2$N-Co-(NH$_2$-C$_5$H$_8$-NH$_2$)$_3$

OH$_2$ OH$_2$

Structure I

OH$_2$

          NH$_2$-C$_5$H$_8$-NH$_2$

(H$_2$N-C$_5$H$_8$-NH$_2$)$_2$-Co   Co-(NH$_2$-C$_5$H$_8$-NH$_2$)$_3$

          NH$_2$-C$_5$H$_8$-NH$_2$

OH$_2$ OH$_2$

Structure II

H$_2$ H$_2$

N-C$_5$H$_8$-N   OH$_2$

(H$_2$N-C$_5$H$_8$-NH$_2$)$_2$-Co-NH$_2$-C$_5$H$_8$-NH$_2$-Co-(NH$_2$-C$_5$H$_8$-NH$_2$)$_2$

OH$_2$ N-C$_5$H$_8$-N

H$_2$ H$_2$

Structure III

H$_2$ H$_2$

N-C$_5$H$_8$-N   OH$_2$

(H$_2$N-C$_5$H$_8$-NH$_2$)$_3$-Co-NH$_2$-C$_5$H$_8$-NH$_2$-   Co   -(NH$_2$-C$_5$H$_8$-NH$_2$)

NH$_2$-C$_5$H$_5$-NH$_2$ OH$_2$
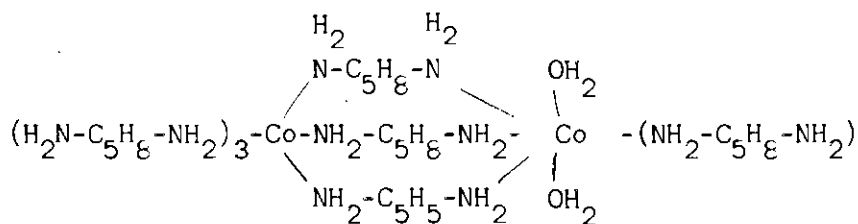
Structure IV

Figure 9. Possible Structures of the Complex Ion
Co$_2$(cptdin)$_7$(H$_2$O)$_2^{6+}$.

millimicrons respectively. Thus the visible spectra of structure IV

would be expected to contain components similar to $Co(NH_3)_4(H_2O)_2^{+3}$ and

$Co(NH_3)^{+3}$ and therefore would be very broad and perhaps even unsymmetri-

cal.

Likewise structure II contains two types of cobalt; one coordin-

ated to two water molecules and the other coordinated to one water mole-

cule. The long wave length maxima of the analogous compounds,

$Co(NH_3)_5(H_2O)^{+3}$ and $Co(NH_3)_4(H_2O)_2^{+3}$ occur at 490 and 498 millimicrons.

Therefore the visible spectra of structure II would also be expected to

be broad.

Structure I contains cobalt coordinated to two water molecules.

The analogous compound $Co(NH_3)_4(H_2O)_2^{+3}$ absorbs at 498 millimicrons. Struc-

ture III contains cobalt atoms coordinated to one water molecule and the

analogous complex, $Co(NH_3)_5(H_2O)^{+3}$ absorbs at 490 millimicrons.

As shown in Figure 4 the long wave length maximum of $Co_2(cptdin)_7$

$(H_2O)_2^{6+}$ occurs at 490 millimicrons. The visible spectrum of the complex

which most closely resembles $Co_2(cptdin)_7(H_2O)_2^{6+}$ is $Co(NH_3)_5(H_2O)^{3+}$.

The half band width of the 490 maximum in the latter complex is 130 mil-

limicrons which is to be compared to a half band width of only 117 milli-

microns for the former complex. Thus the half band width of $Co_2(cptdin)_7$

$(H_2O)_2^{6}$ is even less than $Co(NH_3)_5(H_2O)^{3+}$. Because the maximum is so

narrow and because it occurs at 490 millimicrons, structures II and IV whose

absorption maxima would be expected to be broad, are all but ruled out.

Structures I and III are still distinct possibilities for the structure

of $Co_2(cptdin)_7(H_2O)_2^{6+}$ and it is for this reason that the number of

uncoordinated NH_2 groups was determined.

A mixture of compound one and two showed two uncoordinated NH_2 groups per cobalt and a mixture of compound two and three also showed two uncoordinated NH_2 groups per cobalt or a total of four uncoordinated NH_2 groups per cation. This is good evidence that structure III is the correct structure for the three geometrical isomers.

A scale model of structure III shows that the three bridging amine molecules must be of the same configuration, i.e., all levo or all dextro. The four remaining amine molecules may be levo or dextro but there is considerably less steric hinderance between the bridging amine molecules and the singly coordinated amine molecules when all have the same configuration.

Amine extracted from the resolved third, second and a mixture of the first and second components showed a specific rotation of 42 degrees. Ideally the specific rotation of the recovered amine should be compared with the specific rotation of amine resolved with an optically active acid. Because it was impractical to totally resolve the amine with d-tartaric acid or d-10-camphorsulfonic acid another stratogem was used. Dextro amine recovered from the complexes (specific rotation +42 degrees) was reacted with d-10-camphorsulfonic acid and approximately 25 percent of this salt precipitated from solution. The amine recovered from this salt showed a specific rotation of +42 degrees. In the unsuccessful attempt to totally resolve the amine it was shown that the insoluble diastereomer contained the dextro amine. Now if the complex in question contained six amine molecules of one configuration and one of the other configuration a rotation of +42 degrees for the recovered amine would correspond to a specific rotation of +59 degrees for the optically pure amine. And should

the complex contain five amine molecules of one configuration and two of the other configuration the specific rotation of the optically pure amine would be +98 degrees. While the difference in solubility was not great enough to easily resolve the amine, the difference is great enough to observe a change in rotation of the amine whose specific rotation was 42 degrees if it contained substantial amounts of levo amine, especially since only 25 percent of the salt was precipitated. But there was no change in rotation of the amine on recrystallization of the camphorsul- fonic acid salt; therefore the amine in the complex was assumed to be optically pure. It should be noted that Jaeger obtained a specific rotation of 36 degrees for the amine but this result is not comparable because Jaeger's value is that of the amine in water.

At this point enough data had been collected to unequivocally eliminate all plausible structures except structure III. Closer inspec- tion showed that there are three geometrical isomers possible for such a structure. These structures depend on the position of one water molecule in relation to the other water molecule. The water molecule may be _gauche_ to one another or they may be _trans_ to one another. One such _gauche_ isomer is shown in Figure 10. The _gauche_ isomers are very similar to one another while the _trans_ isomer is in a class of its own. Because the two _gauche_ isomers are so very similar it is believed that they correspond to the compounds whose specific rotations are -418 and -478 degrees. The _trans_ isomer is believed to be the compound whose specific rotation is greater than -600 degrees. This assignment is further substantiated by the fact that the first compound from the chromatography column eluted considerably before the second two and it was comparatively well separated
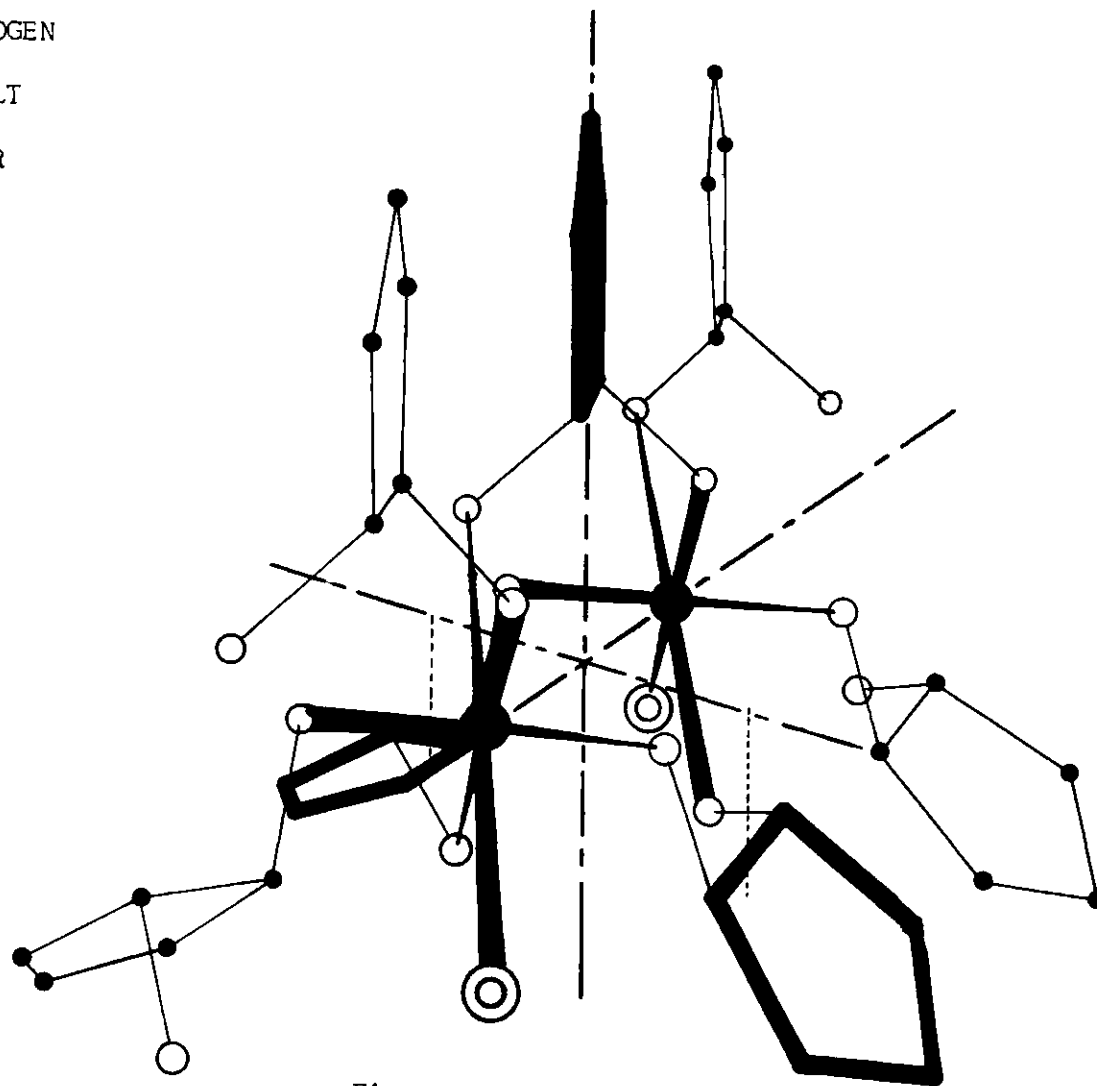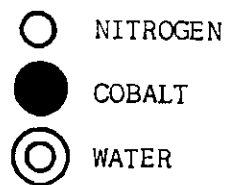
Figure 10.

Proposed Structure of the $Co_2(cptdin)_7(H_2O)_2^{6+}$ Ion.

from the latter two compounds. In contrast, the latter two compounds

were only partially separated from one another. There is no obvious

reason why the compounds occur in the ratio of 1:4:5. One would expect

that on a statistical basis they would occur in the ratio of 1:1:1.

However a free energy difference of less than one Kcal per mole between

the _trans_ isomer and the two _gauche_ isomers would account for the

observed ratio.

The elucidation of the structure of these three complexes has

removed the last support of the idea that interaction of asymmetric

ligands reduce the number of coordination complexes to two, viz., D-ddd

and L-lll or D-lll and L-ddd. Previously Dwyer and coworkers had shown

the number of isomers is not limited to two but in fact almost all pos-

sible isomers occurs in an equilibrium mixture. To be sure all do not

form in identical amounts but as shown by Corey and Bailar (2) the limit-

ing factor is merely repulsion of the various protons with one another.

Most significantly it is not some mysterious property related solely to

asymmetric ligands.

Our investigation has shown that Jaeger erred in several instances.

The _trans_-1,2-cyclopentanediamine which he used, very likely, was con-

taminated with _cis_-1,2-cyclopentanediamine. The assumption that _trans_-1,2-

cyclopentanediamine functions as a bidentate ligand is in error at least

in the case of the pink complexes. It is believed that the pink complex

which Jaeger assigned the formula $Co(cptdin)_3Cl_3 \cdot 4H_2O$ is the same one as

$[Co_2(cptdin)_7(H_2O)_2] Cl_6 \cdot 2H_2O$ because the optical rotatory dispersion

curves of the two are so similar. In any case the theories and ideas

derived from Jaeger's investigation are of little value.

Corey and Bailar (2) indicate the reason that $Co(d\text{-cptdin})(l\text{-cptdin})_2^{3+}$ was not isolated by Jaeger is that the cyclopentane ring has a fixed gauche configuration. Cyclopentane rings in amine molecules of opposite configuration would repell one another and account for the nonexistence of such cations. In fact no such cation exists but simply for the reason that cyclopentanediamine is not bidentate. Nevertheless such reasoning can be applied to the bridging amine molecules in $[Co_2(cptdin)_7(H_2O)_2]Cl_6$.

The amine molecules in the cation possess the same configuration. In the case of the bridging molecules it is because the cyclopentane rings possess a fixed skewed configuration and must be skewed in the same direction to prevent substantial steric hinderance.

The geometrical isomers might best be visualized as three octahedra joined together at the faces by cyclopentanediamine molecules as is shown in Figures 11 and 12. In Figure 11, two sets of octahedra are shown, one set disconnected and the other connected. In connecting the two extreme octahedra another octahedran is formed. Figure 12 also shows the three octahedra. Starting at the unjoined apex of one of the extreme octahedra in Figure 10 A it is possible to trace a helix. Because there are three such apexes, three such helices may be traced out.

Figure 12 B shows the two outside octahedra joined as they would appear in $Co_2(cptdin)_7(H_2O)_2^{6+}$. It is seen that the difference in the geometrical isomers is the path of the three helices traced out. In the trans isomer, the helix containing the water molecules contain one amine molecule and the remaining two helices contain three amine molecules. The difference between the two gauche isomers is rather subtile. The three helices contain three, two and two amine molecules respectively.
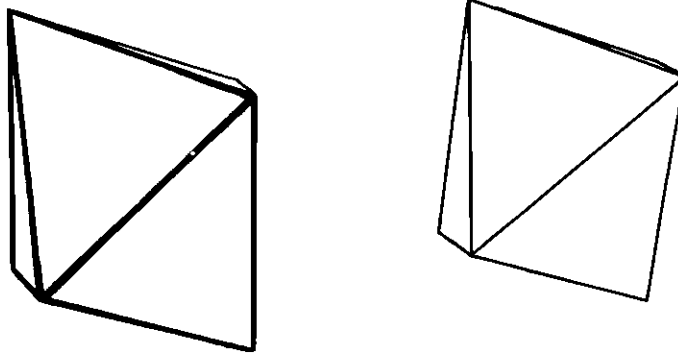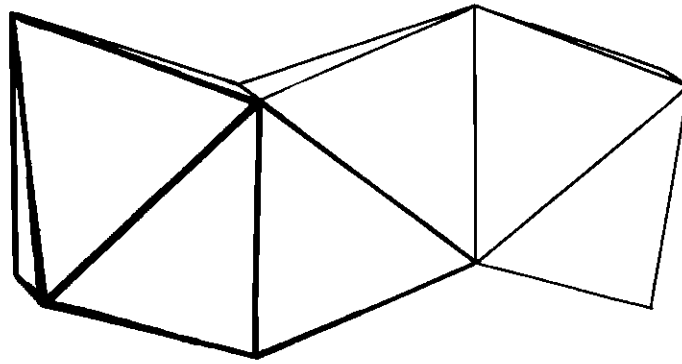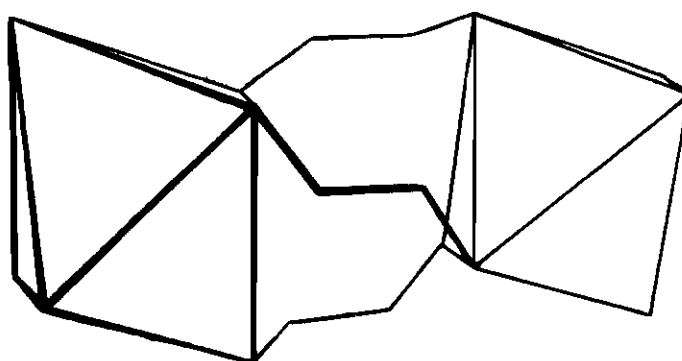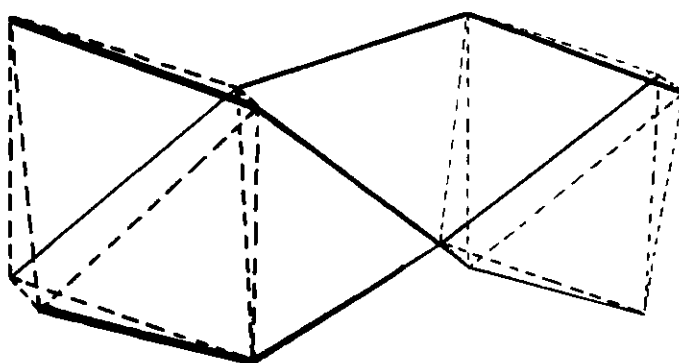
Figure 11. Connected and Unconnected Octahedra.

Figure 12. Octahedra of $Co_2(cptdin)_7(H_2O)_2^{6+}$

But in one isomer a line drawn between the two water molecules bisects a helix, while in the other isomer this same line passes between two helices.

In all three isomers the path length of the three helices covers three octahedra. The two extreme octahedra contain cobalt atoms while the center octahedron is empty. Nevertheless the arguments of Corey and Bailar can be applied to the empty octahedron. The conformation of this octahedron shown in Figure 10 B is the stable lel conformation and right chirality (handedness). Considering only bridging amine molecules for the present, it corresponds to the L-ddd isomer as compared to the tris-ethylenediaminecobalt(III) ion. The ob conformation would correspond to the D-ddd isomer. Such a conformation can be obtained by rotating one extreme octahedron 120 degrees with respect to the other octahedron. The ob conformation is severely hindered and can have no independent existence because it is merely a conformer of the stable lel conformer.

As shown from the amine recovery experiments, the configuration of the singly coordinated amine molecule is identical with the bridging mole-cules. Models show that isomers of the type D-(lll)(dddd) and other mixed complexes might occur. When all the amine molecules possess the same configuration the singly coordinated amine molecules can be positioned so that the cyclopentane rings are turned away from each other and away from the bridging amine molecules. But when one of the singly coordinated amine molecules has a configuration different from the others it must be turned so that its cyclopentane ring faces toward the bridging molecules. When it is turned away from the bridging molecules it encounters even more severe steric hinderance with the other singly coordinated amine

molecules. This steric hinderance between the bridging amine molecule and the singly coordinated amine molecule is quite significant and would probably account for the nonexistence of such mixed isomers.

During the course of this investigation two experimental techniques were developed. In considering the empirical formula of $Co_2(cptdin)_7(H_2O)_4Cl_6$ two things are evident; one, the complex cation is not a monomer and two, some of the NH_2 groups are not coordinated to cobalt. In order to elucidate the structure of the complex cations, the degree of polymerization of the complex and the number of uncoordinated NH_2 groups were determined.

After unsuccessfully attempting to determine the number of uncoordinated NH_2 groups by nonaqueous titration, a slight modification of the van Slyke nitrogen determination was used. Most primary amines react relatively rapidly with nitrous acid to liberate nitrogen but in contrast the NH_2 groups of $Co_2(cptdin)_7(H_2O)_4Cl_6$ react only with difficulty. However on allowing the reaction to continue overnight the uncoordinated NH_2 groups were replaced and their number could be determined quantitatively. Although the van Slyke method worked well its importance is limited because of the comparatively small number of coordination complexes containing uncoordinated NH_2 groups.

The other experimental technique developed promises to be of considerably greater utility. There are relatively few good methods of determining the charge on a highly charged cation in aqueous solution. Attempting to determine the charge on the cation, by measuring the change in solubility of the complex at constant ionic strength in solutions containing an anion in common with the complex failed. And as noted in

Chapter IV other methods were considered but thought to be inapplicable. The method finally developed consisted of calculating the approach parameter $\underline{a}$ of the Debye-Huckel equation for solutions of the complex in a large excess of potassium nitrate, when various possible values of the cationic charge were assumed, and comparing these calculated values of $\underline{a}$ to the value of $\underline{a}$ for pure potassium nitrate.

Ideally, the value of $\underline{a}$ for potassium nitrate should be used in the Debye-Huckel equation and the cationic charge calculated. But because of computational difficulties the procedure described above was employed.

The number of low inorganic polymers is numerous and the Debye-Huckel method should be applicable for determining their degree of poly-merization. While the limits of this method were not determined, it should be applicable to cations charged as high as eighteen.

During this investigation of cobalt(III) complexes of cyclopentane-diamine, a complex believed to be tris-cis-1,2-cyclopentanediaminecobalt(III) chloride was prepared. This is not to be confused with the pink complex Jaeger proposed as tris-1,2-cyclopentanediaminecobalt(III) chloride. In contrast to cptdin, the cis amine (cpcdin) is capable of bidentate forma-tion. The conformation of the chelate ring of $Co(cpcdin)_3^{3+}$ is unusual. Corey and Bailar have calculated the free energies of the lel and ob conformations of five member rings and concluded that the lel conformer was considerable more stable than the ob conformation. Unfortunately they made no effort to analyze an intermediate conformation, the envelope conformation, shown in Figure 13. There is little doubt that the envelope conformation is absent in $Co(en)_3^{3+}$ and $Co(pn)_3^{3+}$. In complexes containing

Figure 13. The Envelope Conformation of the Co-en Ring.

A - axial
E - equatorial
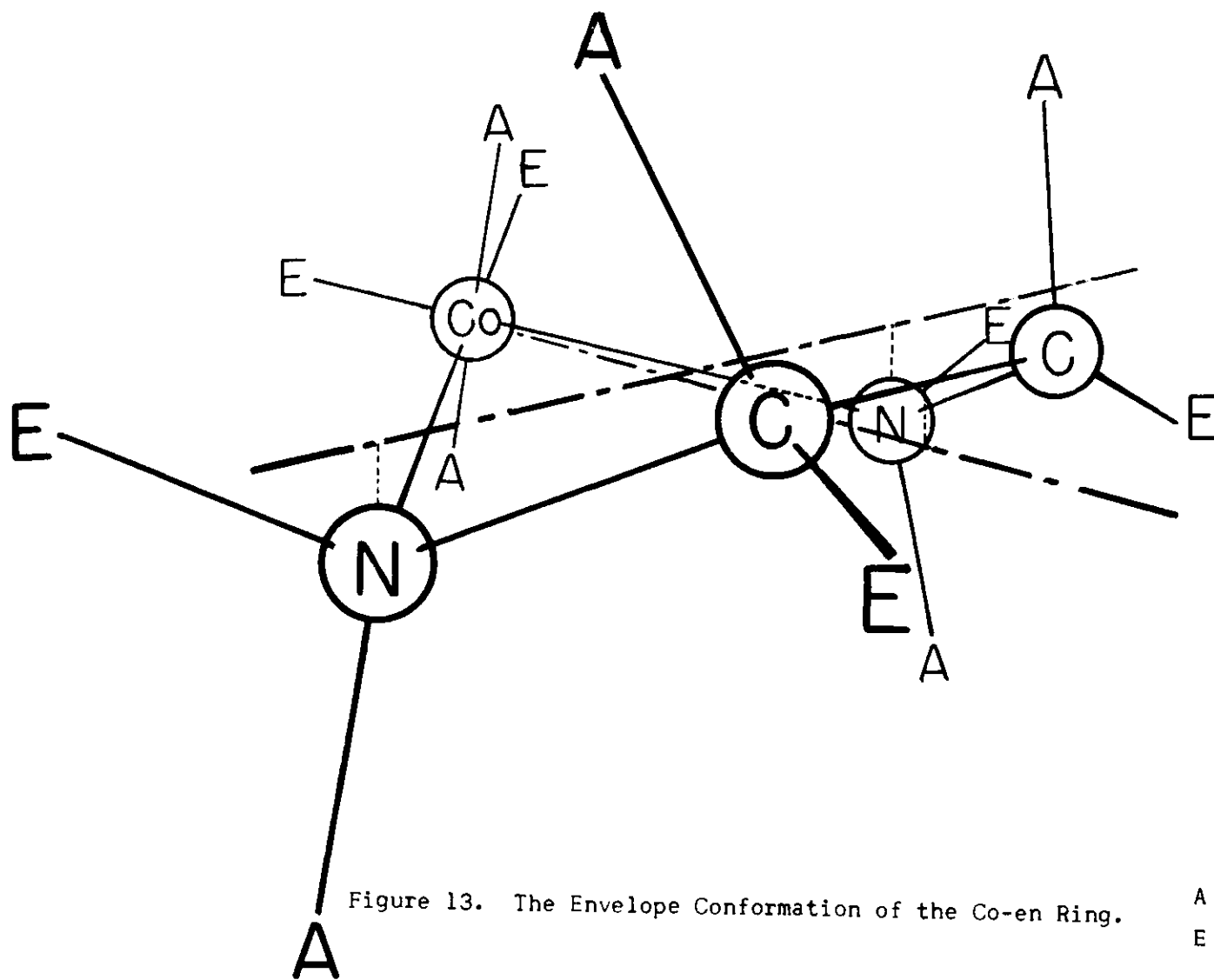
more complicated 1,2-diamines such as meso-butylenediamine and iso-butyl-
enediamine the case for the lel conformation is not clear cut. One of
the methyl groups may be in the stable equatorial position but the other
must be in the less stable axial position. To relieve the hinderance
caused by the axial methyl groups the chelate ring may revert to the
envelope conformation.

The conformation of $Co(cpcdin)_3^{3+}$ is clear cut. The relatively
rigid cyclopentane ring imposes the envelope conformation on the chelate
ring. The only question is whether the cyclopentane ring is axial or
equitorial. Consideration of Figure 13 shows that an axial cyclopentane
ring tilts in toward the complex encountering severe hinderance and
therefore the ring is almost certainly equatorial.

It would be interesting to measure the instability constant of
$Co(cpcdin)_3^{3+}$ whose conformation is known and compare it with the insta-
bility constants of cobalt(III) complexes of iso-butylenediamine and
meso-butylenediamine. From this comparison it might be possible to say
more about their conformations. If the stability constants of the butyl-
enediamine complexes are quite different from $Co(cpcdin)_3^{3+}$, it is quite
likely that the butylenediamine complexes possess the lel conformation.

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