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The ion-exchange chromatographic separation of the components of the product mixture resulting from reaction of trans-dichlorobis (ethylenediamine) cobalt (III) chloride with thiocyanate ion

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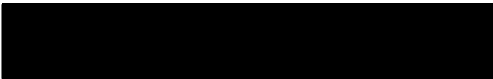
AN ABSTRACT OF THE THESIS OF

William Trew Jordan for the Master of Arts Degree in Chemistry

Date thesis is presented: August 9, 1967

Title: The Ion-Exchange Chromatographic Separation of the
Components of the Product Mixture Resulting From Reaction of
Trans-Dichlorobis(Ethylenediamine)Cobalt(III) Chloride with
Thiocyanate Ion.

Abstract approved:


Theodore A. Michelfeld
Major Professor

THE ION-EXCHANGE CHROMATOGRAPHIC SEPARATION OF THE COMPONENTS
OF THE PRODUCT MIXTURE RESULTING FROM REACTION OF
TRANS-DICHLOROBIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE
WITH THIOCYANATE ION

by

William Trew Jordan

ABSTRACT

The object of the research was to study, by means of ion-exchange chromatography, the product mixture resulting from reaction of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and SCN^- . Cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ had previously been obtained as products of this reaction. However, the possibility of the presence of other products consistent with the nature of the reactants could not be dismissed. These include the dichloro, dithiocyanato, and aqua complexes.

The constituents of the solution resulting from the reaction were separated on a column of Dowex 50W-X8 resin by elution with hydrochloric acid. The eluted fractions were evaporated at room temperature in order to obtain crystals to be used for infrared spectral analysis and identification. Three primary fractions were eluted from the column. The first, eluted with 0.5 M HCl, was identified as trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ by analysis of the infrared spectrum. Two types of crystals were obtained from the second fraction which was eluted with 1 M HCl. The first crystals to form in this solution were orange in color and were identified by examination of the infrared spectrum

as cis-[Co(en)₂(NCS)Cl] Cl. The second crystals obtained from the same fraction were shown to be cis-[Co(en)₂(NCS)Cl] Cl. The crystals isolated from the third fraction, eluted with 3 M HCl, were also identified as cis-[Co(en)₂(NCS)Cl] Cl.

On the basis of observations of the column elution and an analysis of the ultraviolet spectra of the eluted fractions, it was concluded that band #2 was cis-[Co(en)₂(NCS)Cl] Cl and band #3 was cis-[Co(en)₂(NCS)(H₂O)] Cl₂. Aquation of cis-[Co(en)₂(NCS)Cl]⁺ was observed to occur on the column as well as in the eluted solution. In addition, rechlorination of the aquated compound was found to occur in the eluted fraction so that after elution the second and third fractions were mixtures of the unaquated and aquated complexes.

No crystals of dithiocyanato or dichloro compounds were obtained in the separation so that the reaction was demonstrated to be essentially 1:1 between the complex and thiocyanate. Trans-[Co(en)₂(NCS)Cl] Cl was found to comprise forty-nine percent of the typical product mixture. Since other products were present only in very low concentrations, the combined cis-[Co(en)₂(NCS)Cl] Cl and cis-[Co(en)₂(NCS)(H₂O)] Cl₂ contents was estimated at roughly fifty mole percent.

APPROVED:


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Major professor


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Head of Department


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August 9, 1967
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Date thesis is presented

THE ION-EXCHANGE CHROMATOGRAPHIC SEPARATION OF THE
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William Trew Jordan

A THESIS

Presented to the Graduate Faculty

of Portland State College

In Partial Fulfillment of Requirements

For the Degree of Master of Arts

Department of Chemistry

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August 9, 1967

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This thesis is dedicated with love to
my wife, Vicki.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
I. OBJECTIVE OF THE RESEARCH	1
II. ION EXCHANGE	1
III. INFRARED SPECTRA	7
IV. THE REACTION	10
EXPERIMENTAL	12
I. INTRODUCTION TO THE EXPERIMENTAL WORK	12
II. PREPARATION OF THE STARTING COMPOUND	13
III. THE REACTION BETWEEN <u>TRANS</u> - $[\text{Co}(\text{en})_2\text{Cl}]\text{Cl}$ and SCN^-	14
IV. ION-EXCHANGE SEPARATION	14
V. ISOLATION OF CRYSTALS	19
VI. INFRARED SPECTRA	21
VII. ANALYSIS OF THE ULTRAVIOLET SPECTRA	36
VIII. ESTIMATE OF THE <u>TRANS</u> - $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ CONTENT OF THE PRODUCT MIXTURE	44
IX. ANALYSIS FOR COBALT BY ELECTRODEPOSITION	47
DISCUSSION OF THE EXPERIMENTAL RESULTS	49
SUMMARY	55
BIBLIOGRAPHY	56

INTRODUCTION

I. Objective of the Research

In recent years the technique of ion-exchange chromatography has found useful application in the area of coordination chemistry. Previous experimenters¹⁻⁷ have separated geometrical (cis/trans) isomers and performed displacement reactions on ion-exchange columns. It has been the primary objective of the present research to extend the applicability of ion-exchange chromatography to an analysis of product mixtures resulting from reactions which produce coordination compounds.

The initial plan called for the study of a series of reactions originally carried out in the beginning of the twentieth century by the noted Swiss chemist Alfred Werner.⁸ The work herein discussed has been confined to one of these reactions, namely that between trans-dichlorobis(ethylenediamine)cobalt (III) chloride and thiocyanate ion. Specifically, the problem has been to determine what is obtained when the mixture resulting from the above reaction is poured onto an ion-exchange column and then eluted with a suitable solvent. It was hoped that some knowledge of the composition of the product mixture might thereby be gained. That such an effort has, in some measure, been successful is the thesis of this paper.

II. Ion Exchange

The term ion exchange is basically self-explanatory, referring simply to the replacement of one ion by another in association with a

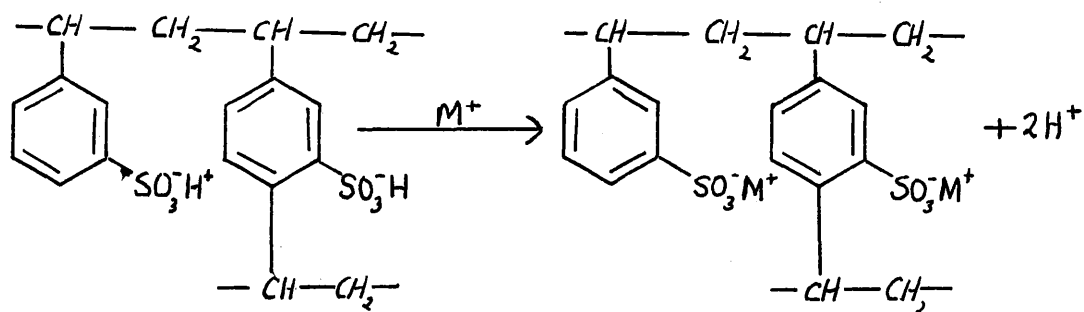
counter ion. This relatively simple concept, however, forms the basis for an impressive number of chemical separations, displacement reactions, and analytical schemes, and is responsible for the existence of a large body of highly developed theory.

While Moses⁹ and Aristotle¹⁰ have been cited by the most scrupulous of historians as the first to recognize and take advantage of the principles involved in ion exchange, it appears that the origin of modern inquiry into ion-exchange phenomena can be traced to mid-nineteenth century England with the discovery of base or cation exchange in soil. In 1845 an English chemist named Spence was hired by landowner H. S. Thompson to find out why ammonia was disappearing from his manure heaps.¹¹ When Spence poured an ammonium sulfate solution through a column packed with soil, calcium sulfate was present in the solution emerging at the lower end. A thorough study of this phenomenon was undertaken in 1850 by J. T. Way¹² who attributed these cation-exchanging properties to the clay or alumino-silicate portion of the soil. The findings of Way and Spence paved the way for further work and, in 1907, Gans,¹³ a German chemist, introduced a synthetic alumino-silicate gel to be used for water-softening.

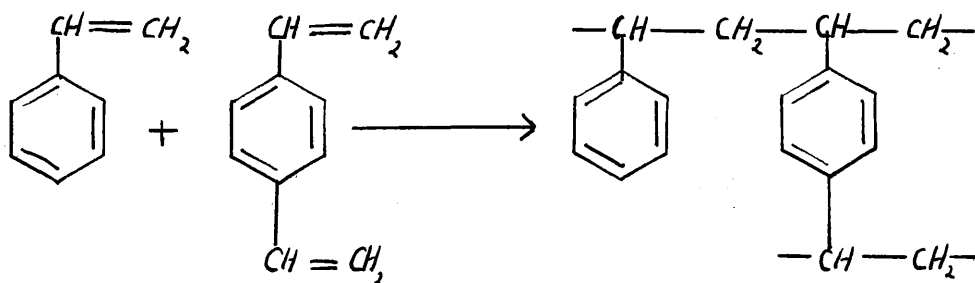
A momentous step in the evolution of ion exchangers was taken in 1935 when two English chemists, B. A. Adams and E. L. Holmes,¹⁴ discovered that certain bakelite resins (in this case crushed phonograph records) could exchange cations. They showed that the ion-exchanging properties of these materials were due to the presence of phenolic -OH groups which, under conditions of sufficiently high pH, could exchange hydrogen ion for another cation. Adams and Holmes proceeded to

synthesize a more efficient resin containing the more acidic sulfonic acid groups, which proved to be the forerunner of one of the most frequently used modern ion-exchange resins.

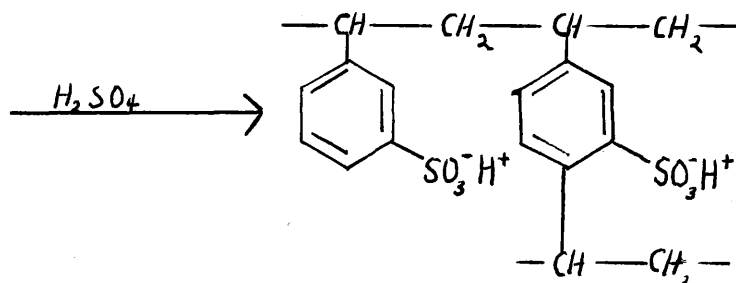
A typical modern ion-exchange resin is Dowex 50W-X4, which was employed in the work presented in this paper. Dowex 50W-X4 is one of a number of crosslinked polystyrene resins which owe their ion-exchanging properties to the presence of sulfonic acid groups.¹⁵



Resins of this type are prepared by polymerizing styrene using divinylbenzene as a crosslinking agent.



and then sulfonating with sulfuric or chlorosulfonic acid.



The degree of crosslinking can be controlled by adjusting the amount of divinylbenzene used. Crosslinking is a necessity since straight chain polyelectrolytes are soluble whereas crosslinked polymers are insoluble, and for most purposes an ion exchanger must be in the solid state. Too much crosslinking is not desirable, however, since the resin must be able to swell in order to accommodate different sized ions and facilitate the mobility of exchanging ions.¹⁶ Generally, a wide selection of resins is available with varying degrees of crosslinking and acid strength. The appropriate resin is chosen for specific task.

That such resins may be used to separate ions in a mixture is due to the fact that different ions are attracted to a particular resin to a different degree. For example, a dipositive ion will be more strongly held by a cation-exchange resin than a monopositive ion. Even ions of the same charge will differ in the degree to which they are held by a particular resin depending on relative size, internal dipole moment, effective charge, and ability of the solvent from which the ion is extracted to attract the ion. Generally, the greater the differences in ion properties, the better the separation which can be obtained.

Chromatographic separations by means of ion exchange are usually carried out in glass columns packed with resin. Several column techniques are available, but the most common one for this type of work, and that which has been used here, is elution development.¹⁷ In this method, a solution containing the ions to be separated is poured onto the top of the column of resin, and as the solution begins to run

through the resin, ions from the solution displace like-charged ions in the resin at the top of the column. When all of the solution has been adsorbed onto the resin, a suitable solvent is allowed to flow through the column bed at a steady rate. Solvent ions displace those of the mixture downward on the column packing, but at different rates depending on the relative ease of displacement of different ions. If the ions in question absorb light in the visible region, then a formation of colored bands will be observed on the column. Elution with the solvent is continued until each band has passed through the column and has been collected in a separate container. Under the proper conditions a complete separation of the components of the mixture may thus be obtained.

Selection of a proper resin and eluting solvent is important. It is desirable that the bands be compact and have sharp boundaries. If the solvent strength is too great or if the exchanging ion of a particular solvent is adsorbed too strongly by the resin in relation to the ions to be separated, the bands will spread and run together and a poor separation will be obtained. On the other hand, the eluting solvent must be of sufficient strength to allow the bands to move and separate continuously. Optimum conditions are arrived at by a process of trial and error, and it is not uncommon to change the strength of the eluent during the elution.

The first reported separation of coordination compounds by ion-exchange chromatography was carried out by King and Dismukes¹ in 1952. Using Dowex-50 resin they separated a mixture of the hexaquoachromium-(III) ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$, and its mono- and disubstituted derivatives,

$[\text{Cr}(\text{NCS})(\text{H}_2\text{O})_5]^{++}$ and $[\text{Cr}(\text{NCS})_2(\text{H}_2\text{O})_4]^+$, by eluting with perchloric acid. As expected, the ions were eluted in order of increasing charge, the monopositive ion coming off first, and the tripositive ion last.

Having succeeded in separating ions of different charges in this manner, King and Walters² predicted separability of geometrical isomers by ion exchange on the basis of differences in dipole moment and went ahead to separate a mixture of cis- and trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ in this way. The trans isomer having no net dipole moment was eluted first with 1 M NaCl and the polar cis isomer was eluted with 3 M NaCl.

Subsequently a number of investigators have carried out ion-exchange separations of geometrical isomers of coordination compounds. A number of such separations have been performed by Mori and coworkers³ at Kanazawa University in Japan. In 1955 they reported separation of cis- and trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ on an ion exchanger of the RNH_3 form, and in 1956⁴ they used amberlite IR-120 to separate cis and trans isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, $[\text{Co}(\text{en})_2(\text{NCS})_2]^+$, and $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$.

In 1957, Hougen, Schlug, and King⁵ separated the previously unresolved cis and trans isomers of dithiocyanatotetraaquachromium(III) ions from a mixture resulting from reaction between chromic perchlorate and potassium thiocyanate, and evaluated the relative amounts of the two isomers in an equilibrium mixture. In 1961, Dimolakis and Myrat⁶ of the Atomic Energy Commission in Athens, Greece separated cis and trans isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ on a column of Dowex 50 resin only four centimeters in length to minimize aquation.

More recently, Michelfeld⁷, at the University of Nebraska, has carried out the separations of a number of geometrical isomers of coordination compounds and estimated the degree to which a separation of each pair may be accomplished. In these and all other separations the trans isomer has always been eluted first.

III. Infrared Spectra

Previous experimenters who have carried out ion-exchange separations of geometrical isomers have made use of the differences in the spectra of the species in the visible and ultraviolet regions for purposes of detection and estimation of the degree to which a separation had been accomplished. The problem here has been a somewhat different one. In previous experiments the compounds to be separated were prepared, purified, dissolved, mixed and poured onto an ion-exchange column so that, unless a side reaction occurred (perhaps on the column), it was known exactly what was present and what, therefore, would emerge upon elution. The objective of the experimental work reported here has been to determine the composition of the product mixture resulting from a particular reaction and although it is well established that cis- and trans- $[\text{Co(en)}_2(\text{NCS})\text{Cl}] \text{Cl}$ crystallize from the product mixture, the possibility of the existence of side products could not be ruled out. It was necessary, therefore, to obtain positive identification of the fractions eluted from the column. For this purpose it has been convenient to rely heavily on infrared spectroscopy.

Fractions eluted from the ion-exchange column were allowed to evaporate at room temperature until crystals were obtained. Crystals

isolated in this manner were then mounted in potassium bromide pellets for infrared studies. Fortunately, a large quantity of work had been done on the infrared spectra of coordination compounds, and a major portion of that on compounds identical and closely related to those obtained here.

In 1954, Faust and Quagliano¹⁸ reported the results of their study of the infrared and ultraviolet spectra of cis- and trans-
 $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ in the solid state. They adapted to coordination compounds the then new and convenient potassium bromide disc method of preparing solid organic samples for infrared spectral study developed in 1952 by Stimson and O'Donnell.¹⁹ Analysis of these spectra showed fewer absorption peaks in the spectrum of the trans compound than in that of the cis compound. This result was attributed to the operation of a natural selection rule, according to which the less symmetrical molecule will exhibit more infrared-active vibrational modes than the more symmetrical molecule.

A generally applicable method had, at this time, not been developed for distinguishing geometrical isomers of coordination compounds, and it was not long before the possibility of utilizing differences in the infrared spectra as a criterion was explored. Merritt and Wiberly,²⁰ in 1955, studied the spectra of a number of bis(ethylene-diamine)cobalt(III) complexes and concluded that the peak in the six micron region was always displaced toward a lower frequency in the spectrum of the trans isomer.

In an effort to elucidate the nature of the bonding in thiocyanato ligands, Chamberlain and Ballar,²¹ in 1959, investigated

the infrared spectra of a number of ethylenediamine and ammine cobalt-(III) complexes containing coordinated thiocyanate. They were able to make several frequency assignments to NH vibrations by deuterating the ammine and ethylenediamine nitrogens. They also concluded that the region between 1120 and 1150 cm^{-1} could be used to differentiate between cis and trans isomers in compounds of this type where the spectra of the cis compound showed two peaks and that of the trans compound only one.

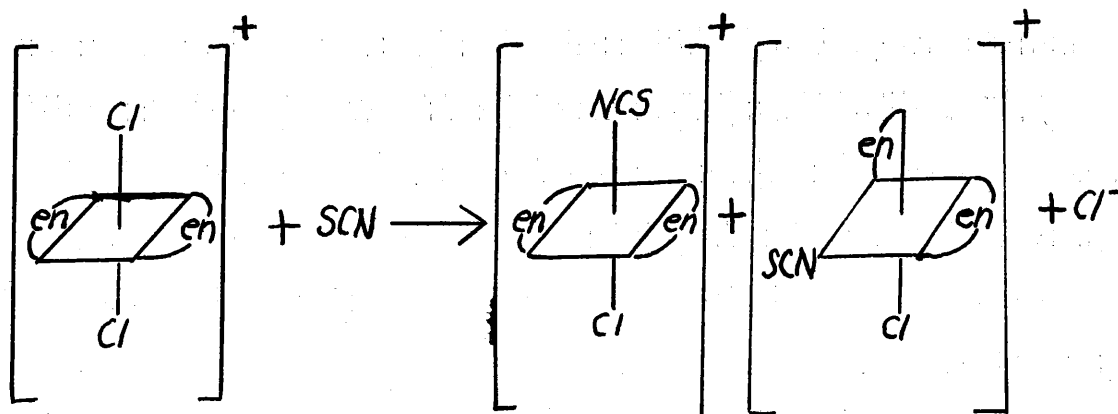
In 1960 Morris and Busch²² studied the infrared spectra of deuterated and undeuterated cis and trans isomers of $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ and $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. They assigned the 3200 cm^{-1} peak to the NH_2 stretch, the 1600 cm^{-1} peak to the asymmetric deformation, the 1350 cm^{-1} peak to the symmetric deformation, and the 800 cm^{-1} peak to the NH_2 rock. In addition, they observed the appearance of two peaks in the spectrum of the cis isomer and only one in that of the trans in the 1600 cm^{-1} region.

In his investigation of differences in the spectra of cis and trans arrangements of ethylenediamine chelate rings, M. E. Baldwin,²³ in 1960, raised objections to the criteria proposed by Chamberlain and Ballar and suggested instead that the region 870-900 cm^{-1} , assigned to the CH_2 rock, be employed to distinguish between isomers. In this region he observed a consistent splitting of the absorption peak into two peaks in the spectra of the cis compounds. No such splitting occurred in the spectra of trans complexes. Since the tris-(ethylenediamine)cobalt(III) ion also exhibited the splitting, he assumed it to be due to the proximity of two ethylenediamine chelate rings. However, Riggs and Sherwin,²⁴ in 1965, observed similar

splitting to occur in diamine-ethylenediamine complexes and, therefore, concluded that the effect of interaction of *cis* NH_2 groups on the CH_2 vibration was responsible for the splitting. They also demonstrated that differences in symmetry were not responsible for the different number of peaks.

IV. The Reaction

The reaction which has been studied is a simple ligand exchange reaction where the stronger thiocyanato ligand has replaced a chloro ligand in coordination to tripositive cobalt. The octahedral trans-dichlorobis(ethylenediamine) cobalt(III) chloride and potassium or sodium thiocyanate are mixed in equimolar portions in solution and heated. Werner,⁸ who first carried out the reaction in 1912, isolated cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ from the cooled mixture. The cis compound crystallized rapidly, while the much more soluble trans isomer precipitated with further evaporation.



The cis isomer has been resolved into its optically active components and has been shown to aquate, rapidly with heating, in aqueous solution.²⁵

EXPERIMENTAL

I. Introduction to the Experimental Work

As stated previously, the basic plan of the research was to run the reaction and then separate the products by ion-exchange chromatography. The products thus separated would then be identified by some means. It was expected that cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ would be isolated in this manner, but these compounds are not exclusive possibilities. It is not unreasonable to presume that both chloro groups might be replaced by thiocyanate on a significant fraction of the complex ions leaving some of the reactant untouched, in which case both the dichloro compounds and the dithiocyanato compounds would also be present in the reaction mixture. Therefore, a list of possibilities would include the following:

cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (If isomerization of the reactant takes place)

trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$

cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$

trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$

cis- $[\text{Co}(\text{en})_2(\text{NCS})_2]^+$

trans- $[\text{Co}(\text{en})_2(\text{NCS})_2]^+$

In addition, mono- and diaquated products of any of the above cannot be excluded. The most likely ligands to be replaced by water, however, are the chloro groups. Ethylenediamine is a very strong chelating agent, and the thiocyanato ligand has been reported to be highly resistant to aquation even in boiling water.²⁶ Both cis- and trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ are known to aquate readily to cis- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{++}$,²⁷

and cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ has been shown to aquate, particularly at elevated temperatures, to cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})_2]^{++}$. The trans isomer also aquates but at a much lower rate than the cis form and appreciably only at temperatures above 50 degrees.²⁸ The latter compounds (especially cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})_2]^{++}$) might be considered probable components of the product mixture since cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ are known to be present and the reaction is carried out in aqueous solution and requires heat. Fortunately infrared spectra can distinguish all of the above-named compounds.

II. Preparation of the Starting Compound

Trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was prepared by the method of Bailar.²⁹

Six hundred grams of a 10 per cent solution of ethylenediamine is added, with stirring, to a solution of 160 g. of cobalt chloride 6-hydrate in 500 ml. of water in a 2 l. beaker or bottle. A vigorous stream of air is drawn or passed through the solution for 10 or 12 hours. (Longer aeration causes undesirable secondary reactions to take place.) Three hundred and fifty milliliters of concentrated hydrochloric acid is added, and the solution is evaporated on a steam bath until a crust forms over the surface (750 ml.). The solution is allowed to cool and stand overnight before the bright-green square plates of the hydrochloride of the trans- form are filtered. These are washed with alcohol and ether and dried at 110°. At this temperature, the hydrogen chloride is lost, and the crystals crumble to a dull-green powder. Yield 83 g. (52 per cent based on the ethylenediamine).

These directions were followed closely. However, after filtering the crystals, the filtrate was evaporated further until it crusted over again, whereupon a second batch of crystals was obtained. This process was repeated successfully a third time but the crystals obtained on a fourth attempt were contaminated with light-yellow-

green needle-shaped crystals. Using half amounts of those given in the above instructions, a total yield of 58 grams or 72.6 per cent was obtained.

The compound was analyzed for cobalt by an electrodeposition method.³⁰ The per cent cobalt calculated for $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)\text{Cl}_2]\text{Cl}$ is 20.6, and the per cent found was 20.5. (see page 47).

III. The Reaction between trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and SCN .⁸

In a typical reaction, 20 g. (.072 mole) of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was dissolved in 30 ml. of water. Moderate heating was necessary to achieve complete solution. Immediately upon addition of a solution of 6.8 g. (.070 mole) of KSCN in 15 ml. of water, fine green crystals of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{SCN}$ formed profusely. The resulting bright-green slurry was heated with constant stirring until complete solution of the green solid was obtained at about 85 degrees. The solution was then allowed to cool. A large quantity of purple crystals of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ precipitated within an hour. The crystals were filtered on a Büchner funnel, washed with 95 per cent ethanol, and dried in air. The deep-violet filtrate yielded more of the purple crystals upon further standing. In one particular instance where the solution was allowed to stand overnight before any crystals were filtered, approximately 18 g. of the compound was obtained. The purity was not, however, determined.

IV. Ion-exchange Separation.

A number of ion-exchange separations of the product mixture

resulting from the above reaction were carried out. The earliest ones were of an exploratory nature, the objective being to see how many bands formed, what they looked like, to what extent they could be separated, and what kind and strength of eluting solvent should be used to perform an optimum separation. Some later column separations were carried out to isolate material for identification purposes. Finally, three separations were performed for the sole purpose of estimating the relative proportion in which the products were formed. It is useful to describe only one typical separation here. Any variations observed will then be discussed.

Most of the column separations were carried out in 50 ml. glass burets. A glass wool plug was inserted above the stopcock to retain the resin. The resin (Dowex 50W-X4 and 50W-X8 were used) was washed with the solvent to be used initially for eluting, and then poured in a slurry into the column. More solvent was introduced through the top of the column and allowed to run through the resin, the solvent level never being allowed to fall below the top of the column of resin. When the resin had settled well, a second glass wool plug was inserted at the top of the resin column to prevent its disruption when introducing the solution to be analyzed, and to filter out insoluble matter such as dust. The solvent was then allowed to flow to the level of the upper glass wool plug and a portion of the solution to be analyzed was poured into the column. When the solution had fallen to the level of the upper glass wool plug, eluting solvent was again introduced and thereafter maintained at a constant level approximately 25 ml. above the resin column. Eluent was introduced through rubber tubing from a

flask placed above the level of the top of the buret. The flow-rate was adjusted by means of a screw clamp to increase very gradually and a constant head was maintained at the desired level by drawing the excess off with an aspirator.

A. A Continuous Elution

In a particular run 1 ml. of product mixture, from which no crystals had yet formed, was pipetted onto a column packed with Dowex 50W-X8 resin to a height of 29 cm. Elution was begun with 0.5 M HCL, a constant head being maintained at 23 ml. above the resin. The flow rate was approximately 0.7 ml. per minute. Early in the elution three colored bands began to form; a broad dark-violet lower band (#1), a somewhat smaller reddish band a short distance behind (#2), and a very narrow red band at the top of the column (#3). As elution progressed, separation improved, and bands #1 and #2 moved gradually down the column, #1 moving most rapidly. Eventually, #2 separated into a slow-moving light-red-colored band (#2b), and a mobile reddish band (#2a). When band #1 had eluted, the strength of the eluent was increased to 1 M. The solvent collected between bands #1 and #2a was colorless, indicating that a complete separation of these fractions had been accomplished, and that no aquation had occurred in band #1. Band #2b became more diffuse, and the area between band #2a and band #3 (which had begun to move slowly after the change in eluent strength) was lightly pink-colored rather than the off-white color of the resin. After band #2a was collected the acid strength was increased to 3 M, and bands #2b and #3 were eluted. Band #3, as did all bands, spread

out somewhat as it moved down the column. A light pink band remained at the top of the column which could not be collected since it spread and became very diffuse with further elution.

A record of the above separation was kept and is reproduced here. It was run without cessation, requiring a total of 31.5 hours to complete.

RECORD OF ELUTION

<u>Time Elapsed</u>	<u>Comments</u>
0	Elution is begun with 0.5 M HCl.
2 hrs. 35 min.	Bands #1, #2, and #3 have clearly separated. #3 looks quite small at this point.
5 hrs. 50 min.	#1 is well separated from #2 which has split into a strong lower and a weak upper band.
12 hrs. 20 min.	The region between #2 and #3 is light pink instead of the off white of the resin, indicating incomplete separation.
14 hrs. 40 min.	Band #1 is completely eluted.
15 hrs.	Eluent is changed to 1 M HCl
19 hrs. 25 min.	#2a has eluted. #2b is very faint, diffuse.
25 hrs.	Eluent is changed to 3 M HCl.
31 hrs. 30 min.	#3 has eluted. Shut off.

B. Interrupted Elutions.

The above separation was run without stopping the flow of eluent through the column at any time, but most of those carried out were

(due to the length of time necessary to complete a separation) shut off a number of times when they couldn't be checked within an hour. In columns which were eluted over a greater length of time, with frequent interruption, it was observed that two or three more bands formed between the #2b and #3 bands on the column at the expense of band #2a. Since these bands appeared to split off from band #2a, they were labeled #2b, #2c, and #2d, three being the most observed, and usually just two. In one of the last separations made, the #2d band was much stronger than band #2a by the time #2a eluted. It eventually became clear that the new bands were appearing when elution was resumed following an interruption, indicating that something had happened to the material in band #2 during a stationary period. The bands formed in this manner appeared to elute at about the same rate and with the same strength acid as band #3. In all of the separations it was noted that the region between bands #2a and #3 was a light pink color.

C. Other Comments on Elutions

In some of the column elutions which were performed it was observed that a light violet band separated from the rest of the solution and eluted within one half hour of commencement of elution. A sufficient amount of this fraction to obtain crystals was never collected, but it is highly probable that it was a neutral but polar compound.

In addition to the light pink band which remained at the top of the column after elution of band #3, some very dark brown material was

absorbed on the top of the column, and could be moved a little only with 6 M or stronger HCl.

Other solutions were tried as eluents but none was found to be as satisfactory as HCl. Sodium chloride was found to be too strongly favored by the resin as opposed to the compounds to be separated, as evidenced by the fact the bands spread and ran together when it was used. Sodium thiocyanate proved to be somewhat better than sodium chloride, and was used to advantage in preparing the thiocyanate salts of the complexes for infrared spectra. A problem with using salts as eluting agents was that when the eluted fractions were evaporated to obtain crystals, crystals from the eluent would precipitate before or coprecipitate with the desired salt. It was thought that perhaps use of a neutral eluent might be preferable to a strongly acidic one but essentially the same results were obtained and the compounds in question appear to be quite stable in strongly acidic media.

V. Isolation of Crystals.

In order to obtain pure crystals for infrared spectral analysis, it was necessary to evaporate the fractions eluted from the ion-exchange column. In the first attempts to obtain crystals in this manner, the solutions were evaporated at low heat on a hot plate until they became sufficiently concentrated for crystallization to occur. Clear, colorless crystals were obtained from the first fraction. It was suspected, and subsequently confirmed by a positive flame test for potassium, that these were crystals of potassium chloride. When the solution was evaporated further, violet crystals coprecipitated with

the colorless ones.

Evaporation of the second fraction over a hot plate resulted in the formation of small green crystals about the same color as the starting compound, trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$. This was a surprise since the solution from which the crystals precipitated was reddish in color whereas trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ is green in solution. Cis- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, however, is dark violet and it seemed reasonable to hypothesize that the trans form had isomerized to the cis which has been reported to be the more stable form in acid solution.³¹

Since it appeared that heating might be causing rearrangements to occur, room temperature evaporations in a fume hood were attempted. Under these conditions, uncontaminated violet crystals were obtained from the first fraction. It is likely, however, that colorless crystals of potassium chloride were not isolated, not because of the method of evaporation used, but because a different strength eluent was used to elute fraction #1, achieving a separation from potassium ion. Additionally, a lower acid strength would have a lower chloride ion concentration, requiring more evaporation to reach saturation, although, this factor would tend to affect both KCl and the violet compound in the same way.

The crystals isolated from band #2a by slow evaporation at room temperature were significantly different from those obtained by evaporation over a hot plate. After relatively little evaporation had taken place, flaky orange crystals formed on the top of the solution. These were collected on a filter. Upon further evaporation, however, fine reddish crystals were obtained and it appeared that either two

different compounds were present in fraction #2a or one compound was crystallizing in two different forms. No green crystals were obtained in the room temperature evaporations. Slow evaporation of fraction #3 yielded crystals similar to the reddish crystals isolated from #2a. Generally, a sufficient amount of solution was not obtained to isolate crystals from fractions #2b, #2c, and #2d.

VI. Infrared Spectra

The potassium bromide pellet method was used to prepare crystalline samples for infrared spectra. Spectra were recorded on Perkin-Elmer 137 Infracord and Beckman IR-12 recording spectrophotometers. The IR-12 was the more useful of the two since it resolved a greater number of absorption peaks and gave more precise wave number readings. Precise readings were necessary since the spectra of the compounds to be separated were similar in many respects. Nevertheless, the spectra obtained from the Infracord were of use for comparison purposes, and a number of these spectra are reproduced here. Significant points concerning the analysis of the infrared spectra are noted below.

A. The infrared spectra of the violet crystals from fraction #1 obtained by elution with HCl, and therefore assumed to be the chloride salt (see figure 1), showed single absorption peaks around 1600 cm.^{-1} and in the $1100\text{--}1150\text{ cm.}^{-1}$, and $870\text{--}900\text{ cm.}^{-1}$ regions, thus indicating that it is of the trans configuration by the criteria of Morris and Busch,³² Chamberlain and Bailar,³³ and Baldwin³⁴ respectively. If the compound were of the less symmetrical cis form, two absorption peaks would appear in each of these regions.

B. Since a single strong thiocyanate C-N stretching peak was observed in the 2100 cm.^{-1} region, the trans-dichloro complex was ruled out, leaving as the only two possibilities trans- $[\text{Co(en)}_2(\text{NCS})\text{Cl}]\text{Cl}$, and trans- $[\text{Co(en)}_2(\text{NCS})_2]\text{Cl}$. The former was suspected, and subsequently confirmed by comparison of the frequencies of absorption peaks in the spectrum (see figure 2) of crystals isolated by evaporation of band #1 (obtained by elution with NaSCN, and therefore, assumed to be the thiocyanate salt) with peaks reported by Chamberlain and Bailar³⁵ for trans- $[\text{Co(en)}_2(\text{NCS})\text{Cl}]\text{SCN}$.

TABLE 1: COMPARISON OF PEAK FREQUENCIES IN THE SPECTRA OF TRANS- $[\text{Co(en)}_2(\text{NCS})\text{Cl}]\text{SCN}$ AND THE VIOLET CRYSTALS FROM BAND #1

<u>trans</u> - $[\text{Co(en)}_2(\text{NCS})\text{Cl}]\text{SCN}$	Violet Crystals
732 cm.^{-1}	732 cm.^{-1}
787	787
1122	1127
2058	2060
2141	2140

C. As will be recalled, two types of precipitate were obtained from fraction #2a. Analysis of the infrared spectrum of the orange crystals (see figure 3) which formed first suggested that the compound was a cis isomer since two peaks appeared in each of the critical regions, around 1600 cm.^{-1} , $1100\text{--}1150\text{ cm.}^{-1}$, and $870\text{--}900\text{ cm.}^{-1}$ of the spectrum recorded on the IR-12. There was one strong thiocyanato peak in the neighborhood of 2100 cm.^{-1} , ruling out the dichloro compound. The cis-dithiocyanato compound was ruled out as well since this would cause the appearance of two strong peaks in the $2000\text{--}2200\text{ cm.}^{-1}$ region. Comparison of the spectrum of this compound with that of

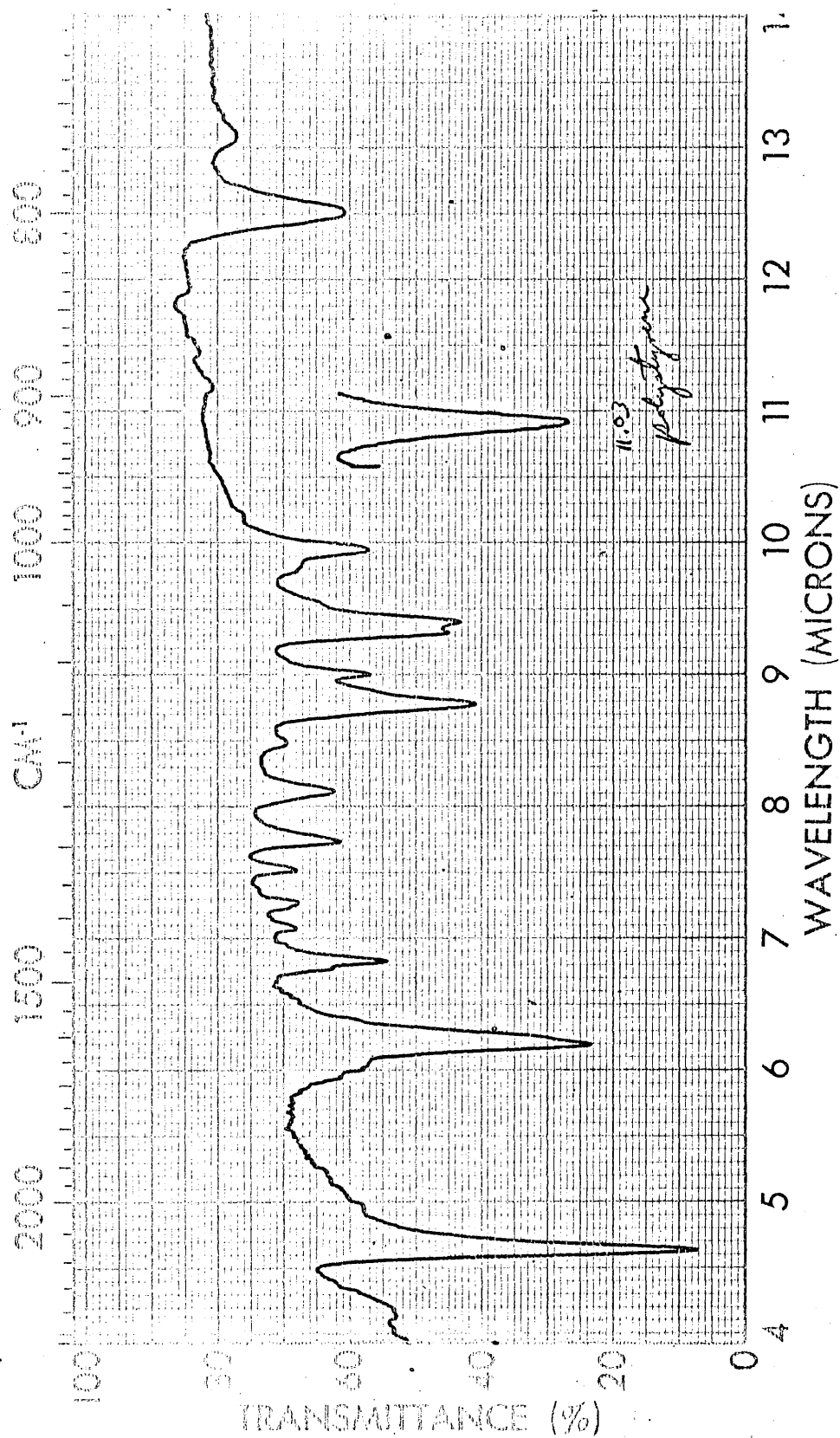


FIGURE 1. A portion of the infrared spectrum of the crystals from fraction #1 eluted with HCl recorded on a Perkin-Elmer Infracord.

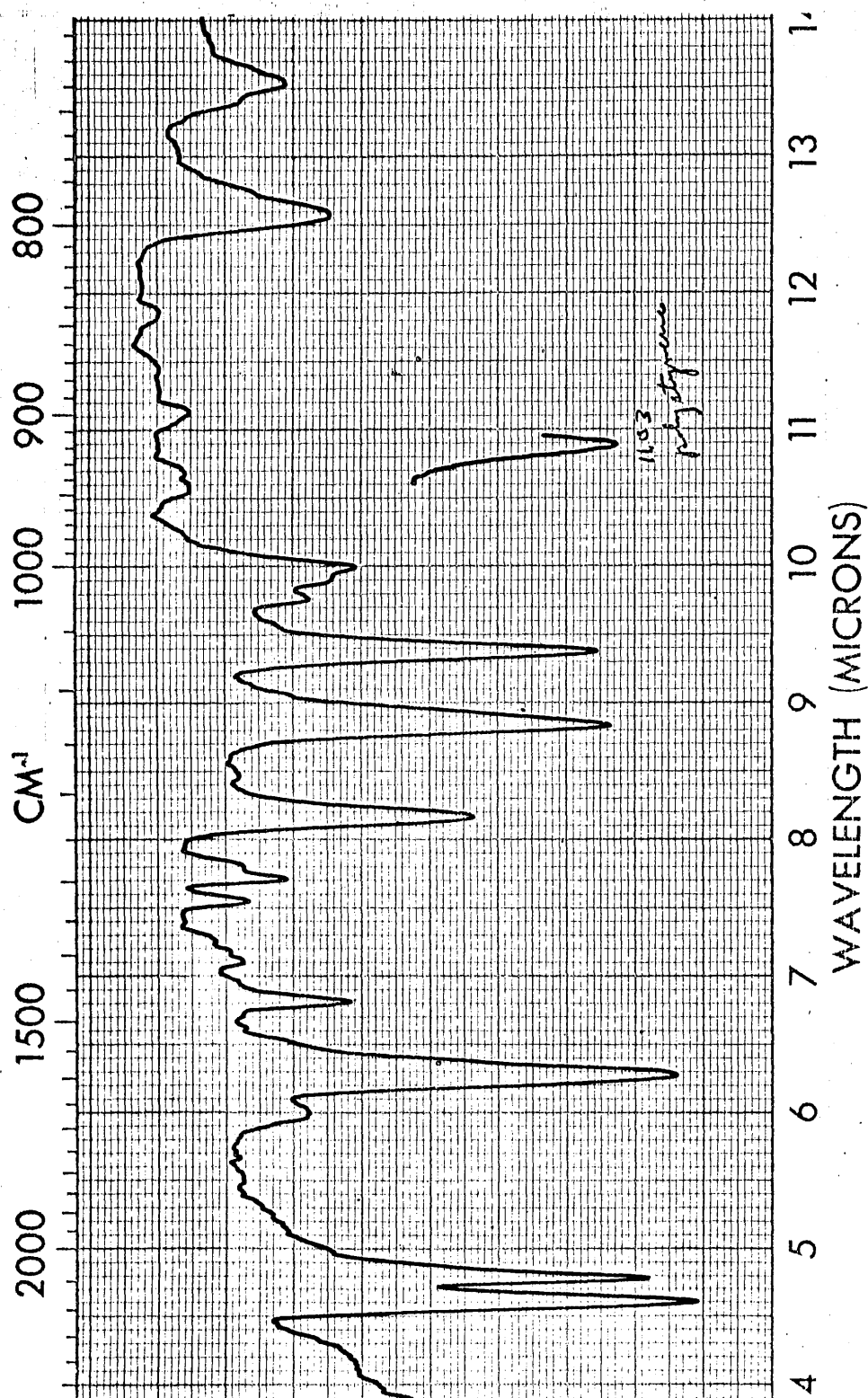


FIGURE 2. A portion of the infrared spectrum of the crystals from fraction #1 eluted with NaSCN recorded on a Perkin-Elmer Infracord.

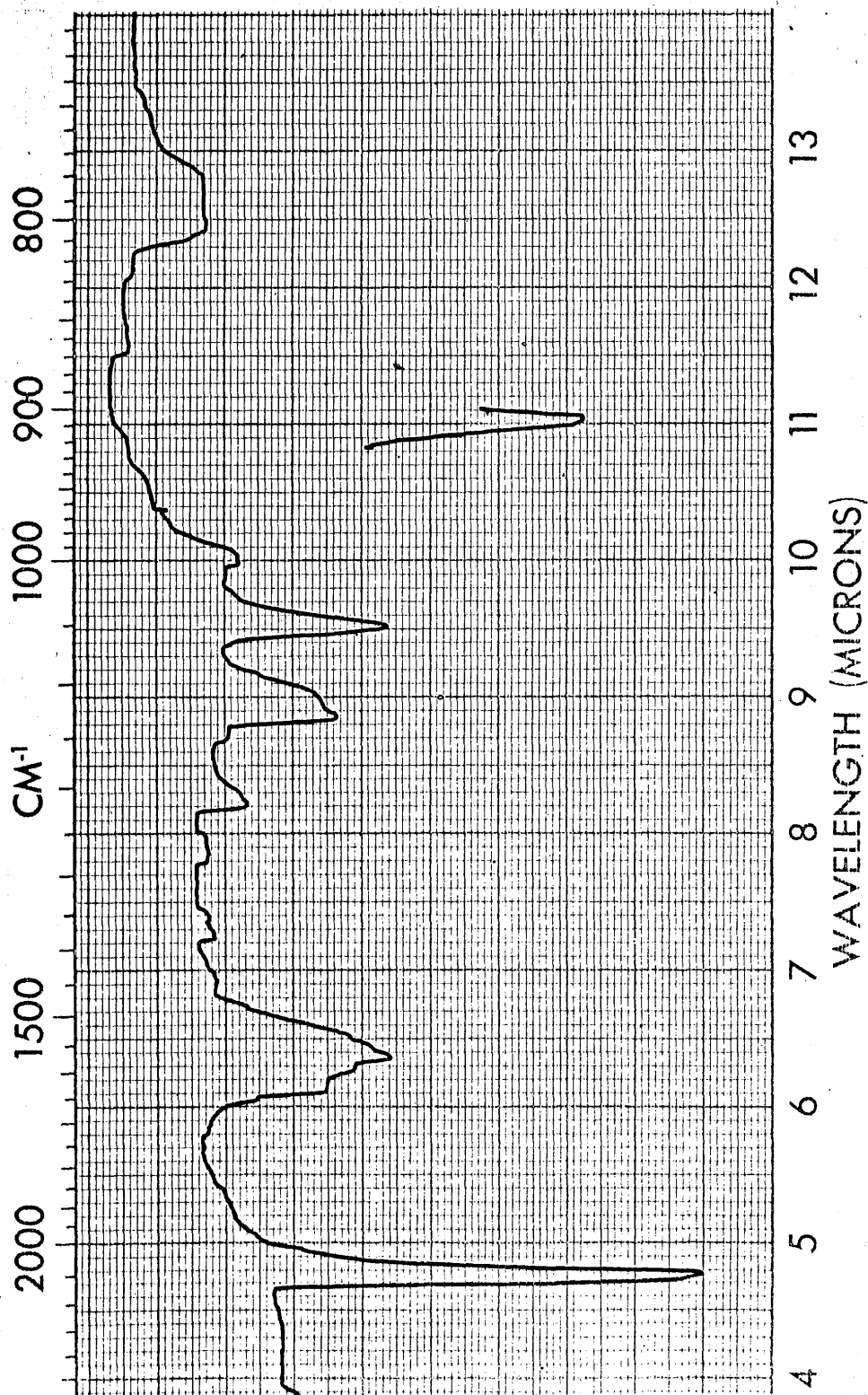


FIGURE 3. A portion of the infrared spectrum of the first crystals obtained from fraction #2a recorded in a Perkin-Elmer Infracord.

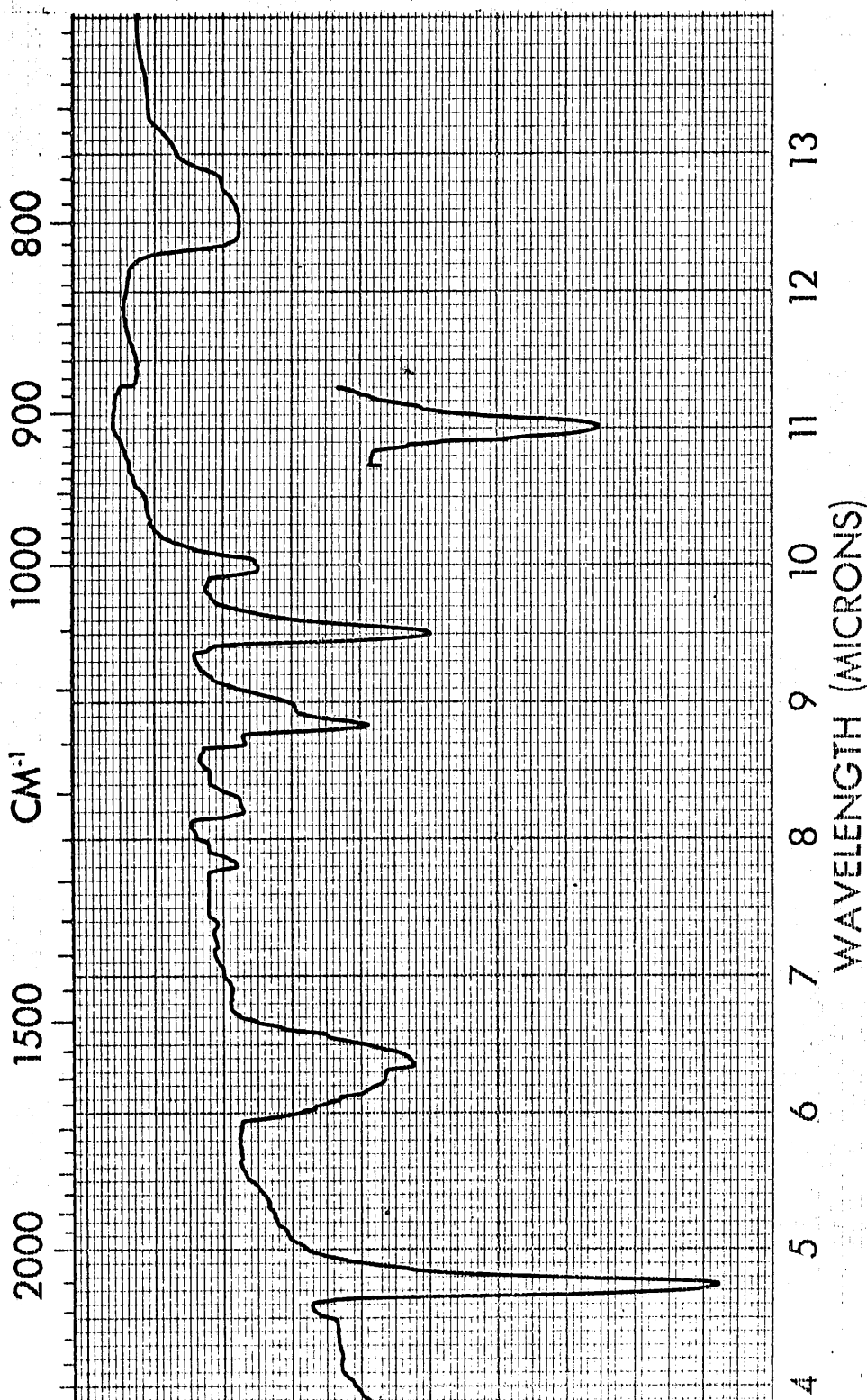


FIGURE 4. A portion of the infrared spectrum of cis-[Co(en)₂(NCS)₂](H₂O)]Cl₂ recorded on a Perkin-Elmer Infracord.

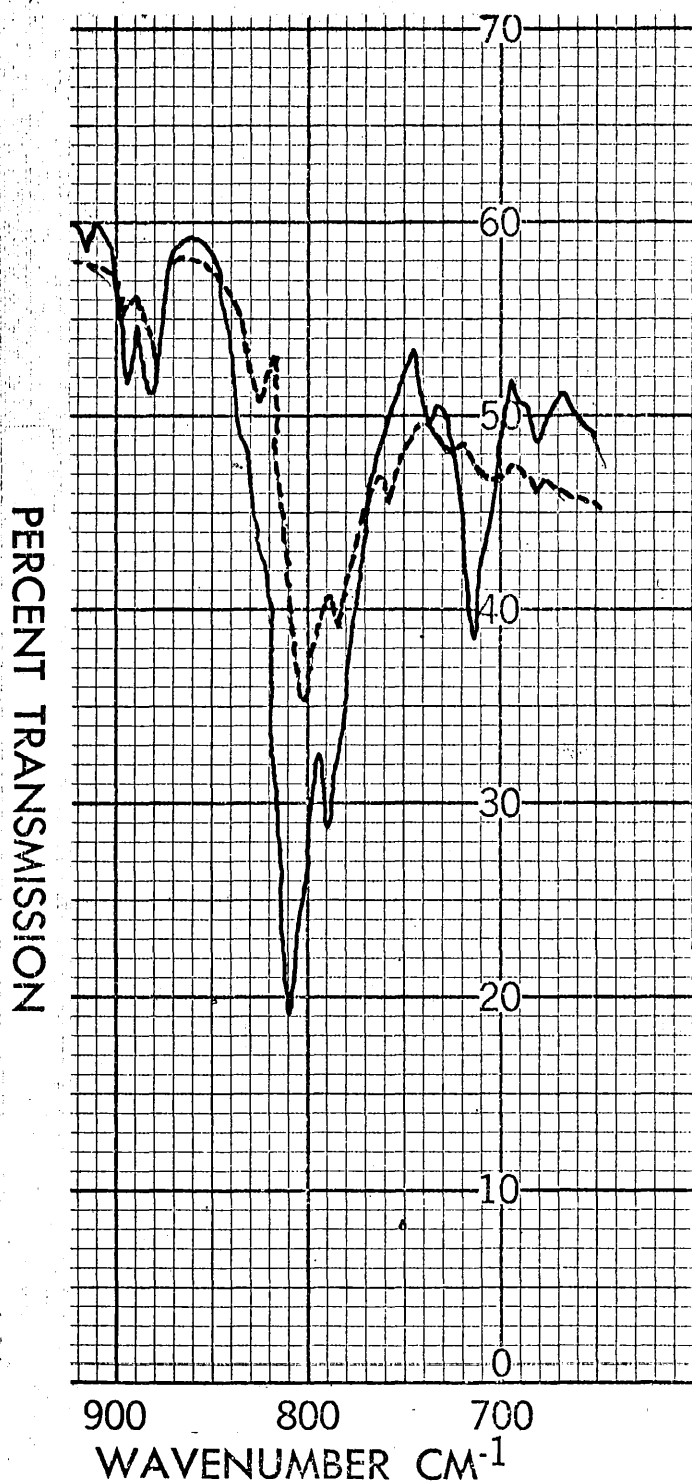


FIGURE 5. The infrared spectra of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ (dashed line) and cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ (solid line) in the neighborhood of 700 cm^{-1} recorded on a Beckman IR-12.

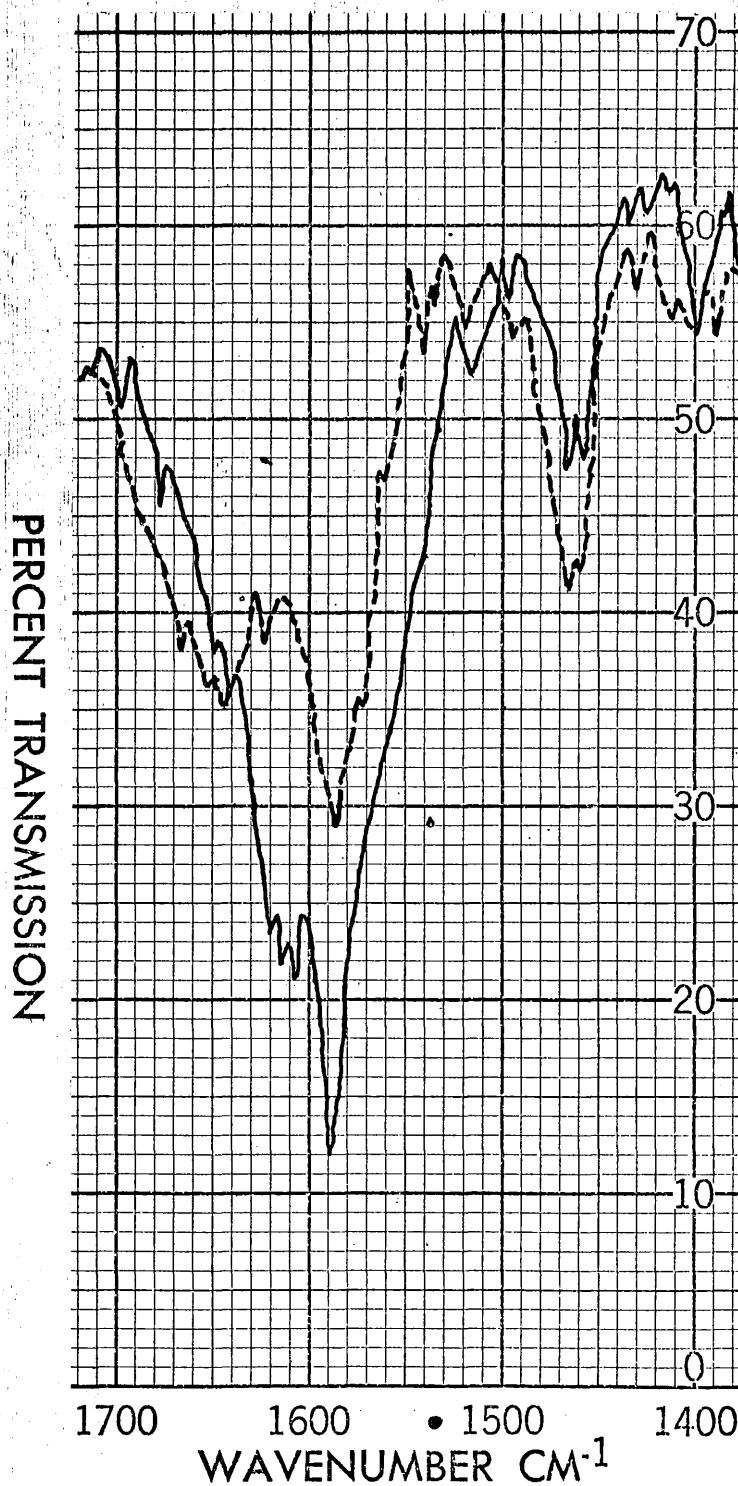


FIGURE 6. The infrared spectra of cis-[Co(en)₂(NCS)Cl]Cl (dashed line) and cis-[Co(en)₂(NCS)(H₂O)]Cl₂ (solid line) in the neighborhood of 700 cm.⁻¹ recorded on a Beckman IR-12.

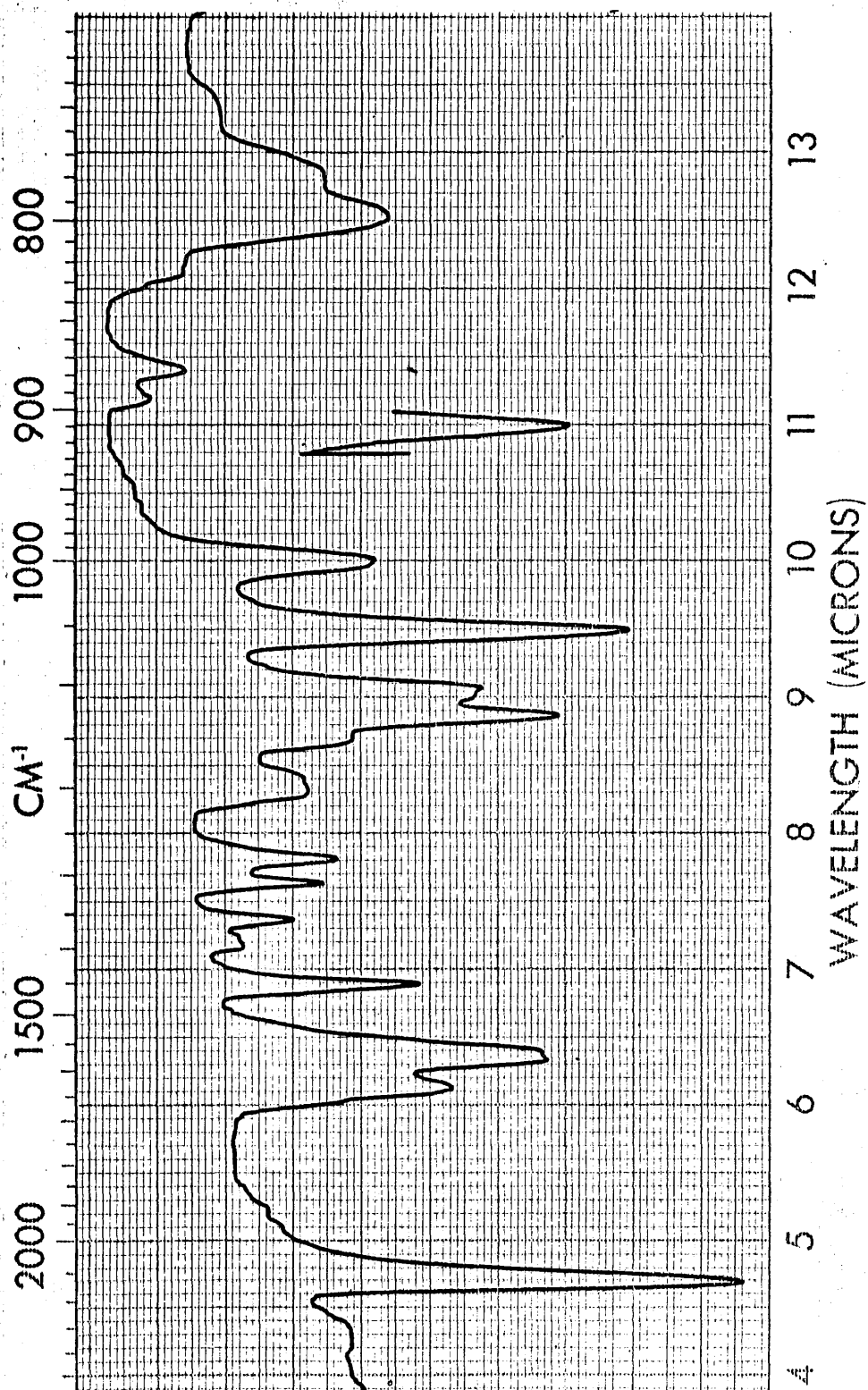


FIGURE 7. A portion of the infrared spectrum of the second crystals obtained from fraction #2a recorded on a Perkin-Elmer Infracord.

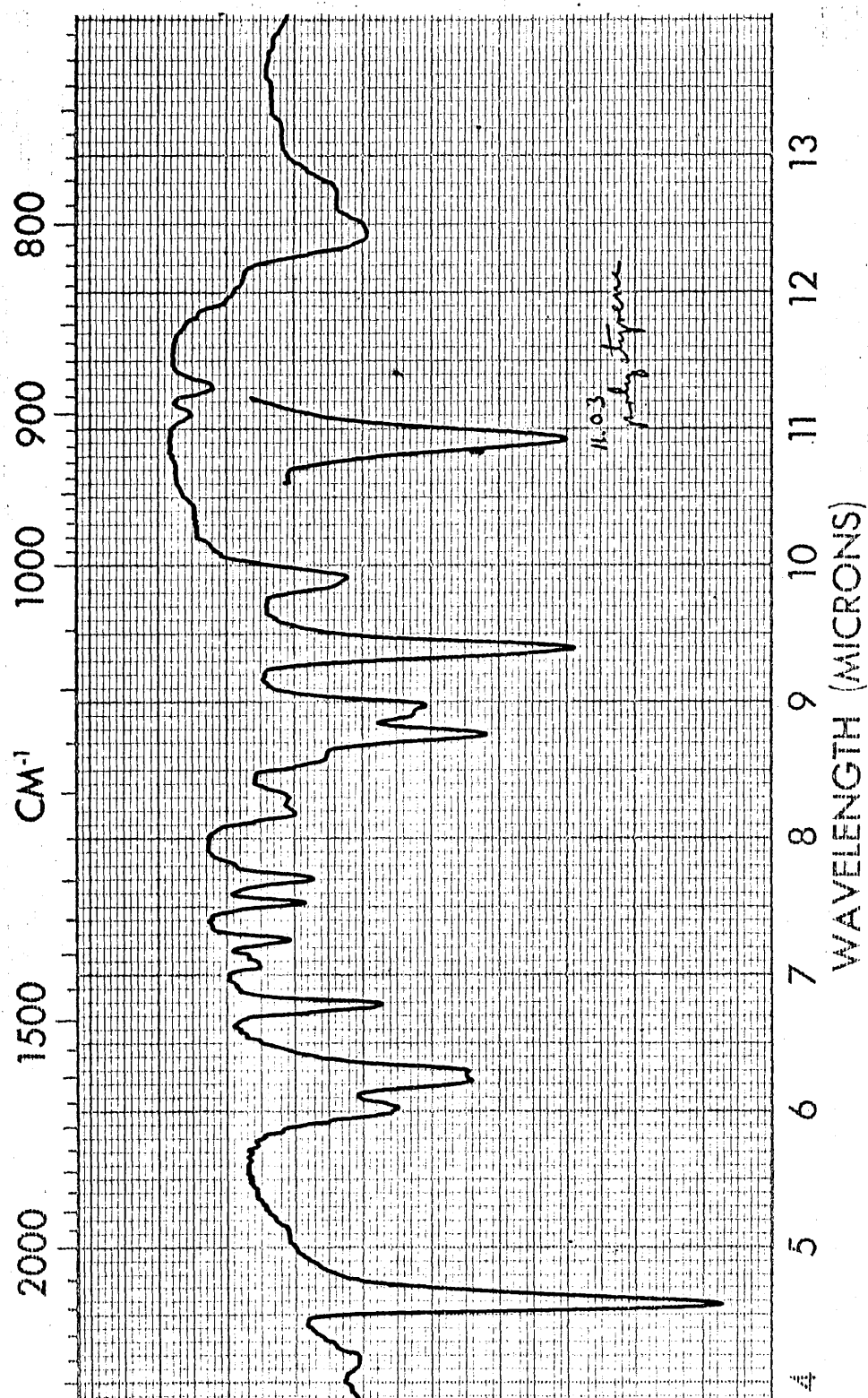


FIGURE 8. A portion of the infrared spectrum of $\text{cis-}[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ recorded on a Perkin-Elmer Infracord.

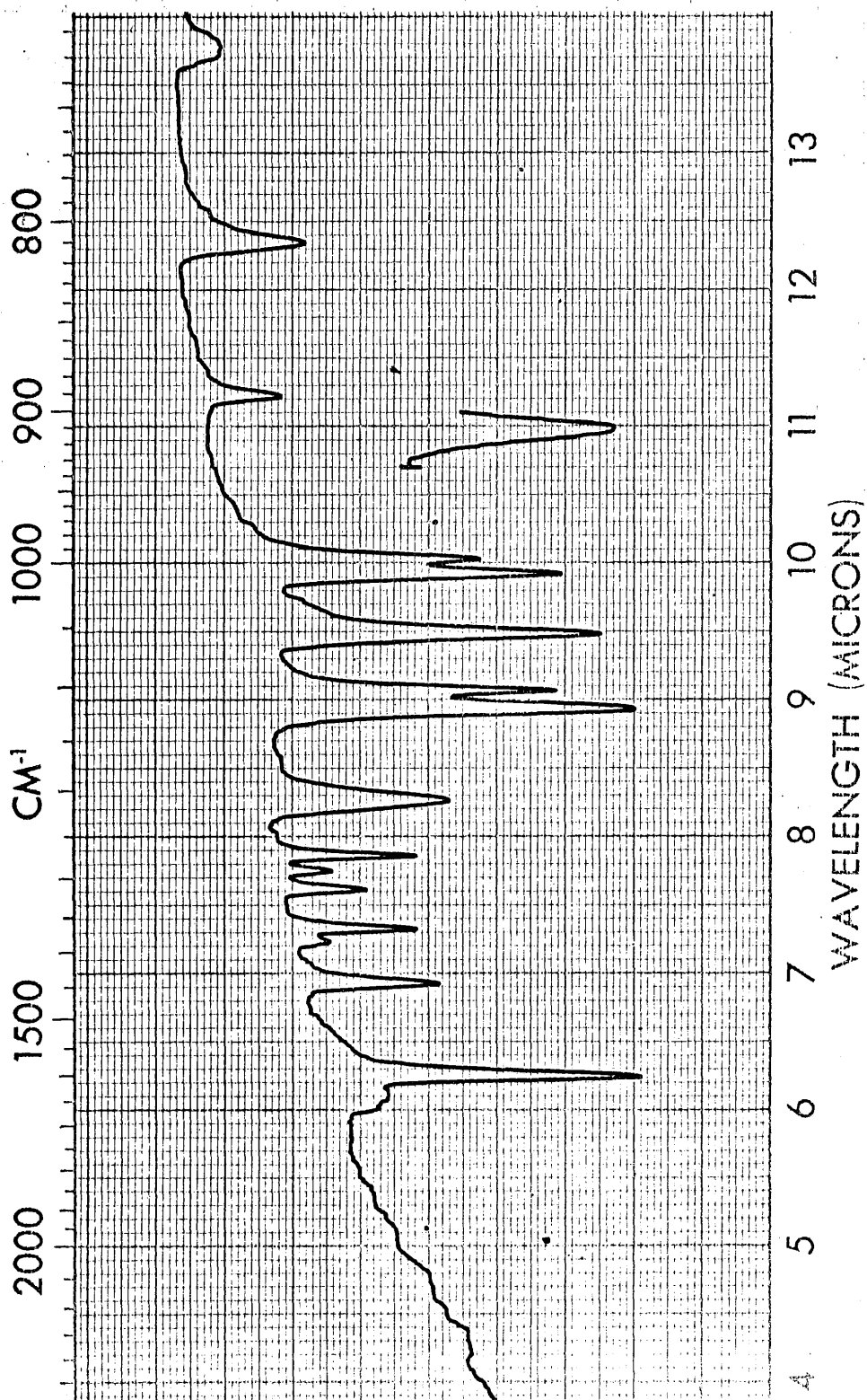


FIGURE 9. A portion of the infrared spectrum of the green crystals obtained from fraction #2a recorded on a Perkin-Elmer Infracord.

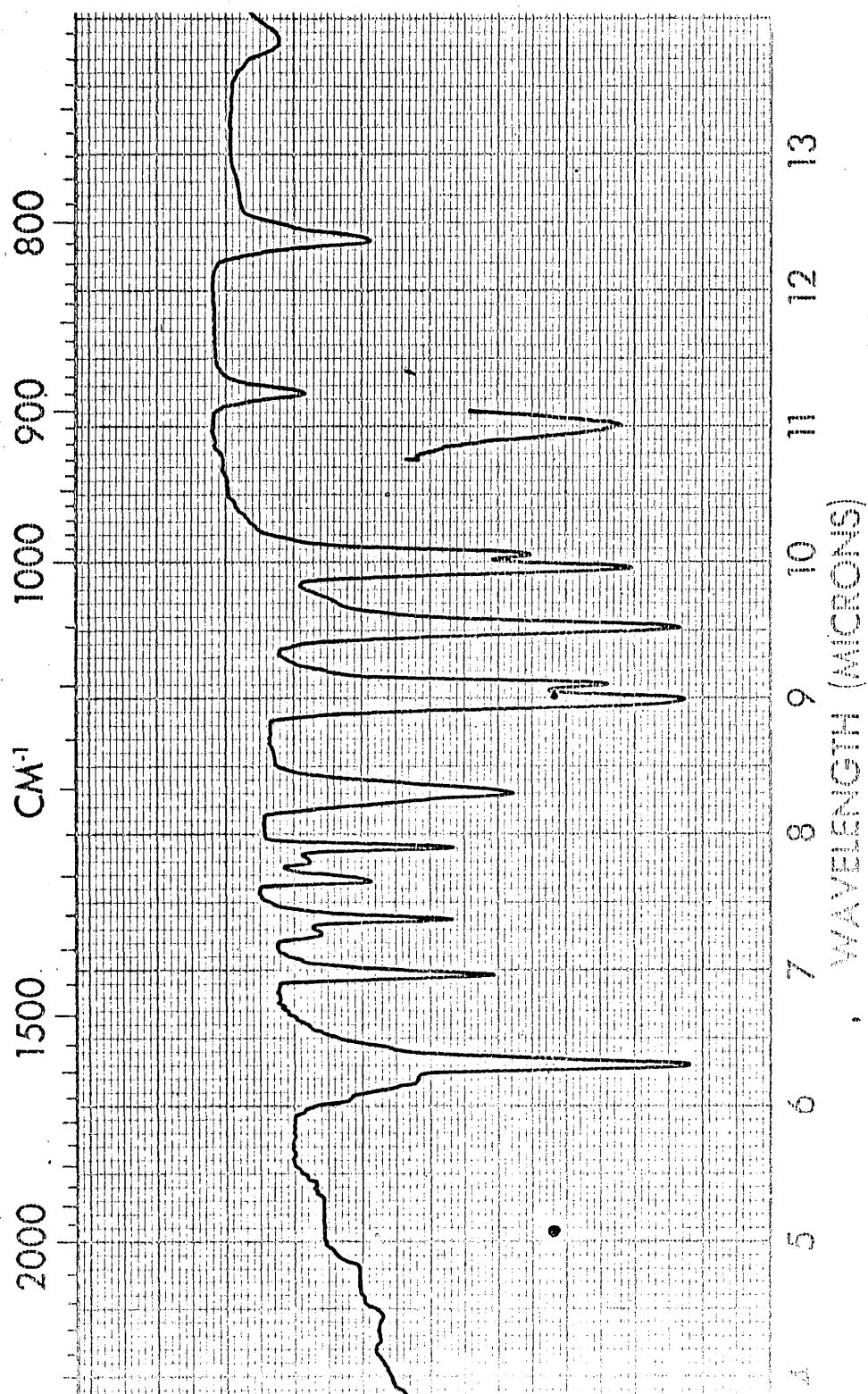


FIGURE 10. A portion of the infrared spectrum of $\text{trans-[Co(en)}_2\text{Cl}_2\text{]Cl}$ recorded on a Perkin-Elmer Infracord.

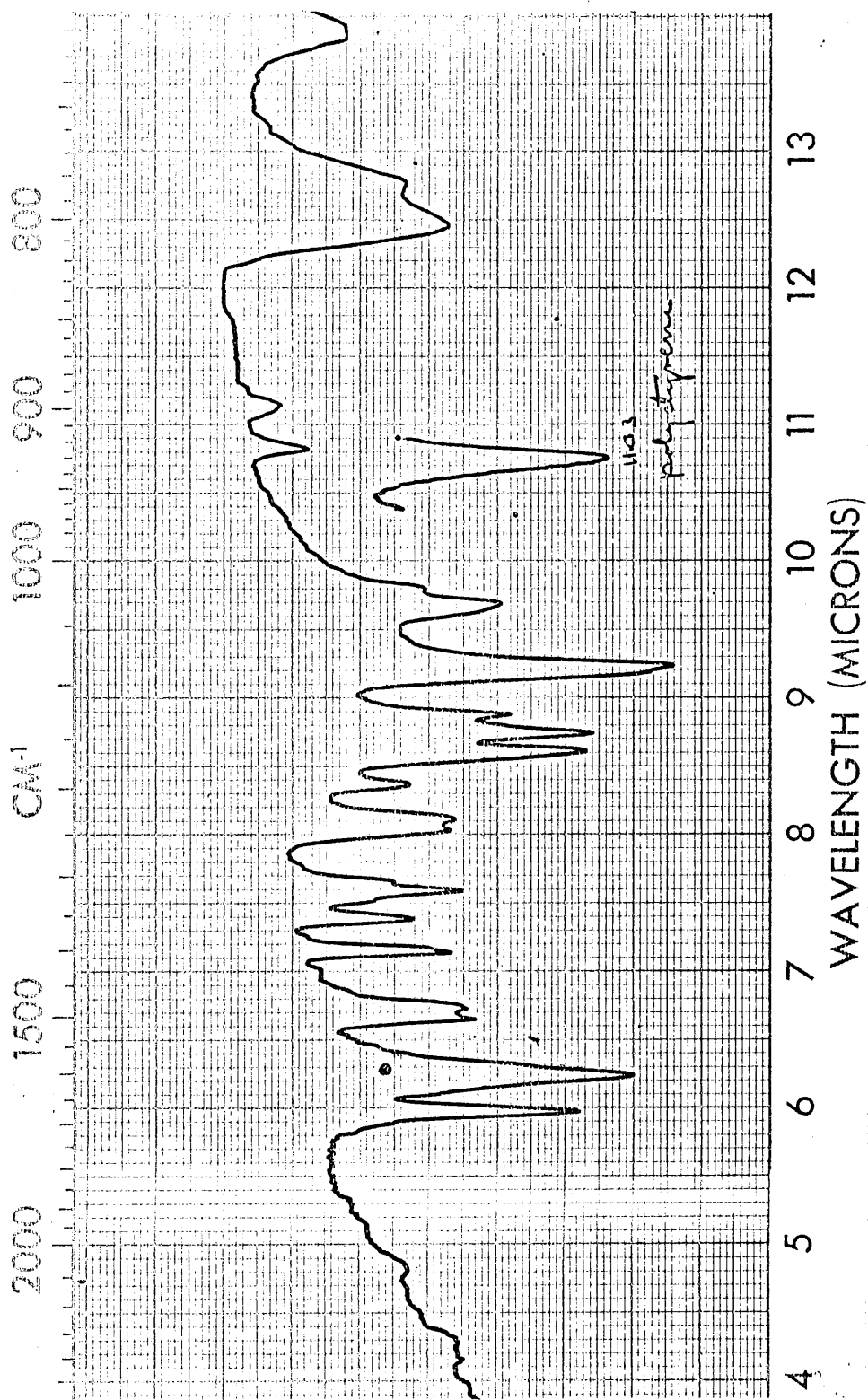


FIGURE 11. A portion of the infrared spectrum of cis-[Co(en)₂Cl₂]Cl recorded on a Perkin-Elmer Infracord.

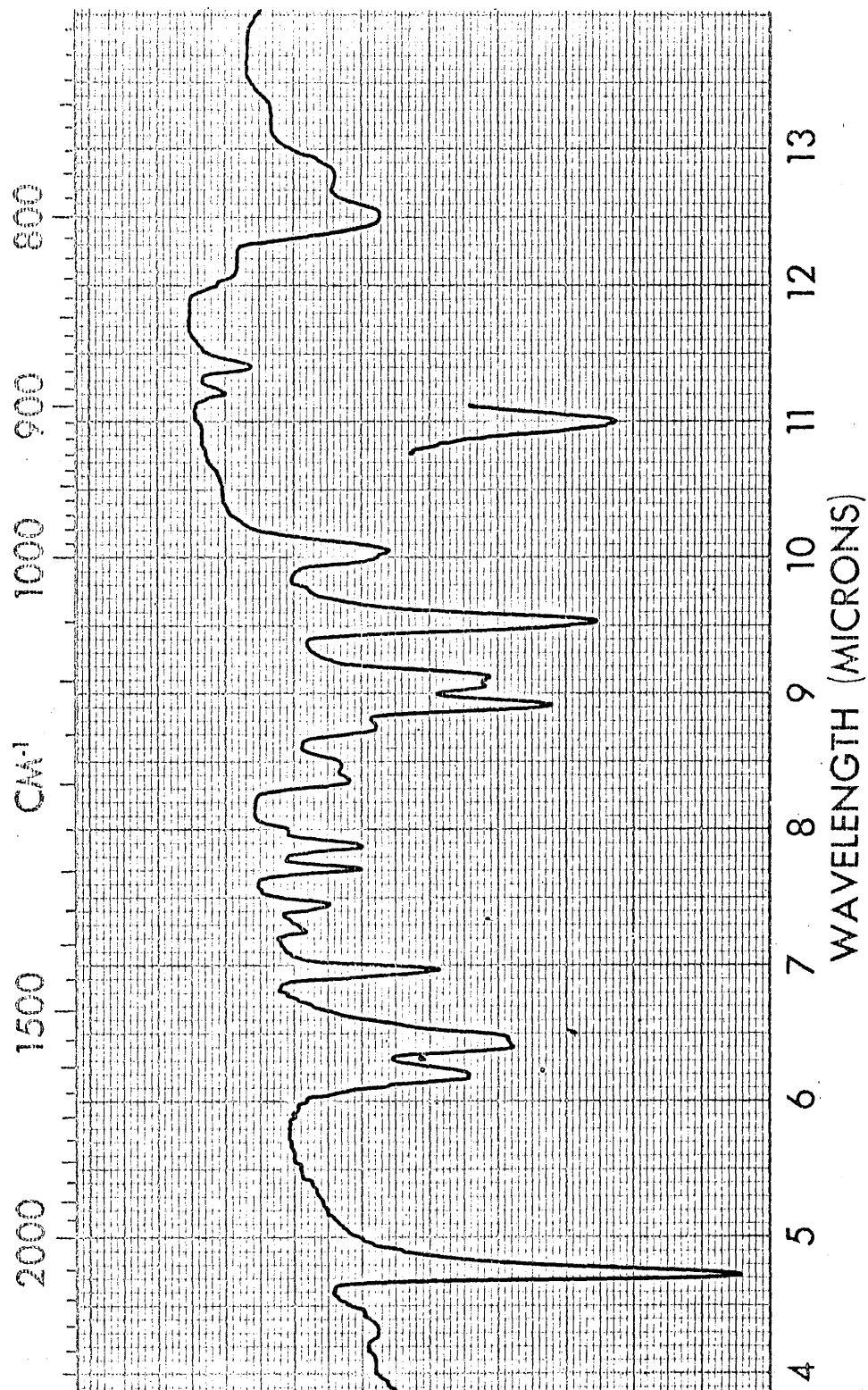


FIGURE 12. A portion of the infrared spectrum of the crystals obtained from fraction #3 recorded on a Perkin-Elmer Infracord.

cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ (see figure 8) indicated that they were not the same. The only remaining possibility appeared to be cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ since the only other available ligand in the acidic aqueous solution was H_2O . In order to test this possibility, cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ was dissolved in water and the solution heated over a hot plate. After about one third of the solution had evaporated, it was set aside to cool. Dark red crystals (only slightly soluble in water) formed after about two hours. Baldwin and Tobe³⁶ have demonstrated that cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ aquates with retention of geometrical configuration to cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]^{++}$. It was, therefore, assumed that the compound which had been prepared as described above was cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$. Additional support for this assumption was obtained from an examination of the infrared spectrum of the compound. The spectrum recorded on the IR-12 indicated the presence of coordinated thiocyanate, confirmed the cis configuration and differed significantly from the spectrum of the unaquated complex. A comparison of the spectrum of this compound (see figure 4) with that of the flakey orange crystals isolated from fraction #2a (see figure 3) indicated that the two compounds were identical.

D. The spectrum of the aquated compound differed from that of the unaquated compound in two noteworthy ways. First, an additional, moderately strong absorption peak appeared at about 715 cm^{-1} (see figure 5). Second, the higher frequency peak of the two in the neighborhood of 1600 cm^{-1} was displaced to a lower frequency by about 35 cm^{-1} (see figure 6). These peaks have been assigned by Morris and

³⁷
Busch to the assymmetric deformation of the NH_2 group.

E. The spectrum of the reddish crystals obtained from fraction #2a (see figure 7) indicated that it was a *cis* compound. It appeared that it might have been contaminated by some of the first compound to crystallize from the same solution. However, a comparison with the spectrum of *cis*- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ (see figure 8) indicated that they were the same compound.

F. A comparison of the spectrum of the green crystals, obtained from fraction #2a by evaporating over a hot plate (see figure 9), with that of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (see figure 10) indicated that they were identical compounds as suspected.

G. A study of the spectrum of the red compound obtained from fraction #3 (see figure 12) indicated that it was *cis*- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$. Two peaks appeared around 1600 cm^{-1} , and in the $1100\text{-}1150\text{ cm}^{-1}$, and $870\text{-}900\text{ cm}^{-1}$ regions. Only one thiocyanate absorption peak appeared in the neighborhood of 2100 cm^{-1} , ruling out the *cis*-dithiocyanato and *cis*-dichloro compounds, and the peak frequencies closely matched those of the infrared spectrum of *cis*- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ (see figure 8).

VII. Analysis of the Ultraviolet Spectra.

Since crystals of the same compound were isolated from separate fractions eluted with, respectively, 1 and 3 molar HCL solutions, it was obvious that some change was occurring in at least one of the fractions after elution from the column. It was thought that an

analysis of the ultraviolet spectra of the complexes in solution might help resolve the problem.

The ultraviolet and visible spectra of cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ in solution have been studied by Basolo³⁸, Shimura³⁹, and Kuroya and Tsuchida⁴⁰. Minor differences in the three reports may be due to solvent differences since Shimura and Kuroya and Tsuchida studied the spectra of the compounds in aqueous solution while Basolo dissolved the compounds in 99 per cent methanol to avoid aquation. Thus Basolo reported a broad peak at 510 millimicrons while Kuroya and Tsuchida reported a peak at 503 millimicrons in the spectrum of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$. A complication in the interpretation of this spectrum occurs in the region between 290 and 300 millimicrons where a broad inflection but no distinct peak appears. Shimura attributes the obscuring of a peak in this region to the interference of "end absorption." He has plotted theoretical peaks to compensate for this interference and thus arrived at a peak of 305 millimicrons. Basolo reported an absorption maximum at 300 millimicrons.

The ultraviolet spectra reported here were recorded on a Bausch and Lomb Spectronic 505 recording spectrophotometer. The spectra (see figure 13) of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ freshly dissolved in water and methanol gave similar inflections but no peaks in the neighborhood of 3000 millimicrons. However, when the water solution was allowed to stand for two days before the spectrum was again recorded (see figure 14), a sharp peak appeared at 310 millimicrons. Apparently, aquation of the complex took place during the interim. Support for this conclusion was obtained by examining the spectrum (see figure 15) of cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ dissolved in water, which also gave a distinct

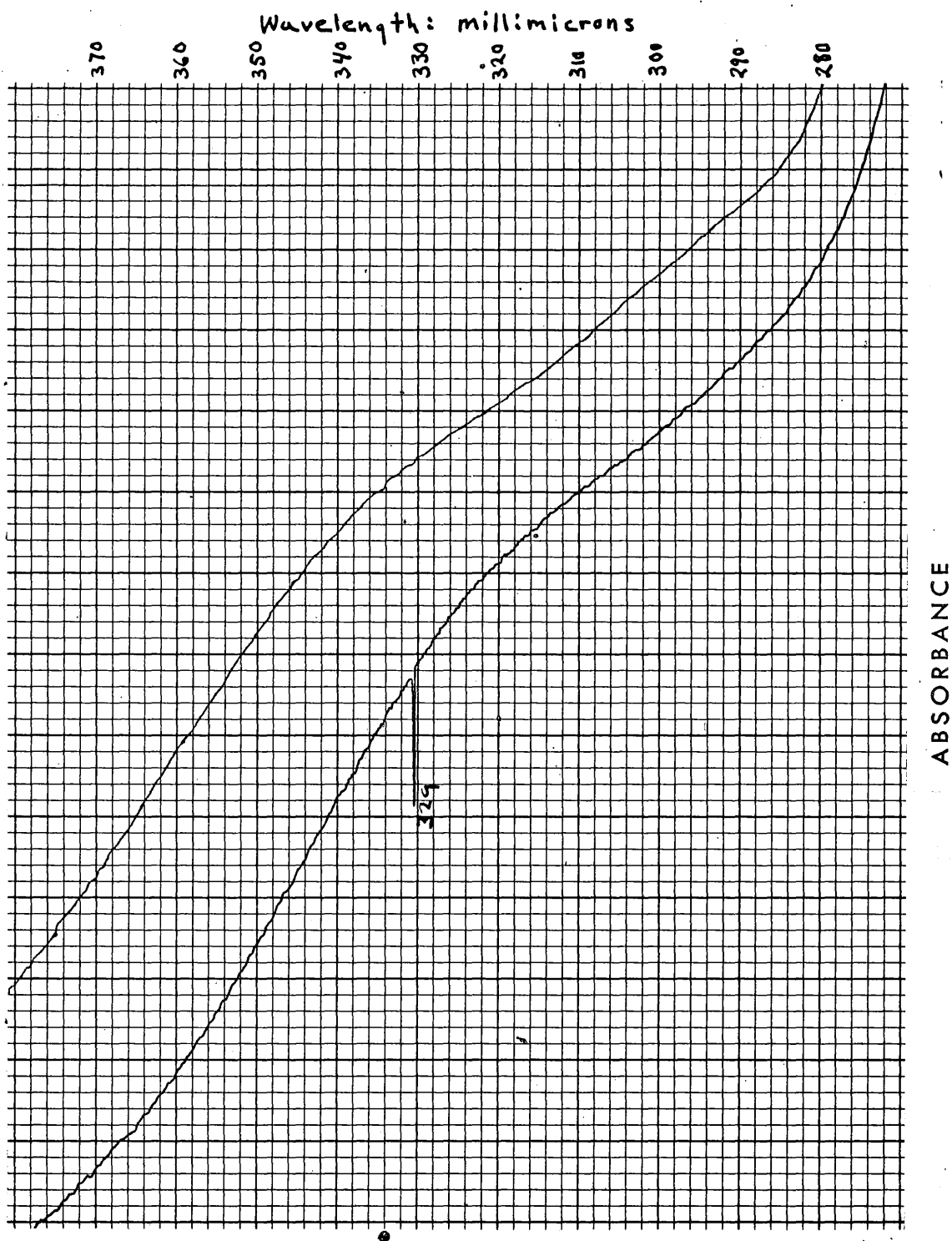


FIGURE 13. The ultraviolet spectra of $\text{cis-}[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ freshly dissolved in methanol (top curve) and water (lower curve) in the neighborhood of 300 millimicrons.

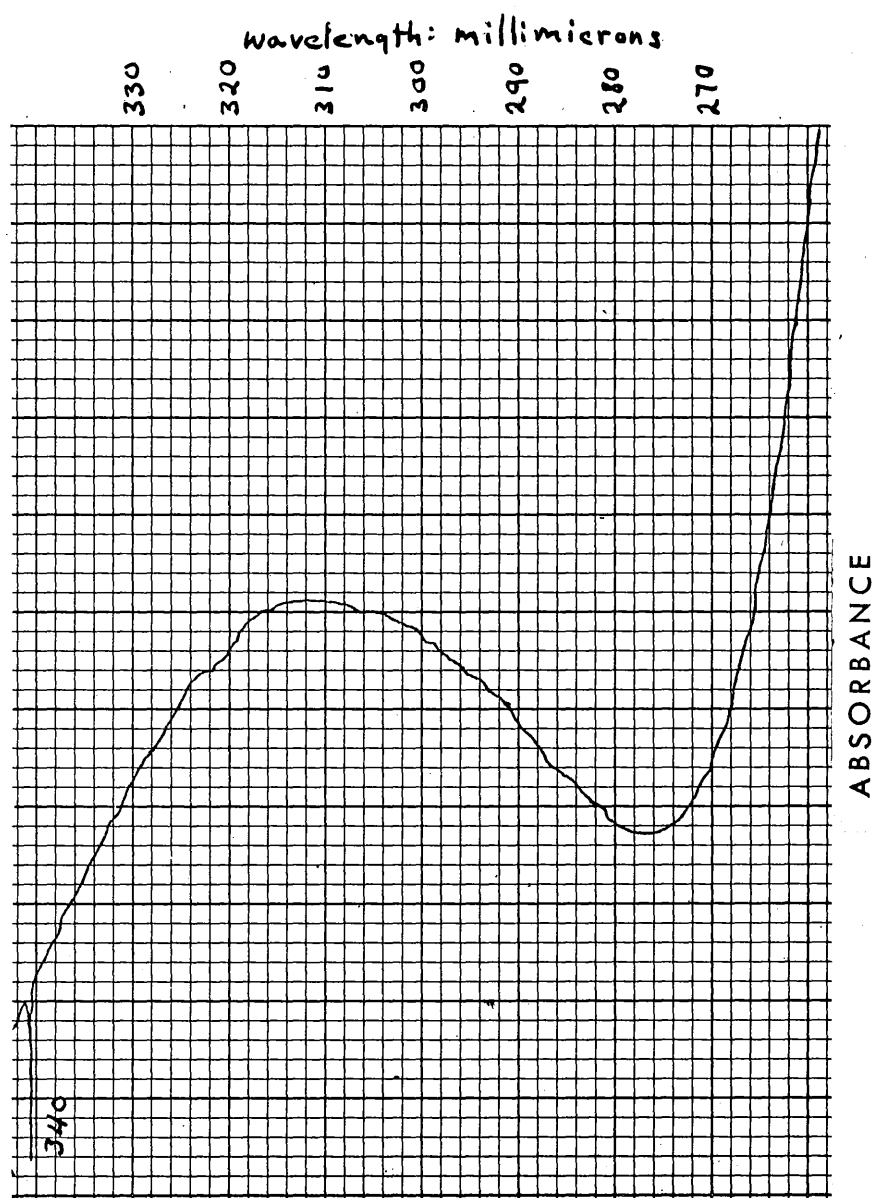


FIGURE 14. A portion of the ultraviolet spectrum of a solution prepared by dissolving in water and allowing to stand two days.

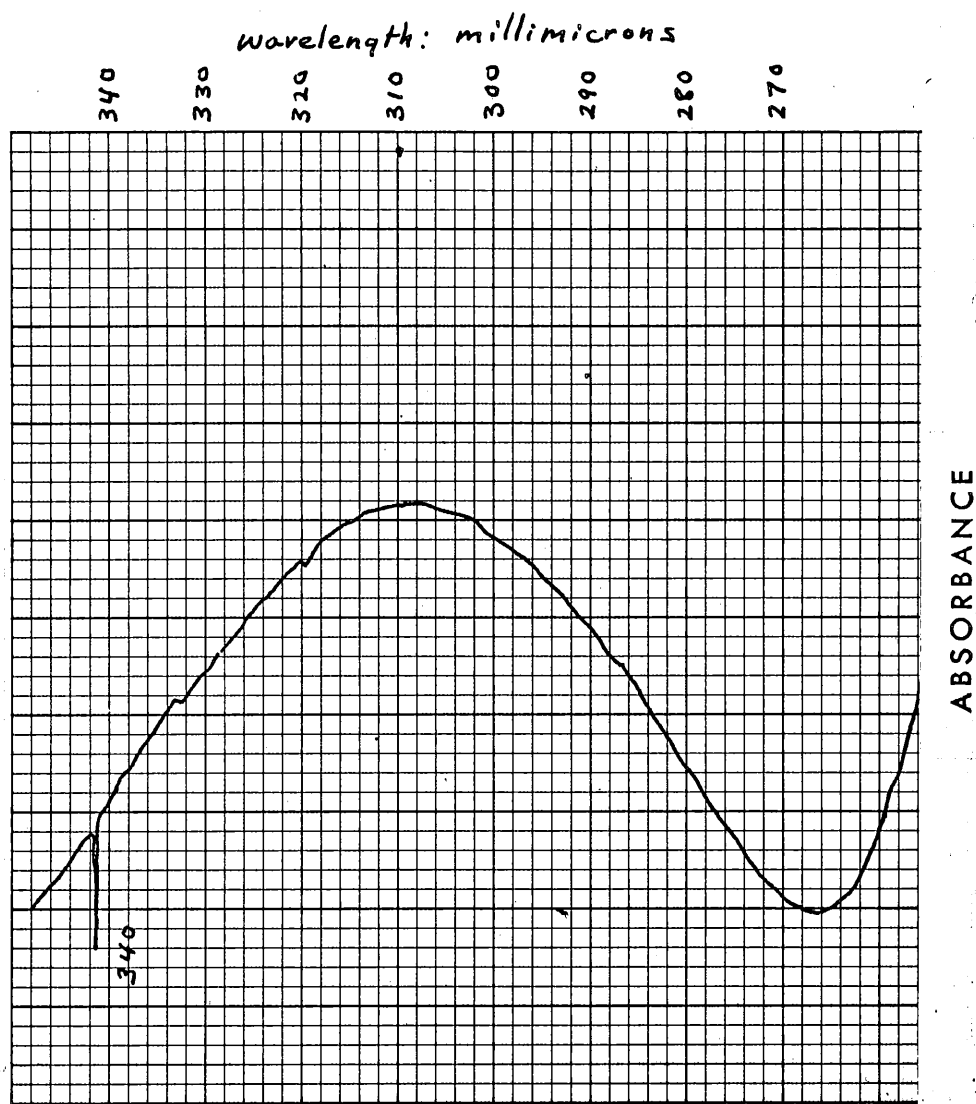


FIGURE 15. A portion of the ultraviolet spectrum of cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ freshly dissolved in water.

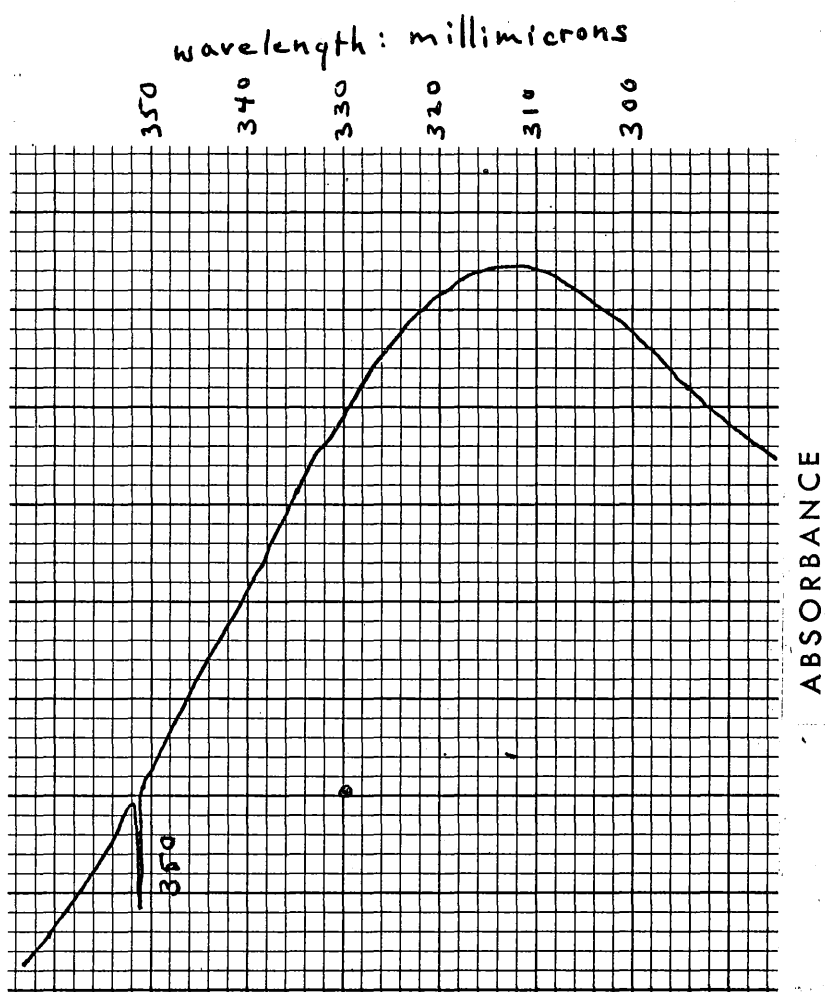


FIGURE 16. A portion of the ultraviolet spectrum of solution #2a.

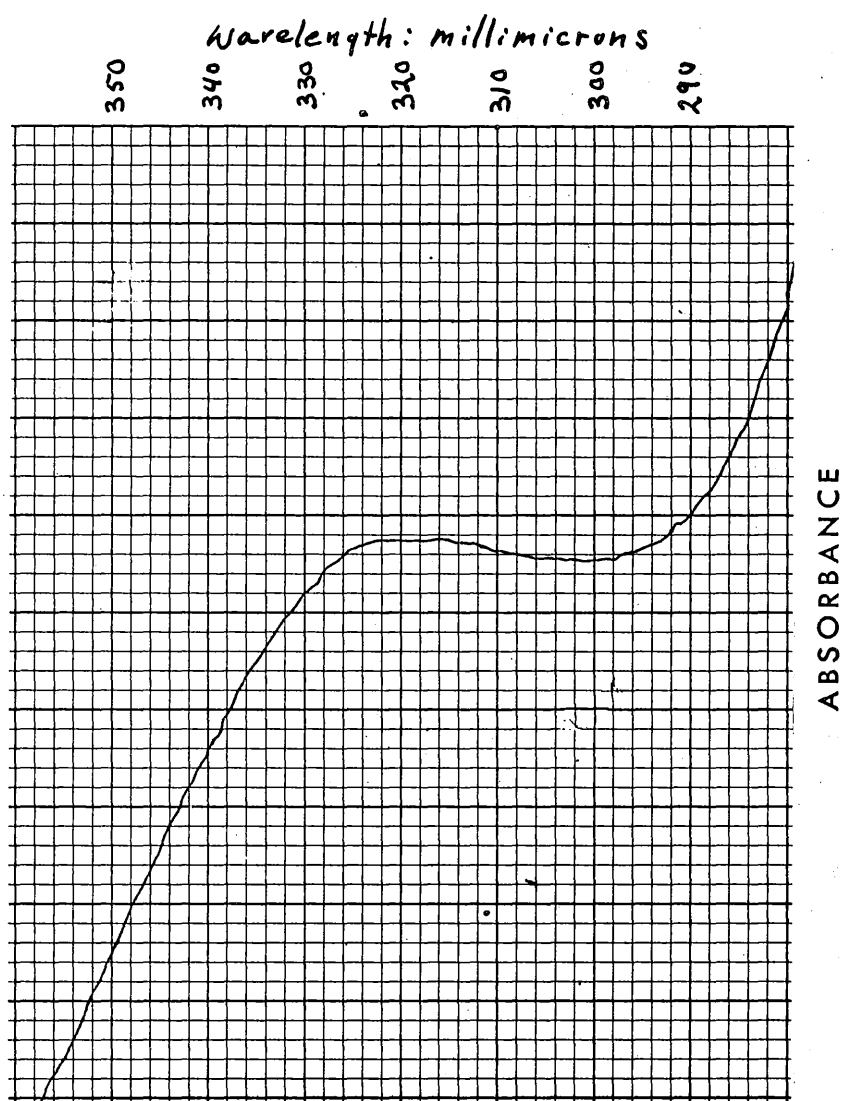


FIGURE 17. A portion of the ultraviolet spectrum of solution #2d.

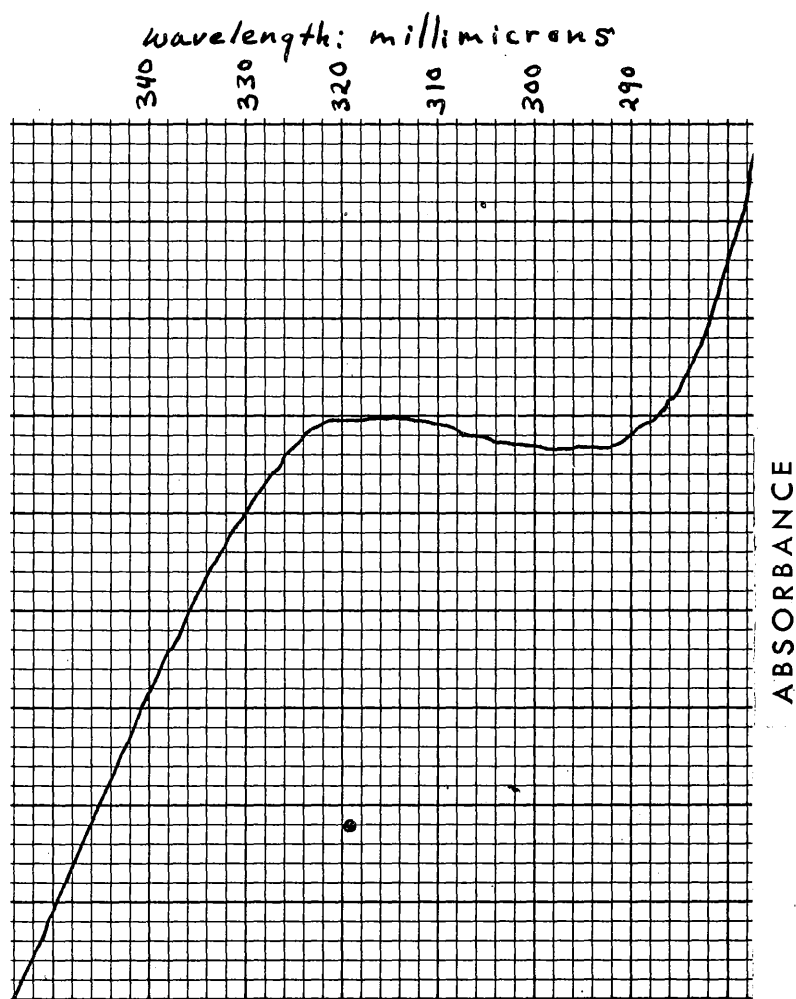


FIGURE 18. A portion of the ultraviolet spectrum of solution #3.

peak at 310 millicrons. The spectra of solutions #2a (see figure 16), #2d (see figure 17), and #3 (see figure 18) gave definite peaks of varying depth and sharpness between 310 and 320 millimicrons suggesting that different proportions of aquated and unaquated complex were present in each solution.

The spectrum of solution #2b gave a peak at about 290 millimicrons indicating that this compound was different from those mentioned above.

VIII. Estimate of the Trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}] \text{Cl}$ Content of the Product Mixture

A sample of the crystals obtained from fraction #1 was analyzed for cobalt by an electroplating method⁴¹ (see page 47) to determine the purity and ascertain a practical molecular weight, to be used in calculating the molarity of a solution of the compound. The percent cobalt calculated for $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)_2(\text{NCS})\text{Cl}] \text{Cl}$ is 19.8, and that found was 19.7.

Fraction #1 appeared to be pure trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}] \text{Cl}$ in HCl. There was no aquation of the compound on the column, and no evidence of aquation after elution. Therefore, it was possible to estimate the concentration of this compound in the product mixture by measuring the intensity of absorption of the eluted solution in the ultraviolet region. The same could not be done with fractions #2 and #3 since they were found to be mixtures of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}] \text{Cl}$ and its aqua derivative, cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})] \text{Cl}_2$.

A product mixture was prepared by reacting 8.57 grams (0.0300

mole) of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ dissolved in 12 ml. of water with 2.92 grams (0.0300 mole) of KSCN dissolved in 4 ml. of water, and diluting to 50 milliliters in a volumetric flask. Thus each milliliter of diluted product mixture contained 0.000600 mole of cobalt compound assuming one cobalt atom per molecule. One milliliter of the diluted product mixture was pipetted onto each of two ion-exchange columns of Dowex 50W-X8 before any crystallization from the mixture had taken place. The first band was entirely eluted from each column with 0.5 M HCl and collected in a flask. The fraction thus collected was diluted to 250 milliliters with 0.5 M HCl in a volumetric flask, and the per cent transmittance at the peak at 555 millimicrons was measured on a Bausch and Lomb Spectronic 20 ultraviolet spectrophotometer.

A concentration versus absorbance curve was plotted (see figure 19) by dissolving a weighed amount of the analyzed trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ in 0.5 M HCl and measuring the absorbance for different dilutions (see table #2). The concentration of the compound in solution #1 was read from the plot, and this value was used to estimate the fraction of trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ in the product mixture (see table #3).

The average value of the mole per cent of trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ found in the particular reaction mixture was 49%.

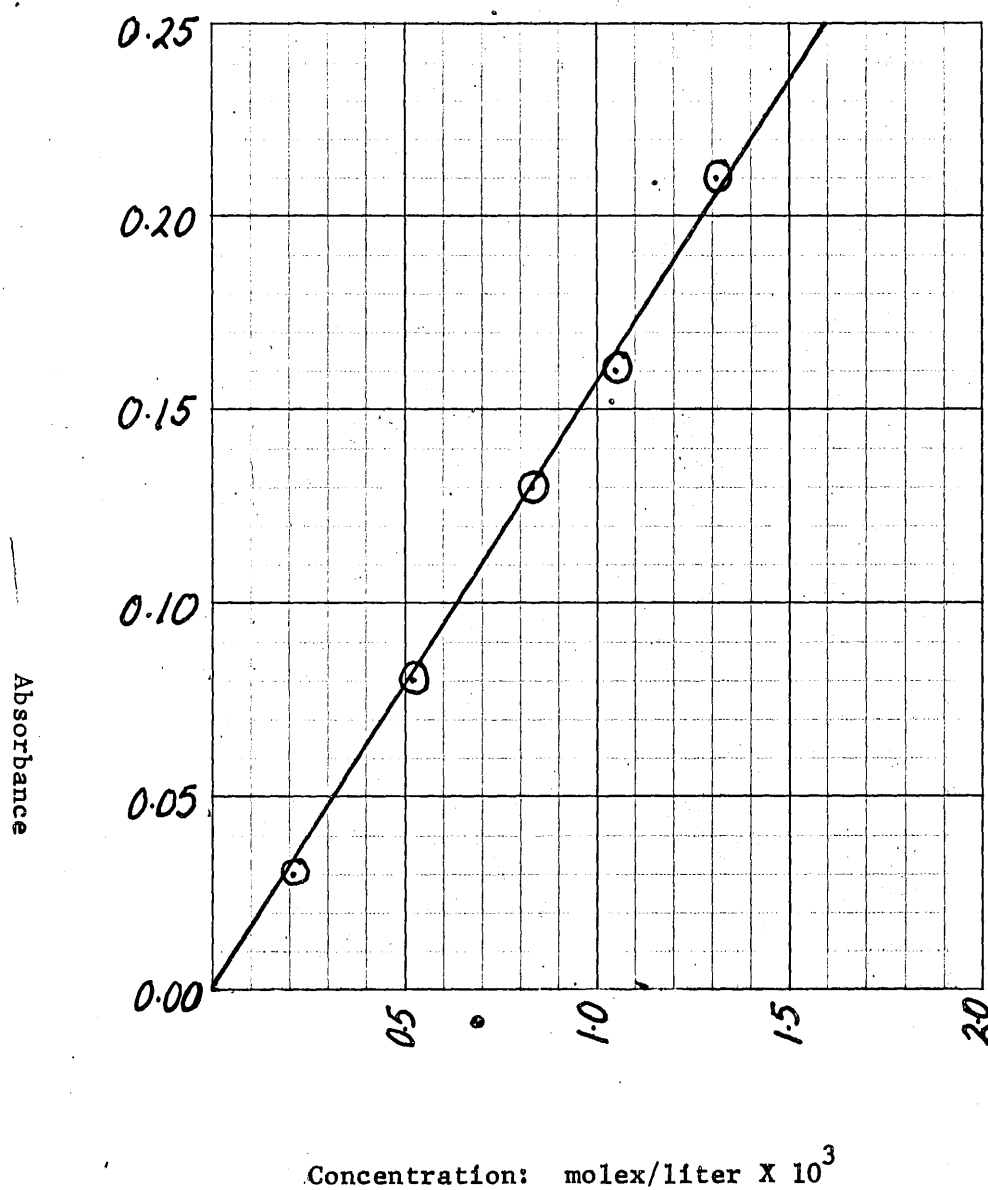


FIGURE 19: Concentration versus absorbance for trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ dissolved in 0.5 M HCl.

TABLE 2: ABSORBANCE MEASUREMENTS AT VARIOUS CONCENTRATIONS
FOR TRANS- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ IN 0.5 M HCl SOLUTION

<u>Concentration</u> <u>grams/liter</u>	<u>Concentration</u> <u>moles/liter X 10³</u>	<u>Per cent</u> <u>Transmittance</u>	<u>Absorbance</u>
0.781	2.62	38	0.42
0.391	1.31	62	0.21
0.312	1.05	69	0.16
0.249	0.84	74	0.13
0.156	0.52	83	0.08
0.063	0.21	94	0.03

TABLE 3: DATA FOR UNKNOWN SOLUTIONS

<u>Per cent</u> <u>Transmittance</u>	<u>Absorbance</u>	<u>Concentration</u> <u>moles/liter</u>	<u>Concentration</u> <u>moles/250 ml.</u>	<u>Mole</u> <u>% in</u> <u>mixture</u>
66	0.18	1.15×10^{-3}	2.87×10^{-3}	48
65	0.19	1.21×10^{-3}	3.00×10^{-3}	50

IX. Analysis for Cobalt by Electrodeposition

Two electrodeposition methods were used to analyze for cobalt. Trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was analyzed by the method of Shreiber.³⁰ Approximately 0.2 grams of the complex was weighed out and dissolved in water in a beaker. About 2 milliliters of ethylenediamine was added as an electroplating agent, and a potential of about 10 volts was applied through the solution between platinum electrodes to obtain a current of about 0.2 amperes. When the color of the complex had disappeared (3-4 hours), the cathode was rinsed in acetone and air-dried before weighing. The per cent cobalt calculated for trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ is 20.6, and that found was 20.5

An attempt was made to analyze trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ by the

above method but a low value was obtained (12 per cent as opposed to 19.8 per cent calculated). A method was, therefore, adapted from Dale and Banks⁴¹ in which the sample is vigorously oxidized before electrolysis. Approximately 0.2 grams of the compound was dissolved in 20 milliliters each of concentrated nitric and concentrated sulfuric acids. The resulting solution was boiled over a Bunsen burner, with intermittent addition of nitric acid, to near dryness. Twenty milliliters more of each acid was added and the evaporation repeated. The residue was dissolved in a minimum of water and the solution again evaporated to fumes of SO_2 . This step was repeated two or three more times. The violet residue was then dissolved in water and transferred quantitatively to an electroplating beaker. About 20 milliliters of 6 M ammonium hydroxide and 2 grams of sodium bisulfite was added. The resulting solution was electrolyzed between platinum electrodes. The current was maintained at 2-4 amperes. When the color had completely disappeared from the solution, plating was assumed to be complete, and the cathode was rinsed in acetone and air-dried before weighing. The per cent cobalt calculated for $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ is 19.8 and that found was 19.7.

In the analysis described above, a Fischer Electroanalyzer was used as a source of voltage.

DISCUSSION OF THE EXPERIMENTAL RESULTS

A number of conclusions appear to be warranted by the experimental results reported in the previous section. The first fraction to be eluted from the ion-exchange column has been identified by infrared spectra and confirmed by a cobalt analysis as trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$. This is hardly surprising since the trans-chlorothiocyanato compound crystallizes from the product mixture studied here, and, in all previous ion-exchange separations of geometric isomers of coordination compounds, the trans isomer has been eluted first.

The identification of the other fractions off the ion-exchange column was less straightforward. The infrared spectra indicate that cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ crystallized from both fraction #2a and fraction #3, and yet, both bands on the column could not have the same composition or no band separation would have occurred. The logical explanation is that band #2a is cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$, and band #3 is cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]^{++}$. It is well established that the cis-chlorothiocyanato compound aquates readily, and it is highly improbable that the dipositive ion would elute more rapidly than the monopositive ion. The above conclusion draws support from the observed behavior of band #2a on the column and an analysis of the ultraviolet spectra of the eluted fractions. It may be recalled that a new band was left behind band #2a whenever elution was resumed after an interruption, and that the new band was eluted at the same rate as band #3. In addition, the area between band #2a and band #3 not occupied by another band was pink rather than the off-white color of the resin. Such behavior may

be explained by aquation of the material in band #2a. The fact that the non-banded region of the resin between band #2a and band #3 was pink suggests that aquation of $\text{cis-}[\text{Co(en)}_2(\text{NCS})\text{Cl}]^+$ in band #2a occurred continually during elution. When elution was resumed after an interruption, the dipositive aquated complex formed during the interim remained behind as a discrete band. The fact that a band thus formed eluted at the same rate as the third band is support for the contention that the two bands were the same material, namely $\text{cis-}[\text{Co(en)}_2(\text{NCS})(\text{H}_2\text{O})]^{++}$. That no $\text{cis-}[\text{Co(en)}_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ was obtained from fraction #3 can be explained by rechlorination of the aquated complex after elution in the 3 M HCl solution. Likewise, the fact that crystals of the aquated complex were obtained from fraction #2a can be explained by aquation of $\text{cis-}[\text{Co(en)}_2(\text{NCS})\text{Cl}]\text{Cl}$ after elution in the 1 M HCl solution. The ultraviolet spectra of the eluted fractions #2a, #2d, and #3 indicate that aquated complex was present in each. Each fraction gave a peak at or very near the peak wavelength of $\text{cis-}[\text{Co(en)}_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ in water at 310 millimicrons. $\text{Cis-}[\text{Co(en)}_2(\text{NCS})(\text{Cl})]\text{Cl}$ gives no distinct peak in the same region. The eluted fractions #2a and #3 must, therefore, be mixtures of the aquated and unaquated complex.

Michelfeld⁷ also observed the occurrence of aquation on an ion-exchange column. In the separation of cis- and $\text{trans-}[\text{Co(pn)}_2\text{Cl}_2]\text{Cl}$ by ion-exchange chromatography he found that no aquation occurred during continuous elution but did occur during the stationary period when elution was interrupted. In the work reported here, aquation

proceeded during both interrupted and uninterrupted periods of elution and it was not readily observable whether or not such aquation took place more rapidly during a stationary period.

It would be interesting to determine whether aquation occurs on ions adsorbed on the surface of resin particles as well as in solution. Such a determination could be made by mixing aqueous solutions of the compound with varying amounts of resin and ascertaining any rate dependence on the resin concentration. The rate of the reaction could be followed conveniently by changes in the ultraviolet spectra. Catalysis by ion exchangers is not at all uncommon, and Helfferich⁴² devotes a complete chapter to the subject in his book on ion exchange. Determination of the rate dependence on the resin concentration might help to elucidate the mechanism of aquation. Adsorption on the resin would naturally hinder access to certain sites on the complex ion.

When the second fraction, which has been identified as a mixture of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ and cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$, was evaporated over a hot plate, green crystals of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ were obtained. Evidently, the thermal energy supplied was sufficient to cause the thiocyanato ligand to be replaced by a chloro ligand in the 1 M HCl solution used as eluent forming cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ which then isomerized to the trans isomer which is the more stable form in acid solution.

Under conditions of room temperature evaporation, no crystals of dichloro or dithiocyanato complexes were obtained. This does not guarantee that these compounds were entirely absent from the product mixture. There is always the possibility that one or more of these

compounds could elute with one of the major fractions and be so soluble or in such low concentration as not to be detected. And #2b, which separated from #2a even during an uninterrupted elution, was never positively identified. Despite these possibilities, it is quite likely that any of the dichloro or dithiocyanato compounds, if present, were there only in very low concentration so that it may be cautiously concluded that an essentially 1:1 reaction took place between trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and thiocyanate ion.

In a typical product mixture, trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ was found to constitute 49 per cent of the products. The composition of the remainder of the product mixture is somewhat in doubt. The primary constituents have been shown to be cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ and cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ and, therefore, the total cis isomer content, both aquated and unaquated, may be estimated at near 50 mole per cent. The remaining constituents were present only in very small quantity and were not identified. They include the material in the first rapidly eluted band (probably a neutral compound), band #2b, the light-pink band remaining after elution of band #3 (probably the diaquated, tripositive ion), and the dark compound which adsorbs strongly to the resin at the top of the column.

It should be pointed out that the conclusions drawn above are valid, in the strictest sense, only for the reaction and separation carried out under the particular imposed conditions. Perhaps, for example, significantly different results would have been obtained had certain other eluting solutions been used. It is thought, however, that the results, for the most part, reflect accurately on the true

composition of the product mixture. Had aquation of the trans isomer taken place, the solution eluted between band #1 and band #2a would have been colored but it was completely colorless. Any equilibration of the cis and trans isomers would have resulted in a spreading and running together of bands #1 and #2a, but this was likewise not observed. Therefore, it is assumed that the mole per cent of this compound was not affected by the separation procedure. That only pure trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ was obtained from the eluted fraction shows ion-exchange chromatography to be a convenient method of isolating the pure trans isomer from the product mixture; it is quite soluble relative to the cis isomer and not readily isolated by evaporation of the mixture.

It was not possible to estimate the cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ concentration of the product mixture because of the readiness with which the compound aquates. It must be higher than would appear from the experimental results, however. The product mixture was diluted with water before being poured onto the column, and some aquation must certainly have occurred on the column before separation of the aquated and unaquated complexes causing the amount of aquated complex to appear erroneously high. Such complications could be avoided by finding a good eluting solvent in which aquation does not occur.

It would be risky to speculate on a mechanism for the reaction studied here on the basis of the experimental results. There are too many complicating factors. In aqueous solution the reaction may proceed through preliminary aquation and then isomerization of the

aquated complex before attack by thiocyanate. A number of exchange reactions proceed through these initial reactions including the isomerization of cis- $\text{Co(en)}_2\text{Cl}_2^+$ to the trans form.⁴³ If one or both of these preliminary reactions took place en route to the final product, then the data reported here would be of little use in suggesting a mechanism. Even if the reaction involved only the starting compound and thiocyanate little could be concluded without rate data and even then the problem is complicated. There are more sites for approach by a nucleophilic reagent in an octahedral system than in the simpler tetrahedral structure and retention and inversion of configuration can take place in both the SN-1 and SN-2 mechanisms with octahedral complexes. In order to avoid the problem of aquation discussed above, brown and Nyholm⁴⁴ studied the reaction between cis- $[\text{Co(en)}_2\text{Cl}_2]^+$ and thiocyanate in methanol solution. The results were found to be consistent with either an SN-1 or SN-2 mechanism.

There is one remaining point, concerning the interpretation of the infrared spectra, which deserves brief mention here. It was observed that an absorption peak appeared at 715 cm^{-1} in the spectrum of cis- $[\text{Co(en)}_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ which was not present in the spectrum of the unaquated compound (see figure 5). This peak may be due to vibration of the bond between cobalt and ligand water.

SUMMARY

The product mixture resulting from equimolar reaction of trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and thiocyanate was separated into its components on an ion-exchange column. The major components were then identified by means of infrared and ultraviolet spectroscopy. The product mixture was found to contain cis- and trans- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ and cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$. The trans compound was found to comprise 49 mole per cent of a typical product mixture, and since other products were present only in very small concentration, the combined cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]\text{Cl}$ and cis- $[\text{Co}(\text{en})_2(\text{NCS})(\text{H}_2\text{O})]\text{Cl}_2$ content was estimated at roughly 50 mole per cent.

The trans isomer was eluted first, the unaquated cis isomer second, and the aquated cis isomer third from the ion-exchange column. This is the order predicted on the basis of relative charge and dipole moment. Aquation of cis- $[\text{Co}(\text{en})_2(\text{NCS})\text{Cl}]^+$ was observed to occur on the column as well as in the eluted solution. In addition, rechlorination of the aquated compound was found to occur in the eluted fractions so that, after elution, the second and third fractions were mixtures of the aquated and unaquated cis complexes.

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