# The Preparation And Determination Of Some Of The Properties Of The Dicarboxylic Amino Acid Chelates Of Platinum(Ii) And Palladium(Ii)

Gordon Harold Williams
*University of the Pacific*

THE PREPARATION AND DETERMINATION OF SOME OF THE

PROPERTIES OF THE DICARBOXYLIC AMINO ACID CHELATES

OF PLATINUM (II) AND PALLADIUM (II)

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Gordon Harold Williams

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*Gordon Harold Williams*,

is approved for recommendation to the
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Department Chairman or Dean:

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Dissertation Committee:

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## ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Coordination compounds each consist of a central atom closely surrounded by a number of other atoms or molecules that have the property of high electron density as contrasted with the central atom which has a low electron density. The central atom is generally a metallic ion, although in a number of coordination compounds, the central atom is a neutral metal atom, and the surrounding species, called ligands, are atoms, ions, or molecules. A coordination compound is distinguished from any other type of chemical compound by the fact that both the central atom and the ligands are capable of independent existence as stable chemical species.

The ligand is always an "electron rich" species and usually contains oxygen, nitrogen, or sulfur atoms. Because of its property of electron richness the ligand is often referred to as an "electron donor". Attempts have been made to explain some of the properties of coordination compounds as the product of a Lewis acid-base type of reaction in which the ligand is the base and the metal is the acid. (10, 25) The words "electron donor" should not be taken in a literal sense since it is not entirely clear as to whether the ligand-metal bond involves the sharing of electrons,

the transfer of electrons, or just a coulombic attraction between the two species.

When the ligand consists of two or more donor groups on the same molecule, the ligand is called a chelating agent. (The name chelate was taken from the Greek word chela and was first applied by Morgan and Drew in 1920.) (16) The coordination compound formed between a chelating agent and a metal is often called a chelate compound or simply a chelate.

Historically, the first chelate compounds to be studied were those made with the chelating agent 1,2-diaminoethane (ethylenediamine). The synthesis of these ethylenediamine compounds was an outgrowth of the studies of ammine complexes. By making various diamino compounds and reacting them with various metals, Werner was able to disprove the linear structure of the ammine coordination compounds that had been proposed by Jorgensen. (28)

Shortly after Werner made the first ethylenediamine compounds it was discovered that glycine had the properties of a chelate. Curtius, in 1890, had reported that the newly isolated amino acid, glycine, would react with copper. (6) Ley, studying the glycine complexes of copper, chromium and platinum fifteen years later was the first to recognize the special significance of the cyclic structure of these chelate compounds. (11) Ley's work can be said to have

begun metal-amino acid chemistry because he showed that the metal-glycine compounds were electrically neutral, did not add ammonia, and were not addition products.

By 1952, Martell and Calvin had listed ninety-nine compounds formed between metals and natural occurring amino acids. (14)  Of these ninety-nine compounds, fifteen contained either aspartic or glutamic acids, the only natural occurring dicarboxylic amino acids.[1]  Since that time additional chelates of aspartic and glutamic acids have been synthesized and studied by Sabine, Nyberg, and Cefola, (22) by Anokhava and Volshtein, (2) and by Spacu and Scherzer. (23)

The dicarboxylic amino acid chelating agents, such as aspartic and glutamic acid, can behave as either bidentate or terdentate chelating agents since both carboxyl groups and the amine group can act as ligands.  When a metal that always forms tetra-coordinate compounds combines with two dicarboxylic amino acids there must be two uncomplexed ligands if the compound is to contain only one metal atom per molecule.  With transition group metals the nitrogen forms a stronger bond than does the oxygen atom.  Thus it appears that such a compound should be expected to contain

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[1]This is not quite true since alpha-amino adipic and amino pimelic acids have both been recently identified in connection with root growth of plants.

two uncomplexed carboxyl groups.  The question was asked,
"Do these carboxyl groups remain uncomplexed or do they com-
plex onto another metal?"

It is surprising that no one has considered that
coordination might have some effect on the strength of the
acid group.  It is the intent of this study to fill this gap
in the knowledge of amino-acid chemistry.

At about the time study began on the effect of chela-
tion on the strength of the uncomplexed acid group, the next
two higher homologs of these dicarboxylic amino acids became
commercially available.  It was, therefore, decided that the
problem of this research should be expanded to include all
four of the acidic amino acids.

The research problem was also defined to include the
systematic synthesis of the platinum and palladium (II)
complexes of the four available alpha amino dicarboxylic
acids,

$$O = \overset{|}{\underset{OH}{C}} - (CH_2)_n - \overset{|}{\underset{NH_2}{CH}} - \overset{|}{\underset{OH}{C}} = O \quad \text{where n equals 1, 2, 3, or 4.}$$
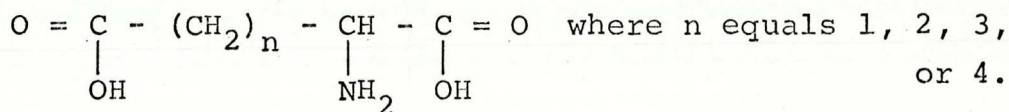
Platinum and palladium were chosen since in the +2 oxidation
state they were known to form only square planar compounds.

While carrying on systematic synthesis of these com-
pounds and measuring the strength of the acids of these

resulting compounds, their respective stability constants would be determined where possible.

# CHAPTER II

## PREPARATION OF COMPOUNDS

The first report of the synthesis of a platinum metal-dicarboxylic amino acid compound was made by Grinberg and Kats in 1955. (9)  They reacted 700 mg. of glutamic acid (4.84 millimoles) with 500 mg. of $K_2PtCl_4$ (1.21 millimoles) in 10 milliliters of water by heating it on a steam bath for 45 minutes.  They reacted aspartic acid with platinum with the same four-to-one mole ratio in the same manner and reported a 20% yield.  No data was reported on the yield of the glutamic acid compound.

Four years later Volshtein and Anokhova reported on their studies of the platinum aspartic acid reaction. (26)  Using the same four-to-one mole ratio they reported synthesizing the trans isomer.  They also reported obtaining the cis form by first reacting $K_2PtCl_4$ with aspargine to form the bisasparginato platinum (II).  The resulting compound was saponified and then acidified to get the cis bisaspartato platinum (II) compound.  No yield data was reported. Later they reported obtaining both the cis and trans isomers in a ratio of three to four. (2)  It was not reported in Chemical Abstracts how these compounds were separated or identified.

In 1962 the palladium glutamic acid complex was first reported. At that time Spacu and Scherzer reported the synthesis using the same four-to-one mole ratio of reactants, although they started with a much more dilute solution. (23) While Grinberg and Kats had used only 10 milliliters of water to 4.84 millimoles of glutamic acid, Spacu and Scherzer had used 250 milliliters of water to 4.00 millimoles of glutamic acid. After several hours the solution was evaporated down to give a concentrated solution with a volume of about 10 milliliters. This same method was used by Luschack in 1963 in the synthesis of both the glutamic and aspartic acid complexes of palladium and platinum. (13)

Other aspartic and glutamic acid complexes have been made in various ways but the compounds were never recovered from the solution in which they were made. Lumb and Martell mixed the solution in a two-to-one mole ratio and then titrated directly in order to obtain a stability constant (See Chapt. V for a critical discussion of their method). (12) Cefola and co-workers developed two interesting methods of synthesis. (2,22) The first method, by which they were able to make the alkaline earth amino acid chelates, reacted the acid directly with the carbonate of the metal of interest. By adding stoichiometric amounts of the reactants to water and boiling to expel the carbon dioxide they

assumed they had the compound they wanted. Their second method, which they used whenever the pure carbonate was not available, reacted the barium amino acid compound with the appropriate metal sulfate. The solid barium sulfate formed would be filtered off leaving the metal chelate in solution. In this manner they assumed that they had made the glutamic acid complexes of manganese (II), iron (II), cobalt (II), copper (II), and zinc (II). They did not separate their compounds from solution, but titrated directly in order to obtain a stability constant.

In all of these studies there has been no data reporting any systematic research to determine the optimum conditions under which these compounds can be prepared. In this study three variables were investigated; these were initial pH of the solution, ratio of the reactants, and initial concentration of the reactants.

Aspartic acid was chosen as the amino acid to study in detail because it formed the most soluble compounds and was the most plentiful acid available. The other acids should form compounds that are similar enough in structure not to differ greatly from those found to be optimal for aspartic acid.

From the following equilibrium involving aspartic acid as an example, it would appear that the hydrogen ion concentration could have some effect on the reaction:

$$2 \ H_2C_4H_5O_4N + PdCl_4^{--} = Pd(HC_4H_5O_4N)_2 + 2H^+ + 4Cl^-$$
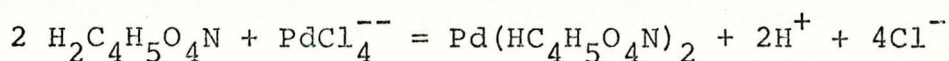
In order to determine the effect of pH on the yield in this reaction one millimole of aspartic acid was mixed into 100 milliliters of water and the pH adjusted with KOH of HCl and then 0.5 millimoles of the palladium compound were added. The solution was evaporated down to about 10 ml. and cooled. The crystals were collected, dried with ether and weighed.

When the pH was below 3 the amount of elemental palladium or platinum formed increased markedly and when the pH was above 8 the metal hydroxide formed in preference to the complex. At pH's of 6 and 7 essentially no compound was formed and no other compound was recovered. It appears as if some other compound must have been formed that was not recovered. Future studies might prove interesting in investigating this observation.

At all pH's the alpha amino adipic acid acted as a better reducing agent than any other amino acid and more metallic platinum and palladium were formed than with any other acids. There is no ready explanation for this observed fact.

The second variable investigated was the effect of differing ratios of reactants on the percent of compound formed. The mass action law would lead one to expect a

## TABLE I

EFFECT OF pH ON THE FORMATION OF Pd(HAsp)$_2$

| Initial pH | Final pH | % recovered |
|---|---|---|
| 3.0 | 2.5 | 39.8% |
| 4.0 | 2.8 | 38.7 |
| 5.0 | 3.8 | 28.7 |
| 6.0 | 4.3 | 0.0 |
| 7.0 | 5.1 | 0.0 |

greater yield if one or the other of the reactants were used
in greater than stoichoimetric amounts. Since the amino
acid is used in twice the amount of the metal, simple equi-
librium considerations would suggest that the amino acid
concentration would have more effect on the equilibrium than
would the metal concentration. Therefore, in this study,
mole ratios of one to one, two to one, three to one, four
to one and five to one were tried. The initial $PdCl_4^{--}$ con-
centration was 0.005 M in each case. Since the pH of aspar-
tic acid solutions are around three, no pH control was main-
tained.

When the mole ratio of reactants was one to one no
product was formed at all. In all the other cases the yield
was nearly forty percent, increasing slightly with an in-
crease in amino acid concentration. This indicates that
some other reaction is also taking place. This side reac-
tion was not investigated since it was outside the scope of
this project, although it will be mentioned again in Chap-
ter III.

Because of the cost of the reagents and the fact that
the amino acid is used in amounts twice as large as the
metal a two to one mole ratio of amino acid to metal was
used in the succeeding studies. The data obtained from
this part of the problem are summarized in Table II.

## TABLE II

EFFECT OF RATIO OF REACTANTS ON THE FORMATION OF Pd(HAsp)$_2$

| Mole ratio H$_2$Asp to Pd | Percent Pd(HAsp)$_2$ recovered |
|---|---|
| 1:1 | 0.0% |
| 2:1 | 39.2 |
| 3:1 | 41.4 |
| 4:1 | 43.7 |
| 5:1 | 43.6 |

The initial concentration of the reactants and their effect on the yield were also studied. A high initial concentration always led to formation of a large amount of metal. This is undoubtedly why previous investigators usually started with dilute solution and then concentrated them.

Starting with a 0.020 M solution of $PdCl_4^{--}$ and a 0.040 M solution of aspartic acid for the first or most concentrated reaction and then going to solutions four times and sixteen times more dilute for succeeding tries, it was found that the yield did not increase appreciably over the 0.005 M solution. Since the volumes involved were so large for the very dilute solutions all future reactions were performed with a 0.005 M solution of metal in the solution.

The method used in the preparation of the compounds used in the further studies in this project was to add 1.25 millimoles of $K_2PdCl_4$ or $K_2PtCl_4$ to a solution made by dissolving 2.50 millimoles of amino acid in 250 ml. of water. The solution was refluxed until almost colorless (20 to 30 hours) and then the volume was reduced to about 25 milliliters by evaporation. This concentrated solution was left in a covered beaker to crystallize (one to three days). The crystals were collected on a filter, washed with a few milliliters of hot water, followed by a rinse with ethanol and then dried with a rinse with ether. The product

was not recrystallized since it was found that there was no change in the infrared spectra.

The solubilities of the various compounds were measured in water by making a saturated solution and measuring out a volume of the solution and evaporating it to dryness on a weighed watchglass. The solubility data and the best results are summarized in Table III.

Observations made during these reactions showed no observable change in pH after the first few minutes of the reaction and no change in the absorption spectra in the ultra-violet and visible region. These observations and the conclusions that might be drawn from them are discussed in Chapter III.

If the solubility data from Table III is combined with the weight of the palladium formed and applied to the percent yield, a rough calculation of percent conversion can be made. These are shown in Table IV as having a range of 38% to 67%. The remaining material must be either unreacted compounds or the products due to some other side reaction.

Palladium and platinum (II) ions always form complexes with a square planar configuration, making two geometric isomers possible. The trans isomer which is the more symmetrical has the two like atoms opposite each other across the metal ion, while the cis isomer, the less symmetrical isomer, has two unlike atoms opposite each other across the metal

## TABLE III

### SOLUBILITIES AND BEST YIELDS

| Compound | Yield | Solubility | Mg. Pd formed |
|---|---|---|---|
| $Pd(HC_4H_5O_4)_2$ | 43.6% | 0.016M | 0.0 mg |
| $Pd(HC_5H_7O_4)_2$ | 46.5% | 0.0074 | 0.0 mg |
| $Pd(HC_6H_9O_4)_2$ | 22.9% | 0.0034 | 11.8 mg |
| $Pd(HC_7H_{11}O_4)_2$ | 49.5% | 0.0019 | 2.0 mg |

## TABLE IV

### PERCENT CONVERSION

| Compound | Millimoles obtained | Millimoles in solution | Palladium recovered | % conversion |
|---|---|---|---|---|
| $Pd(HC_4H_5O_4)_2$ | 0.44 | 0.40 | 0.00 | 67% |
| $Pd(HC_5H_7O_4)_2$ | 0.58 | 0.18 | 0.00 | 61% |
| $Pd(HC_6H_9O_4)_2$ | 0.29 | 0.08 | 0.11 | 38% |
| $Pd(HC_7H_{11}O_4)_2$ | 0.62 | 0.05 | 0.02 | 55% |

ion, or, looking at it another way, has the same kind of atoms adjacent. This can be seen more clearly in the following diagram:

O≡C—O    N—C—
      |        |
      |   M    |
      |  /     |
—C—N    O—C≡O

trans

O≡C—O    O—C≡O
      |        |
      |   M    |
      |  /     |
—C—N    N—C—

cis
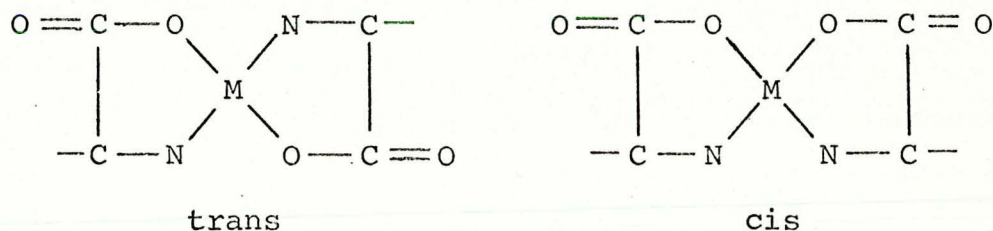
In their study of other amino acid chelates with palladium (II) and platinum (II) Pinkard, et al determined that the cis structure always crystallized first in the form of needles and that the supernatant liquid slowly formed a second crop of crystals which were less soluble, were in the form of plates, and were of the trans configuration. (21) The photomicrographs included in Appendix C show all of the compounds synthesized in this study to be in the form of plates. Modern X-ray methods could determine this aspect of the structure of these compounds very nicely and would make a good auxiliary study related to this investigation.

# CHAPTER III

## PROOF OF STRUCTURE

Dicarboxylic amino acids acting as triprotic acids would have the strongest acid, the carboxyl group, proximal to the amino group. The group of intermediate strength is the carboxyl group distal to the amino group and the group showing the weakest acid is the quaternary amine group.

As a neutral molecule the amino acid exists as a zwitter ion. When the zwitter ion reacts with a metal, there are two possible kinds of reactions. If an ionic compound were made, one would expect the hydrogen ion on the distal carboxyl group to be removed and the zwitter ion character on the other end of the molecule to remain unchanged. This is undoubtably the first step in the reaction between an amino acid and a carbonate mentioned in the last chapter. On the other hand, if a chelate compound were formed, one would expect the hydrogen ion attached to the quaternary amine to be lost so that chelation could form between the metal and both the proximal carboxyl group and the amine group.

By the reasoning that follows and the accompanying data, it is proposed that each of the eight compounds that has been prepared is the bis amino acid metal (II) compound with square planar structure. Probably the amino acids lie

in a trans configuration around the metal and can be repre-
sented structurally by the following formula:

$$HOOC-(CH_2)_n-CH-NH_2 \qquad O-C=O$$

$$O=C-O \qquad \diagdown M \diagup \qquad NH_2-CH-(CH_2)_n-COOH$$

where M is either Pt(II) or Pd(II) and n = 1,2,3, or 4 for
aspartic acid, glutamic acid, alpha amino adipic acid (2
amino hexandioic acid), and alpha amino pimelic (2 amino
heptandioic acid) respectively.

## I.   CARBON - HYDROGEN ANALYSES

Since the compounds all contained organic ligands,
the samples were analyzed for carbon and hydrogen.[1]   Tables
V and VI show the results obtained and the theoretical val-
ues that were expected from the above assumption concerning
the formula of the compounds.   In each of the palladium com-
pounds shown in Table V it can be seen that the measured
results show slightly higher percentages in hydrogen and
slightly lower percentages in carbon than would be expected
when compared to the theoretical values.   This seems to im-
ply that there is some other hydrogen-containing ligand or

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[1]Analyses were made by West Coast Analytical Labora-
tories, Inc., El Cerrito, Calif.   (No longer in business)

contaminant.   The most logical substance appears to be water.
However, if water is to be a ligand in a square planar com-
plex, then either one or both amino acid ligands must not
be acting as a chelate.   Tables V and VI also show the
theoretical percentages of carbon and hydrogen that would
be expected with two amino acids and one water molecule
attached in the coordination compound.   Comparison of these
calculations with the actual analyses show that the carbon
content is now high and the amount of hydrogen is low.

If the analysis either of the carbon or of the hydro-
gen is taken as correct the amount of water necessary to
give this value can be calculated.   These calculations show
that there must be some variable amount of water adsorbed on
the compound.   More value is placed on the calculations
based on the carbon analyses than those based on the hydrogen
because the greater accuracy of the carbon analyses.   These
compounds may have adsorbed water prior to analysis although
they had been stored in a desiccator over calcium chloride
after being prepared and were shipped in closed containers.

The platinum compounds did not show as close an agree-
ment, as can be seen in Table VI, so no additional work was
done toward calculating the amount of moisture that may have
been adsorbed on these compounds.

TABLE V

CARBON-HYDROGEN ANALYSES
PALLADIUM COMPOUNDS

|  | Amino acid | | | |
|  | Aspartic | Glutamic | a-amino adipic | a-amino pimelic |
| --- | --- | --- | --- | --- |
| Reported | | | | |
| carbon | 25.7 % | 29.7 % | 33.1 % | 36.9 % |
| hydrogen | 3.53% | 4.37% | 4.98% | 5.46% |
| Theoretical: (anhydrous) carbon-hydrogen | | | | |
| count | $C_8H_{12}$ | $C_{10}H_{16}$ | $C_{12}H_{20}$ | $C_{14}H_{24}$ |
| percent carbon | 26.0 % | 30.1 % | 33.8 % | 37.0 % |
| percent hydrogen | 3.24% | 4.02% | 4.69% | 5.28% |
| Theoretical (as mono hydrate) | | | | |
| percent carbon | 24.7 % | 28.9 % | 32.4 % | 37.0 % |
| percent hydrogen | 3.51% | 4.34% | 4.95% | 5.52% |
| Water per mole of metal based on the reported values of | | | | |
| carbon | .22 | .37 | .54 | .05 |
| hydrogen | 1.11 | 1.15 | 1.13 | .73 |

TABLE VI

CARBON-HYDROGEN ANALYSES
PLATINUM COMPOUNDS

| | Amino acid | | | |
| | Aspartic | Glutamic | a-amino adipic | a-amino pimelic |
|---|---|---|---|---|
| Reported | | | | |
| Carbon | 20.6 % | 25.2 % | 28.8 % | 30.9 % |
| Hydrogen | 2.53% | 3.17% | 4.01% | 4.29% |
| Theoretical (anhydrous) | | | | |
| Carbon | 21.0 % | 24.7 % | 28.2 % | 31.2 % |
| Hydrogen | 2.61% | 3.28% | 3.92% | 4.44% |
| (as monohydrate) | | | | |
| Carbon | 20.3 % | 25.4 % | 27.2 % | 30.2 % |
| Hydrogen | 2.95% | 3.60% | 4.16% | 4.67% |

Overall, it is felt that the agreement from the carbon-hydrogen analyses are close enough to justify the empirical formula that has been proposed.

## II.  ULTRAVIOLET - VISIBLE SPECTRA

Spectra of each compound were taken from their aqueour solutions using either a Beckman Model DB or Coleman-Hitachi Model 124 spectrophotometer and it was found that all of the palladium compounds showed an absorption peak in the 318 to 320 millimicron region.  This absorption does not occur with either pure amino acid solutions or with the chloro complexes.  It is typical of many coordination compounds, however, and has been explained both by ligand field theory and by molecular orbital theory.

While neither theory has been refined enough to treat square planar complexes mathematically when the coordinating groups are not the same, it can be explained qualitatively. The absorption occurs as a result of electron excitation from the non-bonding orbitals to the anti-bonding orbitals.

The observed energy transition level at 320 millimicrons is 31,000 $cm^{-1}$ or about 3.9 electron volts.  This is a typical value for many coordination compounds and would not have been observed if the compounds had been ionic.  In such a case the palladium would have existed as an aquo

complex and the absorption would have been at about 420
millimicrons.

The platinum compounds did not show this character-
istic absorption in this region. They did not start to ab-
sorb light until near the limit of the intrument, i.e., 200
millimicrons, so it could not be determined whether there
was a peak or not.

The spectrum for palladium aspartate is shown in
Figure 1. The spectra for the remaining palladium compounds
and for a typical platinum compound are included in Appen-
dix A.

### III. INFRARED SPECTRA

Infrared spectral data also are in agreement with
the other data that the compounds are true coordination com-
pounds and not salts. Infrared spectra were obtained for
all eight of the compounds synthesized and for the four
amino acids by using the potassium bromide disc method.
Discs, made containing about one percent of the compound in
analytical grade potassium bromide, were analyzed using a
Perkin-Elmer Model 137B infrared spectrophotometer.

In 1960 Takenishi identified the infrared spectra for
both aspartic and glutamic acids by using both deuterated
amino acids and isotopically labeled nitrogen. (24) These
two amino acids showed absorption peaks at 1500 $cm^{-1}$,
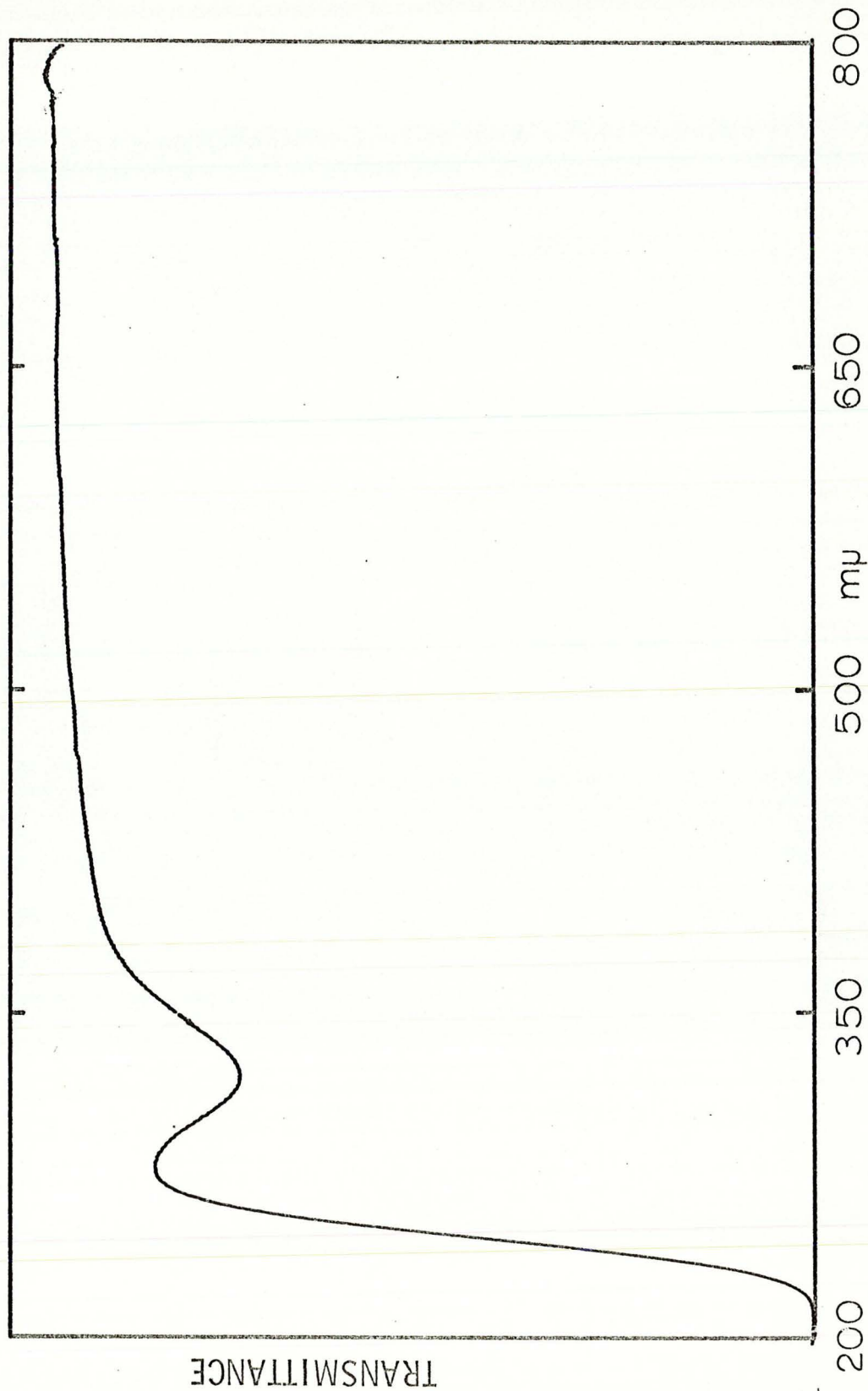
Bis hydrogen aspartato palladium (II)

FIGURE 1

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1150 cm$^{-1}$, and 1120 cm$^{-1}$. This research shows that the two higher homologs also have absorption peaks at these frequencies. These peaks were identified by Takenishi as being caused by the various vibrations of the quaternary nitrogen. The absorption band at 1500 cm$^{-1}$ has been identified in many amino acids as the symmetrical deformation of the quaternary amine which exists in the zwitter ion.

The spectra of all of the various coordination compounds were notable in their lack of an absorption peak at 1500 cm$^{-1}$. This corroborates in part the work done by Nakagawa, et al in 1965. (18)  Their studies were concerned with the valine compounds of platinum, palladium, and other metals.  In particular they identified the symmetrical deformation vibration at 1500 cm$^{-1}$ as being converted to an NH$_2$ scissors vibration and shifted to 1610 cm$^{-1}$ for platinum and to 1630 cm$^{-1}$ for palladium.

This same shifting, although to slightly higher wave numbers, was observed in each of the compounds made in this study.  This fact provides additional proof that these compounds are truly coordination compounds and not ionic salts.

The infrared spectra for aspartic acid and for palladium aspartate are shown in figures 2 and 3 respectively as being representative of the collected spectra.  The remaining spectra are collected in Appendix B.
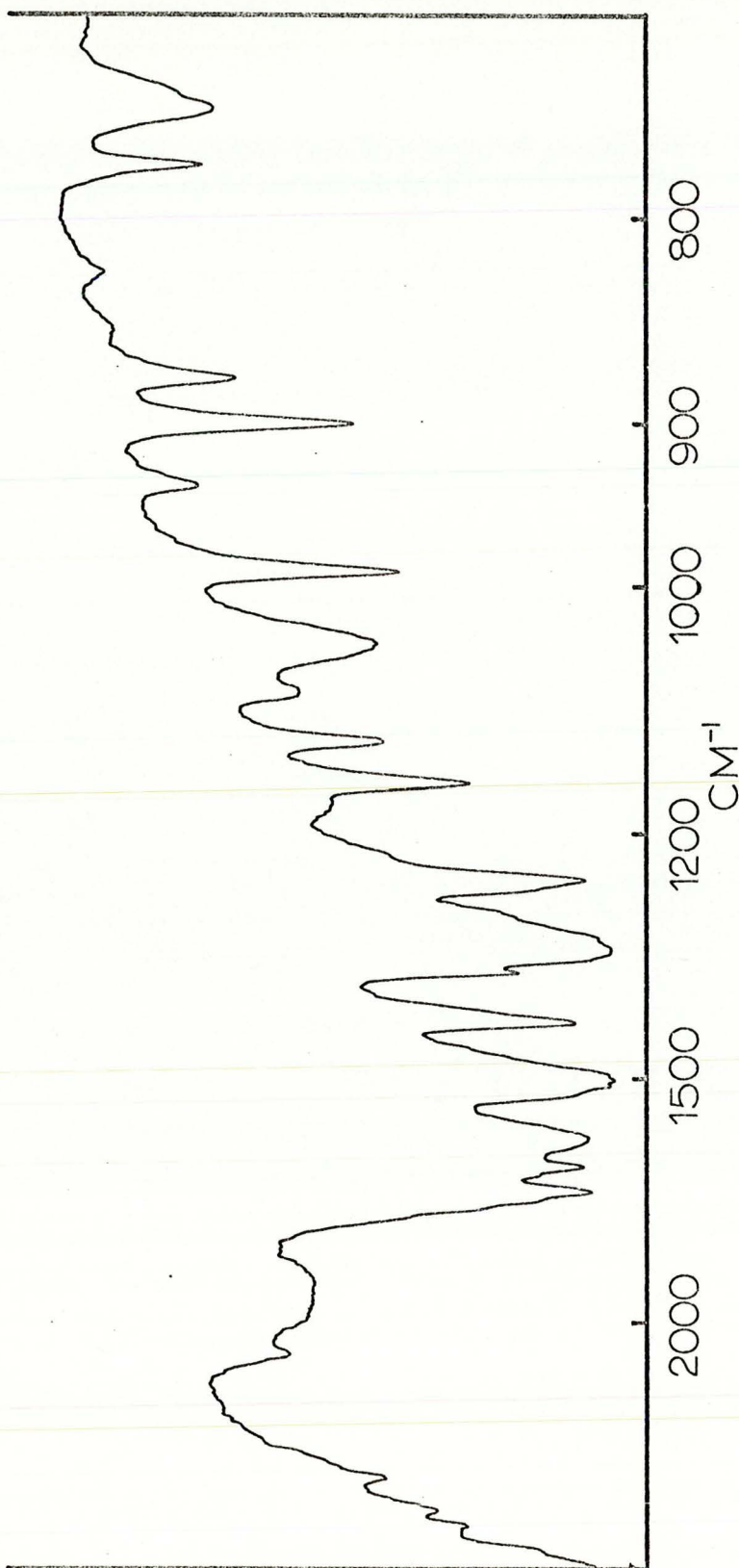
Aspartic acid

FIGURE 2
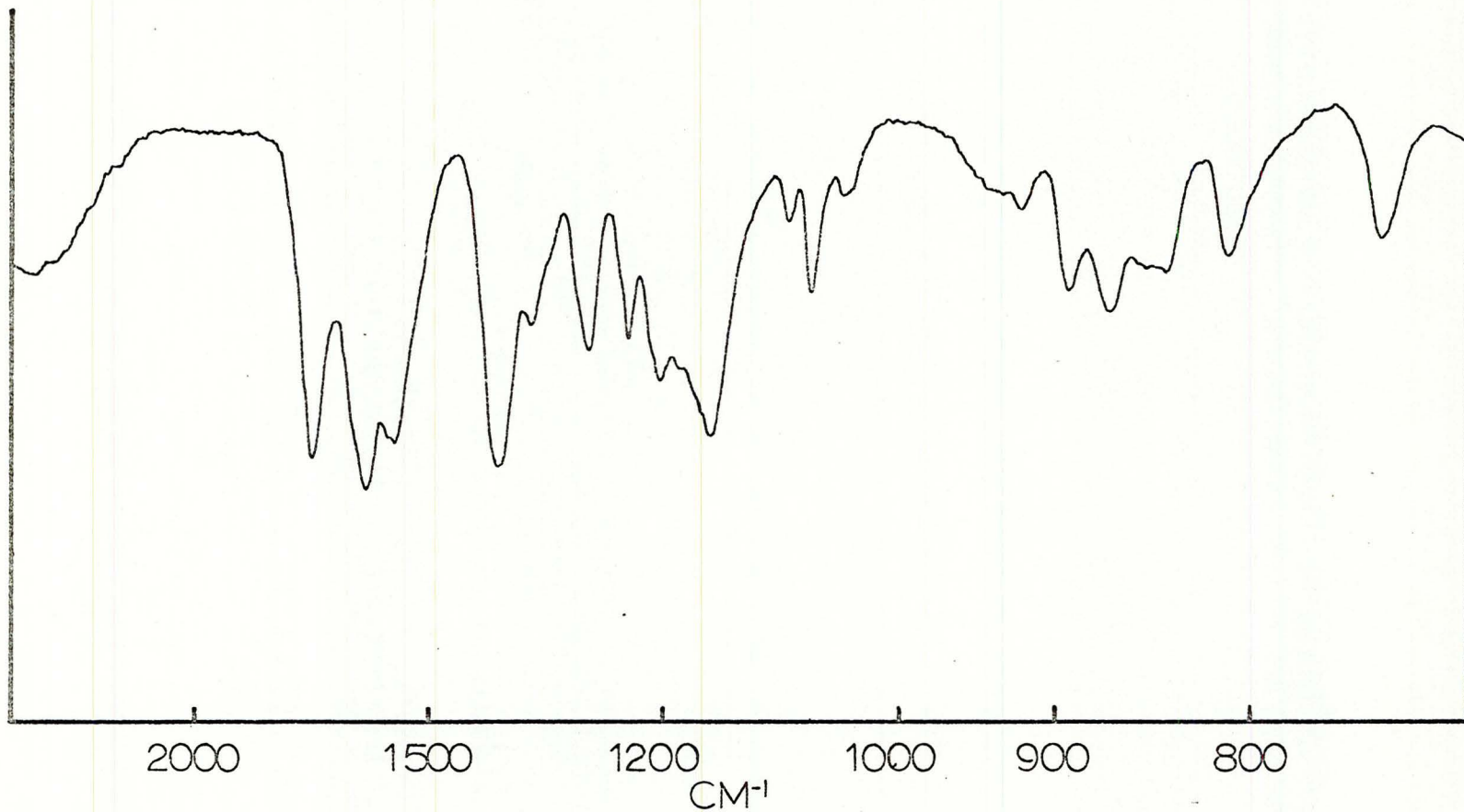
Bis hydrogen aspartato palladium (II)

FIGURE 3

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## IV.  CHANGES IN ACID STRENGTH

Amino acids such as aspartic and glutamic acids and
their higher homologs have three replaceable hydrogen ions.
The carboxyl group adjacent or proximal to an amino group
has a pK of about 2.0 to 2.5, the carboxyl group at the
other end of the molecule has a pK of about 3.75 to 4.75,
and the quaternary amine has a pK in the neighborhood of 9.5
to 10.0.  If it is assumed that the first ionization has
taken place in the neutral, or zwitter ion, form of the
molecule, the easiest hydrogen to replace would be the car-
boxyl group at the end farthest from the amine group.  When
a salt such as monosodium glutamate is formed, it is this
hydrogen ion that is lost.  Titration of monosodium gluta-
mate shows that the pK of the remaining acid group is in
the neighborhood of 10.  As is explained more fully in Chap-
ter IV, the strengths of all of these newly synthesized com-
pounds had pK's which were in the neighborhood of 5.

## V.  CRYSTAL STRUCTURE

If these compounds are similar to those that Pinkard,
et al synthesized in 1934, it would appear that the cis iso-
mer forms rapidly, is much more soluble, and that it slowly
converts to the less soluble trans isomer. (21)  In their
studies of the glycines of platinum and palladium, Pinkard,
et al found that the cis form crystalized into the form of

needles or prisms, while the trans form always crystalized into the form of platelets. Photomicrographs in Appendix C show that each of the eight compounds made in this study also crystalized into platelets.

This same type of data was found by Volshtein and Velikanova in their studies with platinum and alpha amino butyric acid. (27) They reported that the cis isomer was about fifty times more soluble in water than was the trans form.

Additional work could develop a method of obtaining a compound in the early stages of the synthesis to see if a compound with a different crystal structure was obtained.

With these assumptions and their conclusions, the eight compounds made and studied can now be named systematically. The names proposed are as follows:

1. Trans bis hydrogen aspartato palladium (II)

2. Trans bis hydrogen aspartato platinum (II)

3. Trans bis hydrogen glutamato palladium (II)

4. Trans bis hydrogen glutamato platinum (II)

5. Trans bis hydrogen alpha amino adipato palladium (II)

6. Trans bis hydrogen alpha amino adipato platinum (II)

7. Trans bis hydrogen alpha amino pimelato palladium (II)

8. Trans bis hydrogen alpha amino pimelato platinum (II)

# CHAPTER IV

## DETERMINATION OF ACID STRENGTH

The primary problem of this research project was to investigate the effect chelation had on the strength of the uncomplexed carboxyl group remaining when a homologous series of acidic amino acids were complexed with palladium or with platinum. In order to compare the strength of the complexed acids with the uncomplexed acids it is, of course, necessary to know the strength of the uncomplexed acids. Only aspartic and glutamic acids had had any reported values and it was not always possible to determine the condition under which they were measured. The reported values are shown in Table VII.

Because of this lack of data for the higher molecular weight acids and for the sake of consistency, it was decided that the ionization constants for the amino acids should be determined in the same manner as the ionization constants of each of the complexes. In a typical amino acid of this type the strongest acid group is already ionized due to the formation of the zwitter ion. The general structure appears as follows:

$$HOOC - (CH_2)_n - CH - COO^-$$
$$| \atop NH_3^+$$
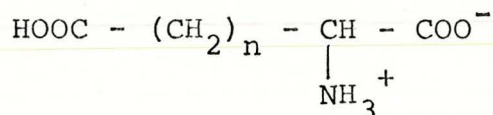
TABLE VII

REPORTED VALUES OF SECOND AND THIRD IONIZATION
CONSTANTS FOR ASPARTIC AND GLUMATIC ACIDS

| Acid | | $pK_2$ | $pK_3$ | reference |
|------|------|------|------|------|
| Aspartic acid | | 3.65 | 9.60 | 5 |
| | | 3.87 | 9.85 | 7 |
| | | 3.65 | 9.63 | 15 |
| | | 3.86 | 9.82 | 8 |
| | | 3.90 | 9.84 | 3 |
| | | 3.78 | 9.56 | 20 |
| | Average | 3.77 | 9.70 | |
| Glutamic acid | | 4.25 | 9.67 | 17 |
| | | 4.32 | 9.60 | 15 |
| | | 4.21 | 9.54 | 20 |
| | Average | 4.26 | 9.60 | |

The strength of the quaternary amine was determined since it involved very little additional effort. This was done by continuing the titration until a second equivalent of base had been added. The strengths of these two acid groups were determined over the range of temperatures from 10°C to 70°C.

The method used for the determination of the ionizations was the potentiometric method of Albert and Serjeant. (1) This method consisted of determining the pH at eight points between the start of titration and the first equivalence point and at eight equivalent points between the first end point and the second end point.

The titrations were all carried out using carbonate-free potassium hydroxide because it causes less electrode error in the alkaline solutions. Although carbonate-free potassium hydroxide is harder to make than carbonate-free sodium hydroxide, its preparation is entirely straight forward and was completed as follows.

The potassium hydroxide was made up to a stronger concentration than would be finally used. Barium hydroxide was added to the solution to react with any carbonate present. The barium carbonate that formed was allowed to settle over night in an inverted Erlenmyer flask. The resulting solution of potassium and barium hydroxides was withdrawn

without disturbing the precipitate through a potassium loaded cation exchange resin into a polyethylene container that had been flushed of any carbon dioxide with nitrogen. The prepared potassium hydroxide was stored in this container until used. The container was fitted with a soda-lime vent tube to prevent contamination with carbon dioxide. The concentration of the potassium hydroxide was determined and the solution was diluted to a concentration of about 0.05 M by adding boiled water. The concentration of this diluted base was then determined potentiometrically against potassium hydrogen phthalate.

All titrations were carried out under temperatures that were controlled to 0.5° in a nitrogen atmosphere. Approximately fifty milliliters of acid solution would be accurately measured into a 400 ml. beaker and covered by inserting a styrofoam cup into the beaker without touching the solution. The styrofoam cup had four holes drilled into the bottom. A center hole was used by the stirring mechanism and three peripheral holes were used by a Thomas combination electrode, the nitrogen inlet tube, and the buret tip, respectively.

Water-pumped nitrogen was used as an inert atmosphere after it had been further purified to remove both oxygen and carbon-dioxide. The tank nitrogen was bubbled

first through a chromium (II) sulfate solution and second
through a sodium hydroxide solution.

The actual titration would be carried out by adding
a small volume of the base to the acid solution noting the
pH on a Beckman Model G pH meter. After an interval of
about one minute the pH would again be noted, and if there
was less than 0.02 pH units of change, the pH would be re-
corded versus the volume of base added. If the pH reading
had changed, then another reading would be taken about a
minute later. This would be repeated until stability was
shown on the pH meter. (Seldom was more than a second
reading required, and never more than a third.) Additional
base would then be added and the operation repeated. By
this method twenty-five to forty readings would be taken
during a single titration.

The data obtained would then be graphed and the pH-
volume data would be extracted at points equivalent to each
five percent of neutralization. The first, tenth, nineteenth
and twentieth points would be discarded. The remaining six-
teen pertinent points were used to calculate eight pairs of
values for the first and second ionization constants. (Sec-
ond and third ionization constants in the case of the amino
acids.)

The acid constants were calculated by the method of Noyes as reported by Albert and Serjeant. (1)  This method averages the salt against the acid and gives reliable results even though the two pK values are separated by less than one unit.  When the pK values are farther apart than 2.7 units there is no need to treat the two ionizations simultaneously, although the method works just as well.

For the calculations used, let:

C = the total concentration (all species)
    of the acid being titrated.

B = the concentration of alkali added
    (assuming no reaction).

Then:

$$X = [H^+](B - C + [H^+])$$

$$Y = 2C - (B + [H^+])$$

$$Z = [H^+]^2(B + [H^+])$$

$X_1$, $Y_1$, and $Z_1$ will refer to readings obtained with less than one equivalent of base and $X_2$, $Y_2$, and $Z_2$ will refer to readings obtained with more than one equivalent of base added to the acid being titrated.

Then:

$$K_1 = \frac{Y_1 Z_2 - Y_2 Z_1}{X_1 Y_2 - X_2 Y_1} \quad \text{and} \quad K_2 = \frac{X_1 Z_2 - X_2 Z_1}{Y_1 Z_2 - Y_2 Z_1} \;.$$

Pairs of readings are selected from either side of the mid-point in symmetrical fashion.  This method involves

a good deal of calculations, but it is entirely straight-
forward. In order to avoid the necessity of making these
many repetitive calculations it was decided to make use of
a digital computer. No program was available for these
calculations so a program in the Fortran language was writ-
ten to utilize the IBM 1620 computer. This program, along
with the output data is included in Appendix D.

Calculations of this type will give a mixed constant
rather than a thermodynamic constant since no activity co-
efficients were used. The hydrogen ion concentration is
expressed in activity rather than in concentration units,
but all other species are expressed in molarity, hence the
use of the term "mixed constant". This constant should be
close to the thermodynamic ionization constant since all of
the concentrations are less than 0.01 Molar and the pH
measurements are accurate only to 0.02 pH units. The pK's
that were determined are reported only to two places to the
right of the decimal point although the program is written
for the computer to list four places. Data for aspartic
acid at 25°C are shown in Figure 4 as raw data, in Figure 5
in titration graph form, and in Figure 6 as computer input
and output form.

As mentioned previously only the second and third
constants for the ionization of the acid were calculated

and these are collected in Table VIII.  The data is collected in Appendix D.

From Table VIII two facts become evident.  First, the ionization constant of the carboxyl group is nearly independent of temperature, and second, the ionization of the quaternary amine changes by at least an order of magnitude between the two extremes of temperature.

| Buret reading | pH |
|---|---|
| 0.00 | 3.05 |
| 0.50 | 3.22 |
| 1.00 | 3.38 |
| 1.5o | 3.55 |
| 2.00 | 3.73 |
| 2.50 | 3.92 |
| 3.00 | 4.09 |
| 3.50 | 4.34 |
| 4.00 | 4.70 |
| 4.25 | 4.87 |
| 4.50 | 5.25 |
| 4.55 | 5.43 |
| 4.60 | 5.46 |
| 4.65 | 5.62 |
| 4.70 | 5.88 |
| 4.75 | 6.22 |
| 4.80 | 6.60 |
| 4.85 | 7.41 |
| 4.90 | 8.42 |
| 5.00 | 8.82 |
| 5.50 | 9.27 |
| 6.00 | 9.52 |
| 6.50 | 9.71 |
| 7.00 | 9.89 |
| 7.50 | 10.03 |
| 8.00 | 10.18 |
| 8.50 | 10.34 |
| 9.00 | 10.52 |
| 9.50 | 10.72 |
| 10.00 | 10.94 |

FIGURE 4

TITRATION DATA FOR
ASPARTIC ACID
$25^{\circ}$ C.
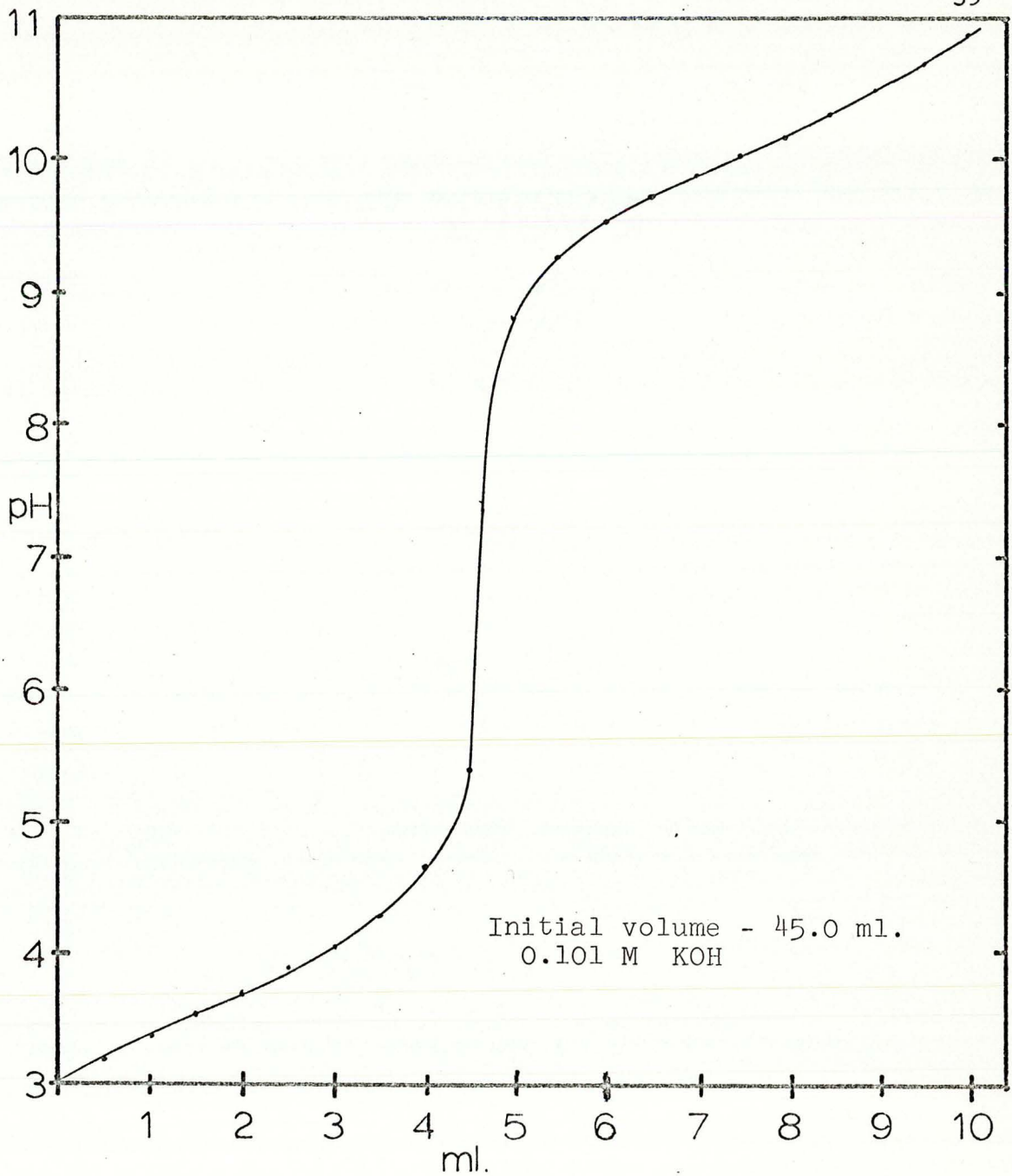
FIGURE 5

Titration Curve for Aspartic Acid at 25° C.

```
45.0 .480 .101ASP25 P38

0.97208.744.17E-044.68E-11
01.4608.262.82E-045.88E-11
01.9407.771.95E-047.95E-11
02.4207.281.38E-041.12E-10
02.9106.809.11E-051.66E-10
03.4006.315.50E-052.00E-10
03.8805.832.75E-053.39E-10
04.3705.349.11E-066.32E-10



45.0 .480 .101ASP25 P38

1.3492E-04     2.4395E-10
1.4174E-04     1.6566E-10
1.4547E-04     1.3827E-10
1.5121E-04     1.2723E-10
1.4952E-04     1.2565E-10
1.4210E-04     9.7499E-11
1.2461E-04     9.9398E-11
1.0540E-04     8.9157E-11

K1=   1.3687E-04   K2=   1.3585E-10
      3.868              9.878
```

FIGURE 6

Computer Input and Output

Aspartic Acid

TABLE VIII

pK VALUES FOR THE AMINO ACIDS AS A
FUNCTION OF TEMPERATURE

| Acid | | 10° | 25° | 40° | 55° | 70° | Average Table VII |
|------|---|-----|-----|-----|-----|-----|-------------------|
| Aspartic | $pK_2$ | 3.92 | 3.87 | 3.91 | 3.90 | 3.94 | 3.77 |
| | $pK_3$ | 10.25 | 9.88 | 9.53 | 9.30 | 9.01 | 9.70 |
| Glutamic | $pK_2$ | 4.31 | 4.40 | 4.39 | 4.14 | 4.35 | 4.26 |
| | $pK_3$ | 10.18 | 9.99 | 9.63 | 9.38 | 8.85 | 9.60 |
| Amino-adipic | $pK_2$ | 4.35 | 4.36 | 4.46 | 4.48 | 4.54 | |
| | $pK_3$ | 9.96 | 9.63 | 9.30 | 9.01 | 8.75 | |
| Amino-pimelic | $pK_2$ | 4.64 | 4.52 | 4.69 | 4.76 | 4.78 | |
| | $pK_3$ | 10.72 | 9.73 | 9.60 | 9.29 | 9.02 | |

The lack of temperature dependence on the ionization constant of the carboxyl group makes it possible to determine the ionization constants of the chelate acids at only one temperature. This carboxyl group is not expected to combine with the metal when the chelate compounds are formed.

The temperature dependence on ionization of the quaternary amine group indicates that the formation of the chelate should proceed faster at higher temperatures since loss of the hydrogen ion from the amine is necessary in order for chelation to take place.

The ionization constants of the acid chelates were measured in the same manner as were the ionization constants for the uncomplexed amino acids. Little or no change in slope of the titration curve was shown at the point corresponding to the half neutralization of the compounds, so it was expected that the two ionization constants would be close together. This would be expected when two acid groups are widely separated on a large molecule as they should act independently of each other. If the molecule is symmetrical there should be no internal effects on one carboxyl group that would not appear on the other group. The question arose then, can the data be treated as if it were from two molecules of just half the size? The ionization constant obtained from the half neutralization point is approximately

the average of the two pK values that were calculated by the equations previously given. The half neutralization point would be the value of the pK for a monoprotic acid of the same normality.

To see what the calculations would produce if a monoprotic acid were treated mathematically as a diprotic acid of half the molar concentration, appropriate data from the titration of KHP with potassium hydroxide were used. $pK_1$ was calculated as 5.08 and $pK_2$ was calculated as 5.67. The handbook value for the pK is given as 5.41 whereas the average of the values is 5.37. From these calculations it will be assumed that any difference in pK values of 0.6 or less is insignificant and can be accounted for by the method of calculation.

Most of the compounds listed in Table IX have their two constants within this factor. While a few values lie slightly beyond this range it is felt that all of these compounds can just as well be treated as monoprotic acids of half the molecular weight when comparing strengths of the acids with the uncomplexed amino acids. When this is done it can be seen that in all cases the complexed acid is weaker than the uncomplexed acid.

Thermodynamically this may be explained by the decrease in entropy of the system since the second carboxyl

group is limited in the amount of freedom that it has in relation to the first carboxyl group.

TABLE IX

IONIZATION CONSTANTS FOR THE CHELATE COMPOUND ACIDS

| Metal | Compound Amino acid | $pK_1$ | $pK_2$ | $pK_2$ uncomplexed amino acid |
|-------|---------------------|--------|--------|-------------------------------|
| Palladium | | | | |
| | Aspartic acid | 3.68 | 4.52 | 3.91 |
| | Glutamic acis | 4.06 | 4.76 | 4.39 |
| | Amino adipic acid | 4.45 | 5.04 | 4.46 |
| | Amino pimelic acid | 4.58 | 5.33 | 4.69 |
| Platinum | | | | |
| | Aspartic acid | 3.77 | 4.14 | 3.91 |
| | Glutamic acid | 4.39 | 5.05 | 4.39 |
| | Amino adipic acid | 4.53 | 5.01 | 4.46 |
| | Amino pimelic acid | 4.75 | 5.38 | 4.69 |

# CHAPTER V

## DETERMINATION OF STABILITY CONSTANTS

There have been many methods developed for determining the stability constants of coordination compounds. Several of these methods were tried and will be discussed in this chapter with reasons given as to why they were less than satisfactory for these particular compounds and then a method will be developed that will give a satisfactory result.

At first, it seemed that the best method would be to take a solution of the complex and titrate it with a standardized acid. By measuring the pH as a function of the amount of acid added to the solution the stability constants could be measured. From the equilibrium:

$$M(H \text{ amino acid anion})_2 + 2 H^+ = M^{++} + 2 \text{ Amino acids}$$
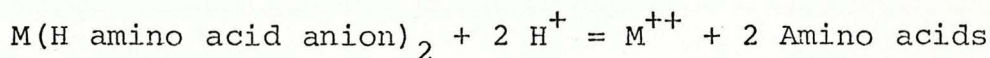
it appeared that both the stepwise and the overall stability constants could be measured in this manner. When titrated with nitric acid (a non-complexing acid), no shift in equilibrium could be detected. A titration using nitric acid versus bis hydrogen aspartato palladium (II) gave no different titration curve than a titration using nitric acid versus a solution of hydrochloric acid which had been diluted to give the same starting pH. The shift in equilibrium is thus too small to be detected by the pH meter available.

Titration with H Cl (a complexing acid) might have shown some reaction since the stability constant for $PdCl_4^{--}$ is about $10^{14}$. No stepwise constants have been reported for the chloro complexes of palladium or platinum so it was felt that no interpretable data would be obtained by this method.

Spectrophotometric methods can often be used to measure changes in concentration where the pH meter fails. In the potentiometric method the range is limited since the compounds themselves are acids with a pH approximately equal to three and the pH meter can measure only down to about one. The spectrophotometric method has an advantage over the potentiometric method in that the hydrogen ion concentration is not being measured and therefore a much higher hydrogen ion concentration can be obtained.

At 320 millimicrons the $PdCl_4^{--}$ ion has almost no absorbance, while the amino acid chelate absorbs strongly. If the chelate solution obeys Beer's Law, the concentration divided by the absorbance should be a constant. However, if the equilibrium is being shifted and a new species with a different absorbance is being formed then a deviation from the constant should be observed. It is proposed that the equilibrium is pH dependent, so the deviation should be expected to increase with an increase in hydrogen ion concentration.

The solution was treated with drops of concentrated sulfuric acid and the hydrogen ion concentration increased from about $10^{-3}$M to about 10M. The results of these tests show that the ratio of concentration to absorbance remains constant over this great range of hydrogen ion concentration. It can be concluded then that within the limits of the spectrophotometer no new identifiable species has been produced.

To investigate this spectrophotometric method farther it was decided to see if a new species would form if the pH was raised. The solution was progressively made more and more basic by the dropwise addition of 6M sodium hydroxide until the pH had been raised to ten. There was no detectable reaction during the time of these measurements (approximately thirty minutes).

It must be concluded that either pH has no effect on the stability of these compounds or that the reaction is too slow to be detected during the time of the measurements.

Polarographic measurements have been used to determine stability constants in many cases. By combining the Ilkovic equation and the Nernst equation the concentration of the cation undergoing reduction can often be determined. This method was not as successful as had been hoped for, but some rough measurements were made. Working with a 0.001 M $K_2PdCl_4$ solution a half-wave potential was measured at about

0.5 volts.  This measurement is in doubt since spontaneous reduction was evident at 0.0 volts.  The amino acid chelates all behaved in a similar manner by reducing spontaneously, but in some cases a half-wave potential was barely detectable at about -0.3 volts when the solution was also 0.001M.

Since the change of potential between one complex and another is being compared, one must work from the chloro complex half-wave potential to the half-wave potential for the uncomplexed metal.  This can be done by using the Nernst equation in the form

$$E_{complex} - E_{metal} = \frac{0.06}{2} \log K_{stability}$$

Palladium has a stability constant of $1.6 \times 10^{13}$ for the chloro complex and using the above equation an $E_{metal}$ is calculated as -0.9 volts.  Using this value and the -0.3 volts for the half-wave potential of the complex a stability constant is calculated as being about $10^{20}$.  Typical polarographic tracings are collected in Appendix E where it can be seen that this method can give only a rough value for the stability constant.

The method most often used to determine stability constants calls for calculating the value $\bar{n}$ (the average number of molecules of ligand bond by one atom of metal).  This is done by measuring the pH when a known amount of hydrogen ion forming ligand is added to a known amount of

metal ion. This method is good and has been used exten-
sively in cases where there are no other competing ligands.
This method is listed in all texts on methods of determining
stability constants and will give stepwise constants if the
constants are not too close together. Cefola and co-workers
obtained a stability constant in this manner in 1959 although
its interpretation leaves some reason for doubt. (5) The
method they developed added the metal chloride to the glu-
tamic acid on a one-to-one mole ratio. This solution was
titrated with standardized sodium hydroxide and the pH of
the resulting solution was plotted versus the ratio of base
to acid in the solution. In cases where there is no chela-
tion an inflection point should appear at 1.0 moles base per
mole of acid due to the neutralization of the carboxyl group.
If all of the amino acid has been chelated, there should be
an inflection point at 2.0 miles of base/mole of acid.

The point they failed to consider is that the metal
is in excess in the solution as a chloro complex and at the
same pH at which they were making their measurements the
metal ion also forms stable hydroxide complexes. These in-
vestigators apparently ignored this effect completely. In
addition, they also failed to take into consideration the
stability of the chloro complex of the metal as a competing
equilibrium with the uncomplexed metal ion.

The method adopted uses the reasoning of Cefola with modifications to take into consideration the variable that should not have been ignored. This method will only give an overall stability constant, but it is consistent with the other data.

To measure the overall stability constant of the metal-amino acid complex, a known amount of the metal chloro complex is added to a known amount of amino acid and the solution is titrated with a standard hydroxide solution. It is important to keep the pH below the point where either the metal hydroxide forms or where the quaternary amine will start to be neutralized. In practice neither of these reactions become important at pH's below 7.5.

During titration the hydroxide first neutralizes the hydrogen that has been freed from the quaternary amine as a consequence of complex formation. In addition the hydroxide neutralizes the uncomplexed carboxyl group both from the complexed and the uncomplexed amino acid. The amount of amino acid that has reacted with the metal can be calculated by subtracting the amount of amino acid originally put into the solution from the amount of base used in the titration. From this the amount of metal-amino·acid compound in solution can be calculated (assuming a one-to-one metal-amino acid ratio) as can the amount of chloride ion in solution. Each

complexed amino acid liberates two chloride ions and this is added to any additional chloride in the solution. The amount of unreacted metal chloro complex and the amount of unreacted amino acid.

Since the stability constant for the chloro complex is known, the concentration of the uncomplexed metal ion can be calculated by using the chloride ion concentration and the concentration of the metal chloro complex. Then, using the concentration of the uncomplexed metal, the metal-amino acid concentration and the concentration of the unreacted amino acid, the stability constant for the metal-amino acid complex can be calculated. These calculations are somewhat tedious but entirely straight forward. One may question the advisability of leaving the hydrogen ion concentration out of the equilibrium expression; therefore, calculations were made both with and without the hydrogen ion concentration in the expression.

A typical calculation is shown here for clarification of the method just outlined above.

Starting with

0.25 millimiles of $K_2PtCl_4$

0.50 millimoles of Aspartic acid

1.25 millimoles of K Cl

dissolved in water to give a total volume of 50.0 ml. The

initial pH was 2.77 and titration took 0.647 millimoles of OH$^-$. It takes 0.50 millimoles of hydroxide ion to neutralize the carboxyl groups, therefore it took 0.647 - 0.500 millimoles of base to neutralize the hydrogen ions liberated from the quaternary amine during the complex formation. The 0.147 millimoles of reacted amino acid formed 0.074 millimoles of metal-amino acid complex leaving 0.353 millimoles of unreacted amino acid and 0.176 millimoles of PtCl$_4^{--}$. In addition, 0.296 millimoles of chloride ions were released from the chloro complex which, when added to the 1.25 millimoles initially in the solution, give a total of 1.546 millimoles.

Molar concentrations of each of these species before titration are as follows:

| | |
|---|---|
| Aspartic acid | $7.06 \times 10^{-3}$ |
| PtCl$_4^{--}$ | $3.52 \times 10^{-3}$ |
| Cl$^-$ | $3.09 \times 10^{-2}$ |
| Pt(HAsp)$_2$ | $1.40 \times 10^{-3}$ |

$$Pt^{++} = \frac{(K_{stab})[PtCl_4^{--}]}{[Cl^-]^4} = \frac{(10^{-16})(3.52 \times 10^{-3})}{9.12 \times 10^{-7}}$$

$$= 3.86 \times 10^{-12} \text{ M}$$

$$K_{stab} = \frac{[Pt(HAsp)_2]}{[H_2Asp]^2[Pt^{++}]} = \frac{1.48 \times 10^{-3}}{(4.98 \times 10^{-15})(3.86 \times 10^{-12})}$$

$$= 7.90 \times 10^{12} \quad .$$

All of these reactions were made up with either 1.25 millimoles of KCl or 1.25 millimoles of $KClO_4$ in order to maintain the same ionic strength. In either case the results were comparable.

The hydrogen ions liberated through complex ion formation cannot be separated from the hydrogen ions on the uncomplexed carboxyl group, so it is impossible to get stepwise stability constants. Even to get an overall stability constant, this method is based on several assumptions. The metal ion concentration must be extremely small so that it may be calculated as previously outlined and it must be assumed that no other complexes are formed in any appreciable concentration. This latter assumption is believed to be true since the slow reaction between hydroxide ions and the metals cannot be detected in titrations in which the amino acid complexes are present

The results of these measurements are summarized in Table X while the complete data is collected in Appendix F. From Table X two things can immediately be seen. The type of amino acid has little effect on the stability of the

compound and the palladium complexes are more stable than the platinum complexes. This latter information may explain why the palladium complexes were much easier to make than the platinum complexes.

## TABLE X

### STABILITY CONSTANTS

| Amino acid | Palladium | Platinum |
|---|---|---|

A. Calculations made without hydrogen ion concentration

| | | |
|---|---|---|
| Aspartic | $4.2 \times 10^{14}$ | $7.9 \times 10^{12}$ |
| Glutamic | $2.0 \times 10^{14}$ | $4.6 \times 10^{12}$ |
| Amino-adipic | $3.4 \times 10^{14}$ | $4.6 \times 10^{12}$ |
| Amino-pimelic | $1.4 \times 10^{14}$ | $1.2 \times 10^{12}$ |

B. Calculations made with hydrogen ion concentration

| | | |
|---|---|---|
| Aspartic | $9.4 \times 10^{9}$ | $2.3 \times 10^{8}$ |
| Glutamic | $4.0 \times 10^{9}$ | $6.4 \times 10^{7}$ |
| Amino-adipic | $3.8 \times 10^{8}$ | $8.1 \times 10^{7}$ |
| Amino-pimelic | $4.9 \times 10^{9}$ | $2.4 \times 10^{8}$ |

# CHAPTER VI

## SUMMARY

Palladium and platinum coordination compounds have
been synthesized from the four dicarboxylic amino acids,
namely aspartic (2-amino 1,4 butandioic acid), glutamic
(2-amino 1,5 pentandioic acid), alpha amino adipic (2-amino
1,6 hexandioic acid), and alpha amino pimelic (2-amino 1,7
heptandioic acid). These acids form chelates between the
number 1 carboxyl group and the amine group with the metals
in the form M(H Amino acid)$_2$. The two amino acids undoubt-
edly form around the platinum and palladium in a square
planar manner leaving the omega carboxyl group uncomplexed.
The two higher homologs of this series have never been pre-
pared as chelates before.

The four amino acids studied show slightly decreas-
ing ionization constants as the chain length increases, the
ionization constant is only slightly affected by tempera-
ture, and the ionization of the quaternary amine groups
shows an increase in ionization constant with an increase
in temperature.

Chelation decreases the ionization constant of the
uncomplexed carboxyl group slightly although chain length
of the acid appears to have no effect on the degree to which
the ionization constant is lowered.

The stability constants of the platinum chelates are about an order of magnitude less than the palladium compounds. The length of the carbon chain of the amino acid has little effect on the stability of the compounds that were made.
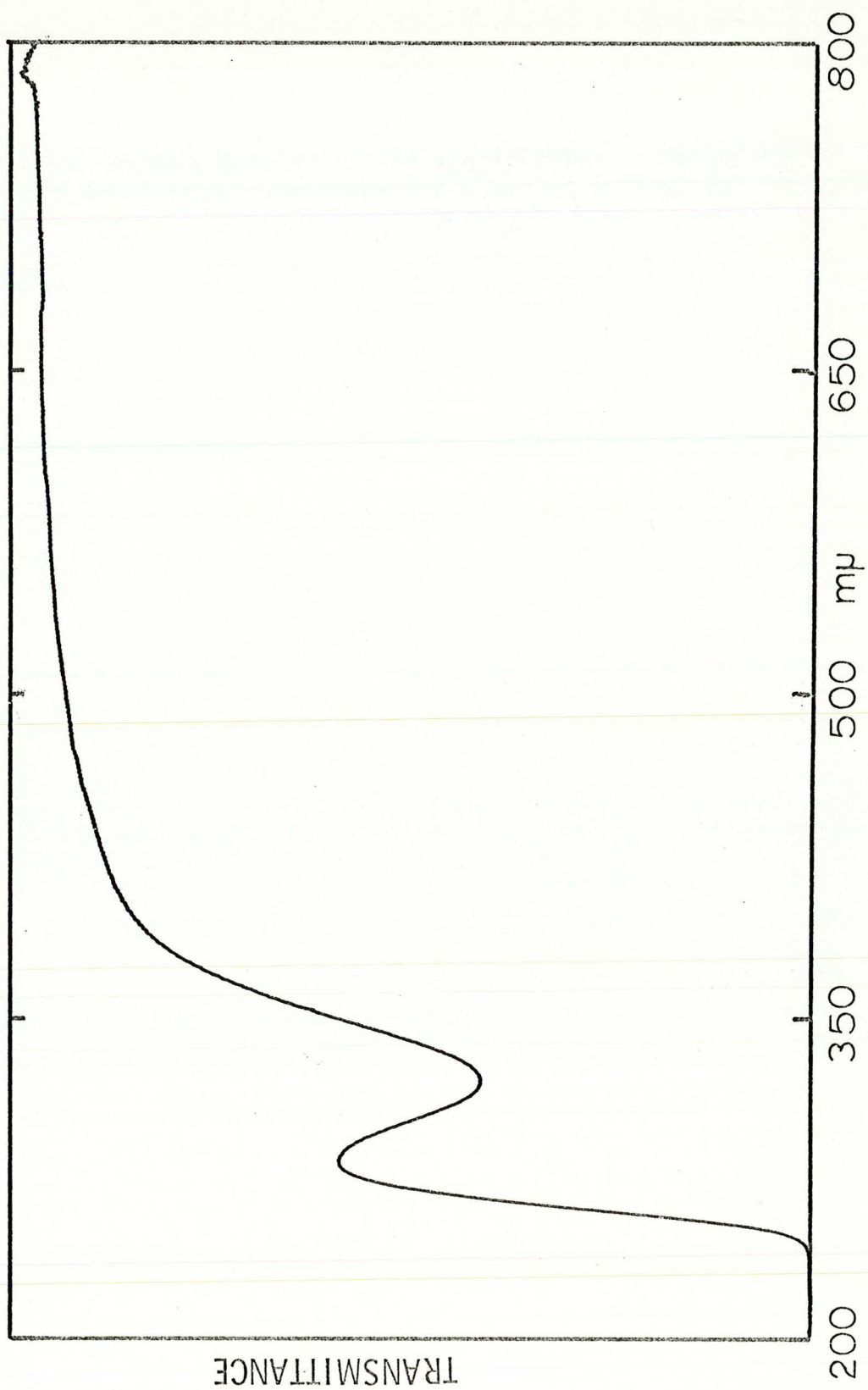
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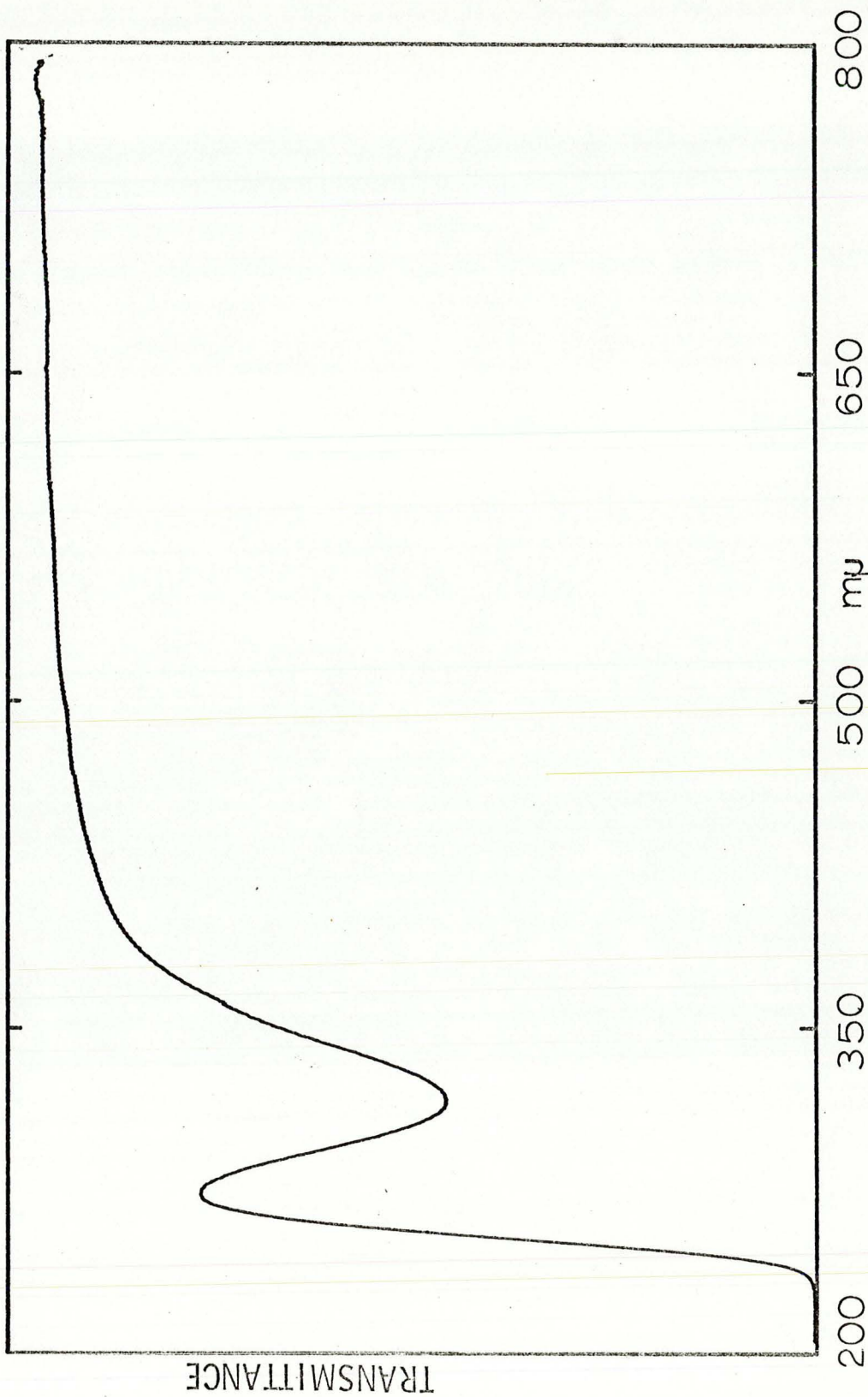
61

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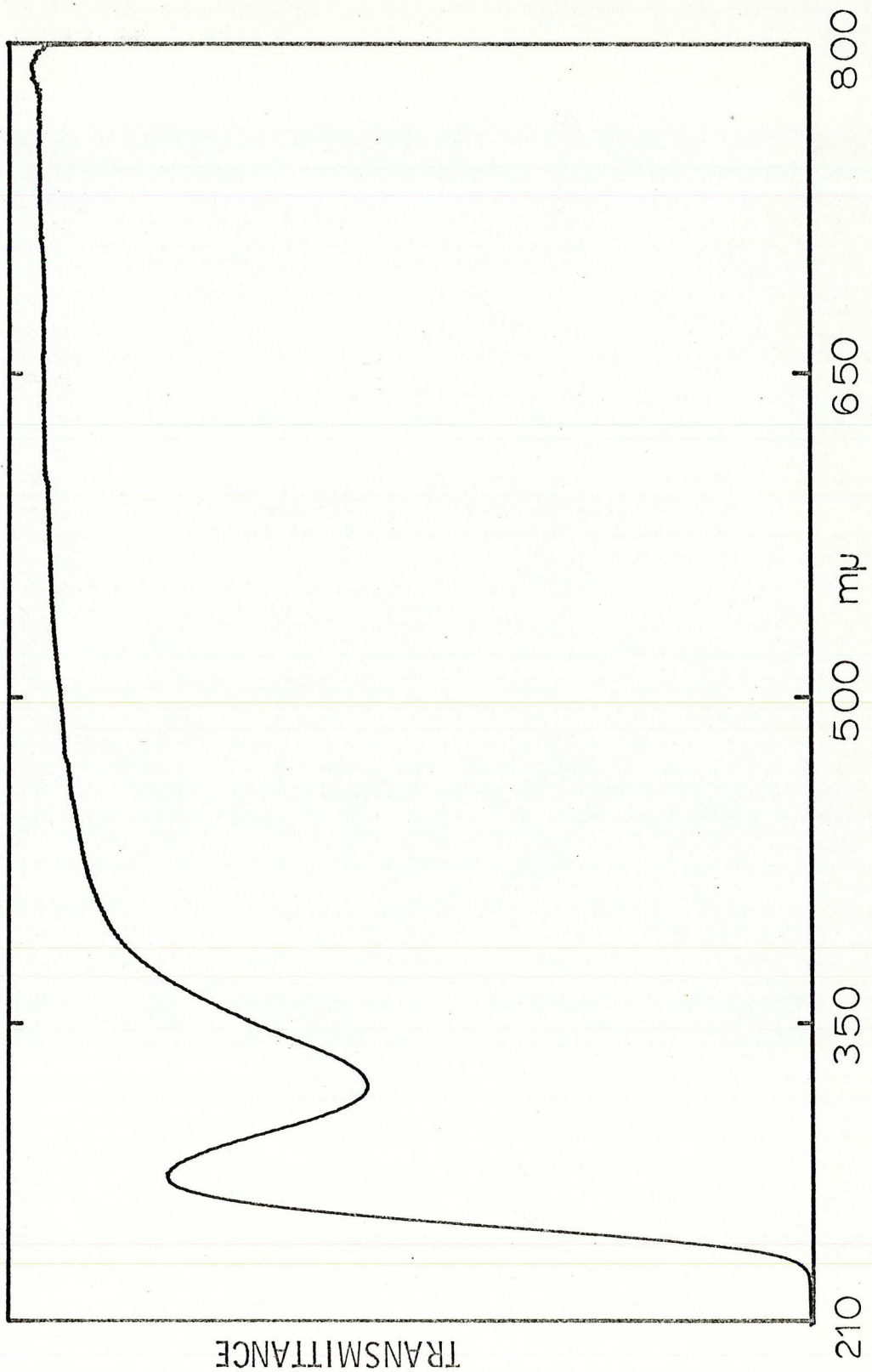28.  Werner, Alfred, "Ethylenediamine Complex of Cobalt" Ber., 34, 2584 (1901).

APPENDIX A

ULTRA-VIOLET AND VISIBLE SPECTRA

TRANSMITTANCE

200    350    500  mµ    650    800

Bis hydrogen glutamato palladium (II)

63

TRANSMITTANCE

200    350    500 mμ    650    800

Bis hydrogen alpha amino adipato palladium (II)

64

Bis hydrogen alpha amino pimelato palladium (II)

TRANSMITTANCE

TRANSMITTANCE

210    350    500    mμ    650    800

Bis hydrogen alpha amino pimelato platinum II)

APPENDIX B

INFRA-RED SPECTRA
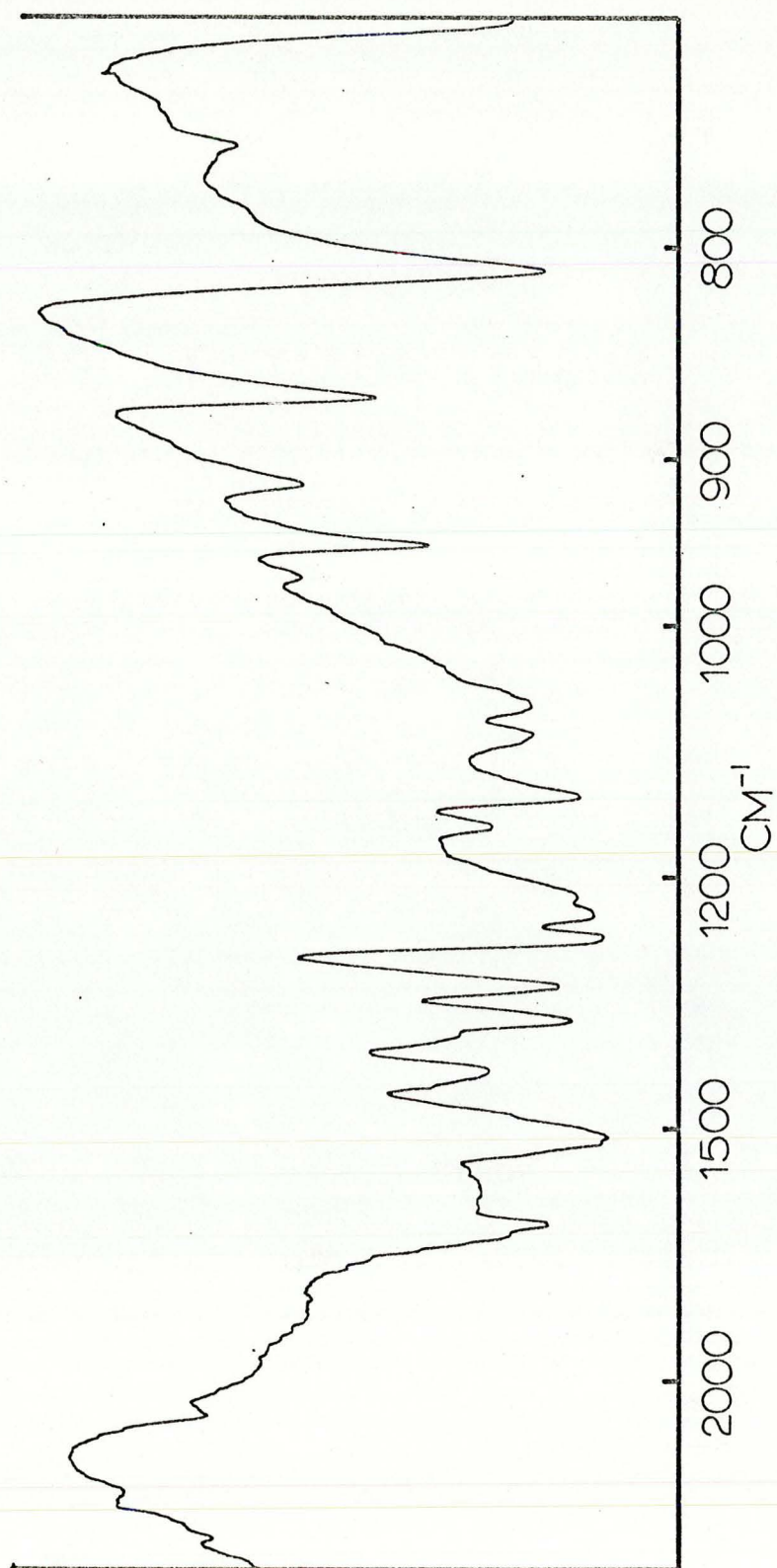
Glutamic acid

Alpha amino adipic acid
(2-amino-1,6-hexandioic acid)

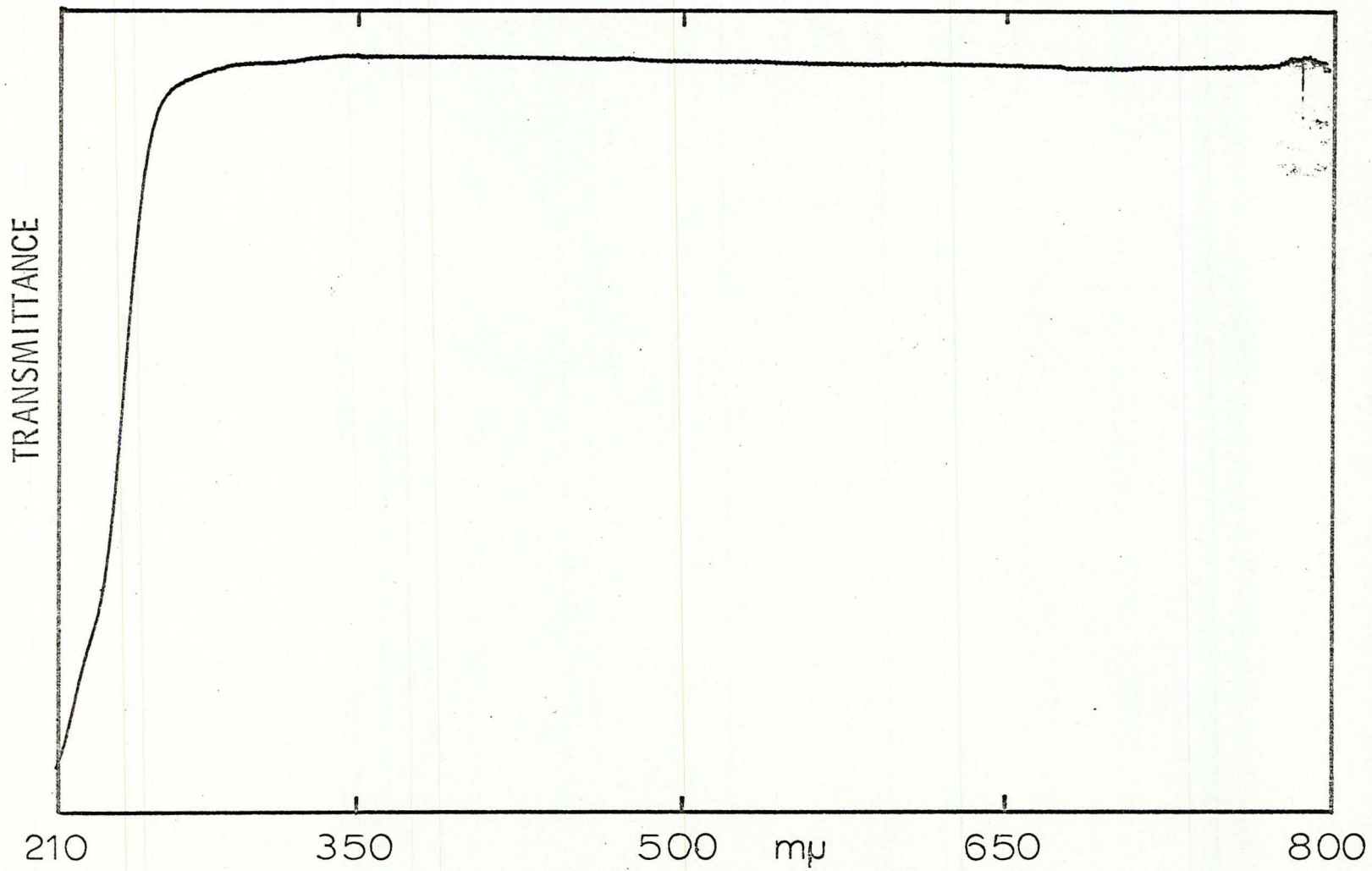Alpha amino pimelic acid
(2-amino-1,7-heptandioic acid )
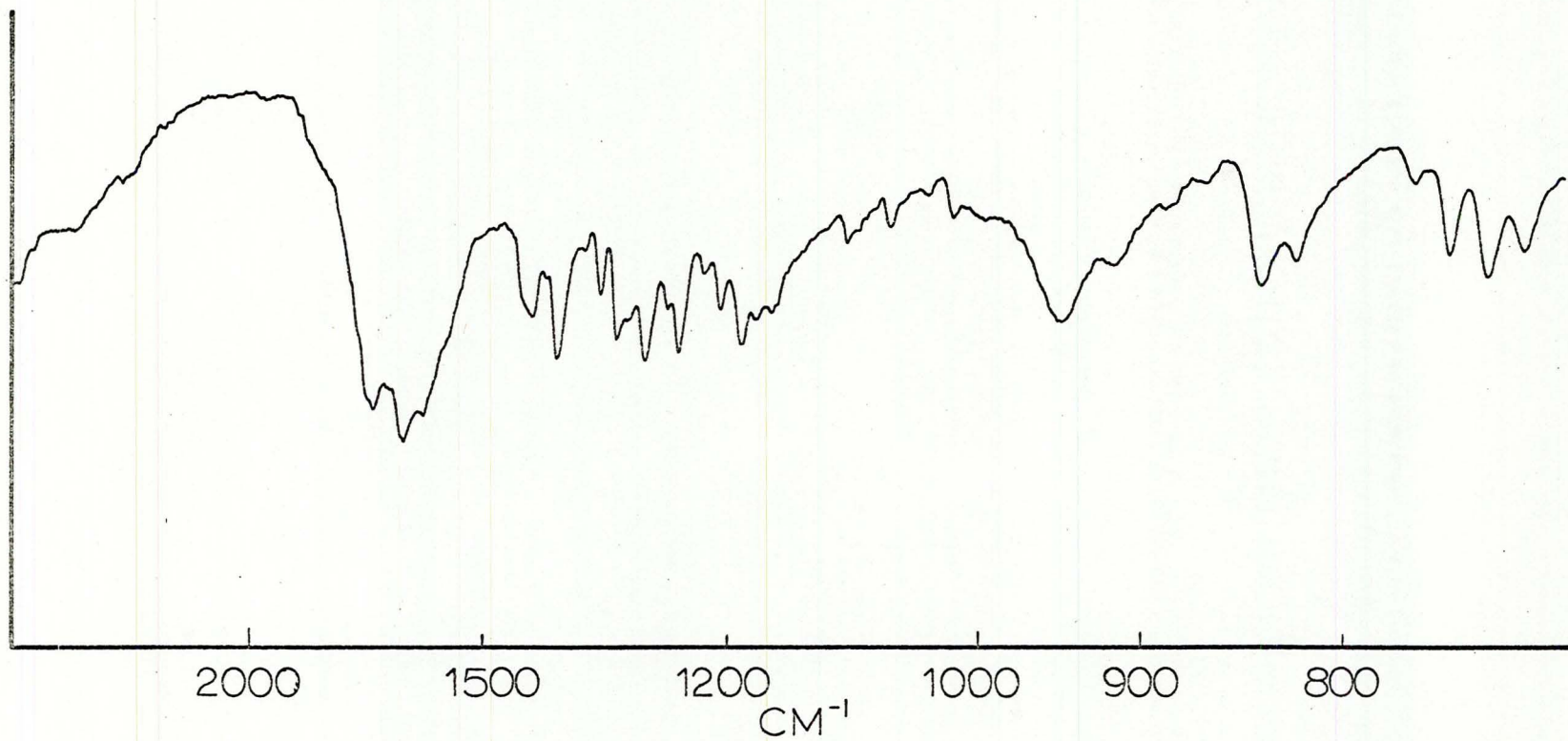
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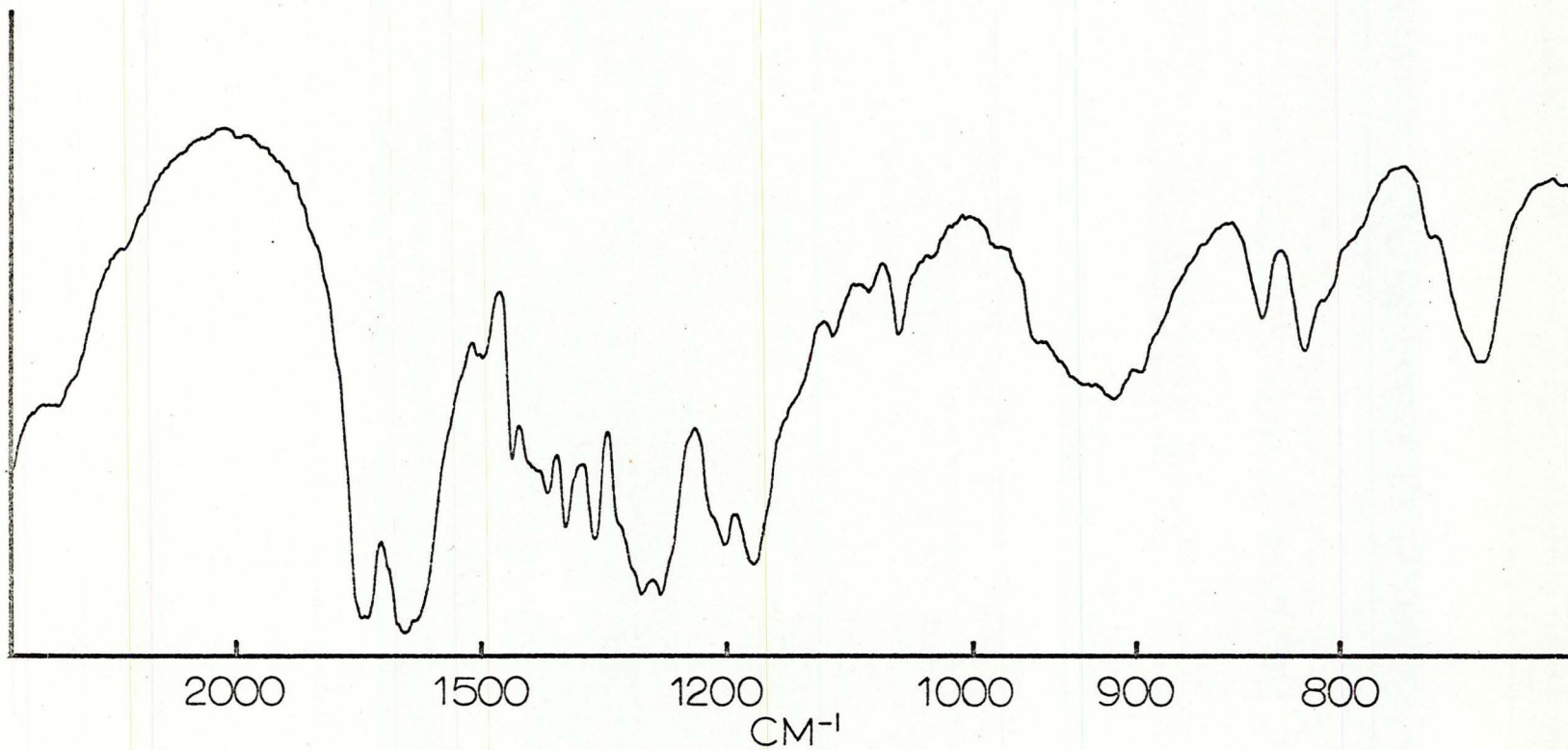
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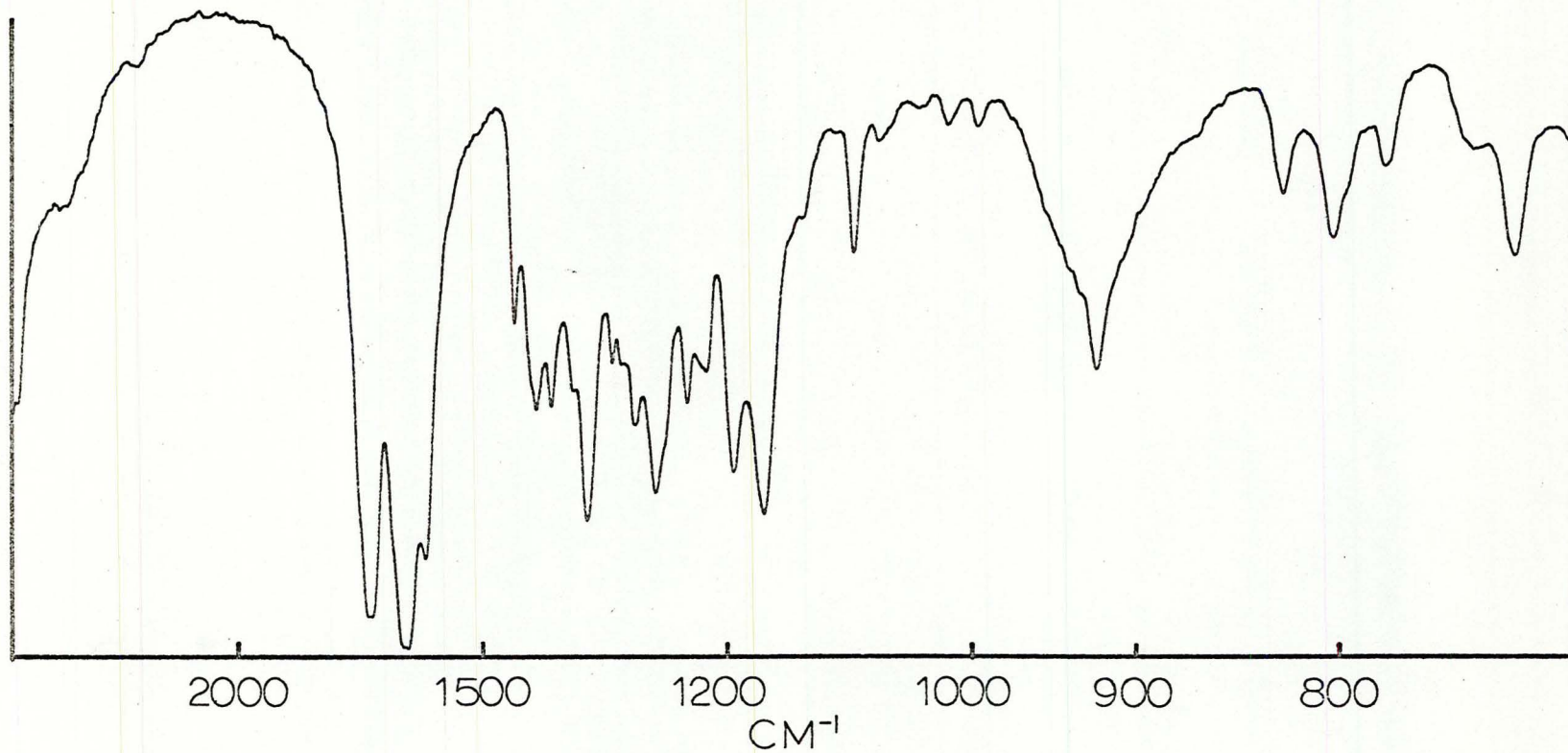
Bis hydrogen alpha amino pimelato palladium (II)

Bis hydrogen aspartato platinum (II)

74
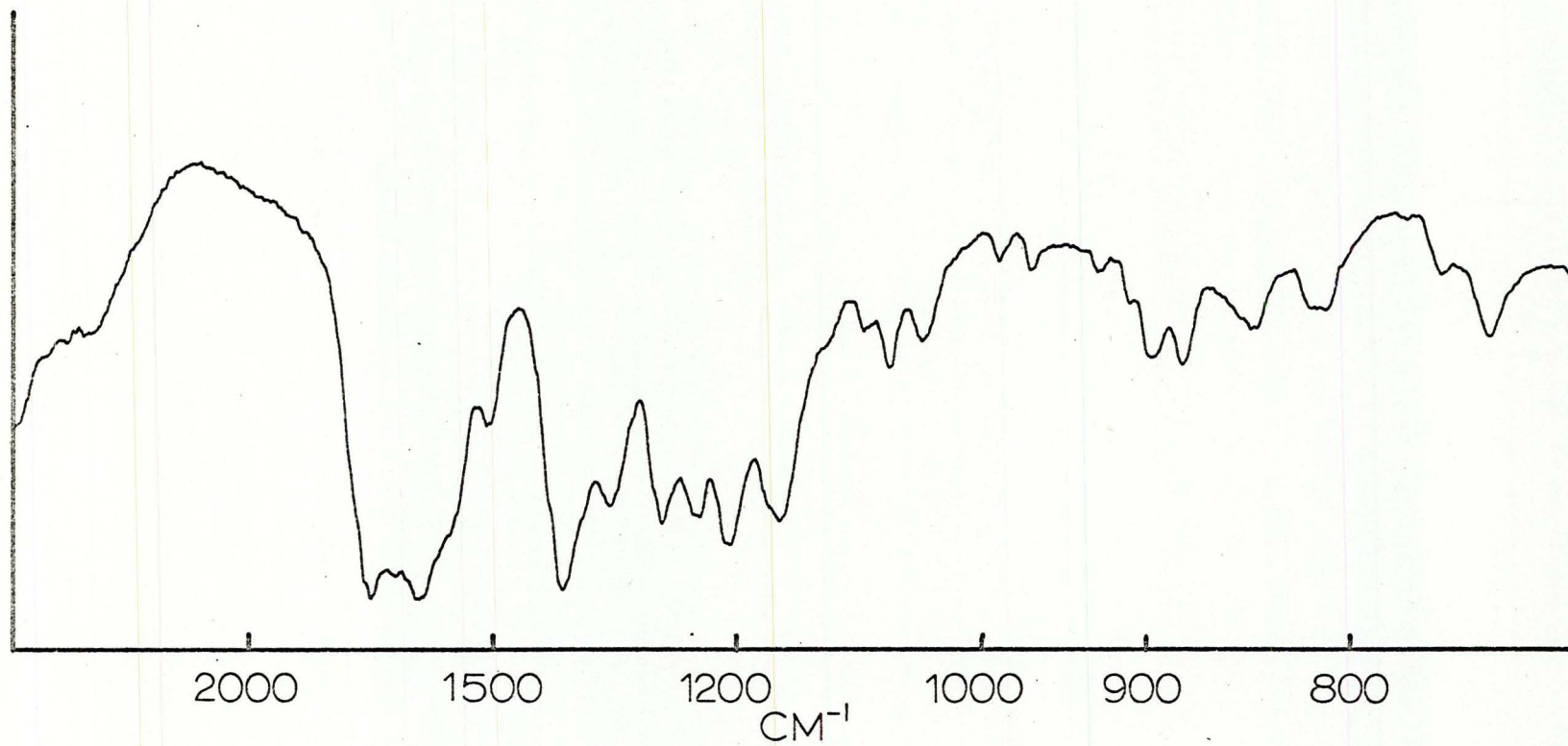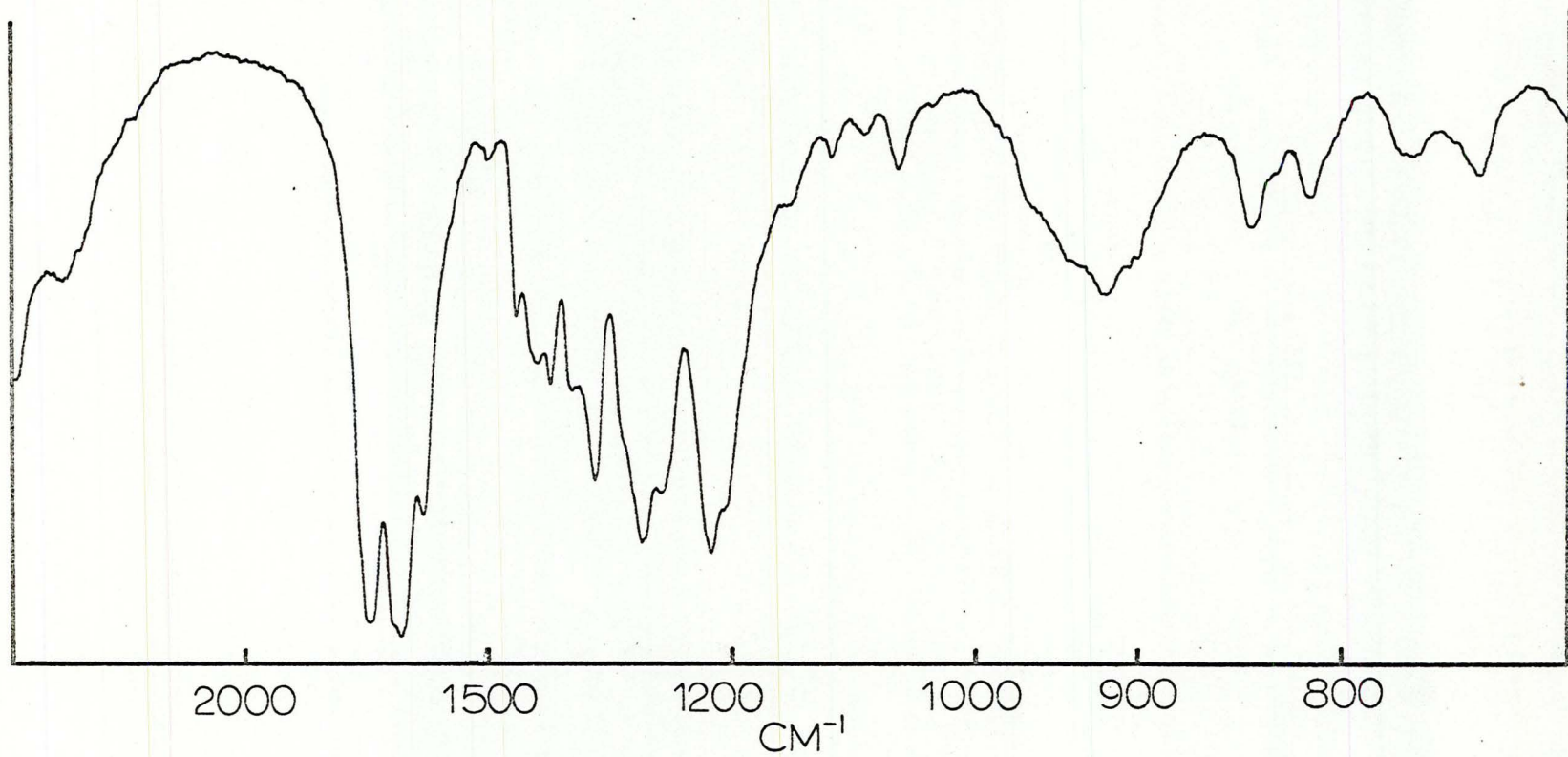
Bis Hydrogen alpha amino adipato platinum (II)
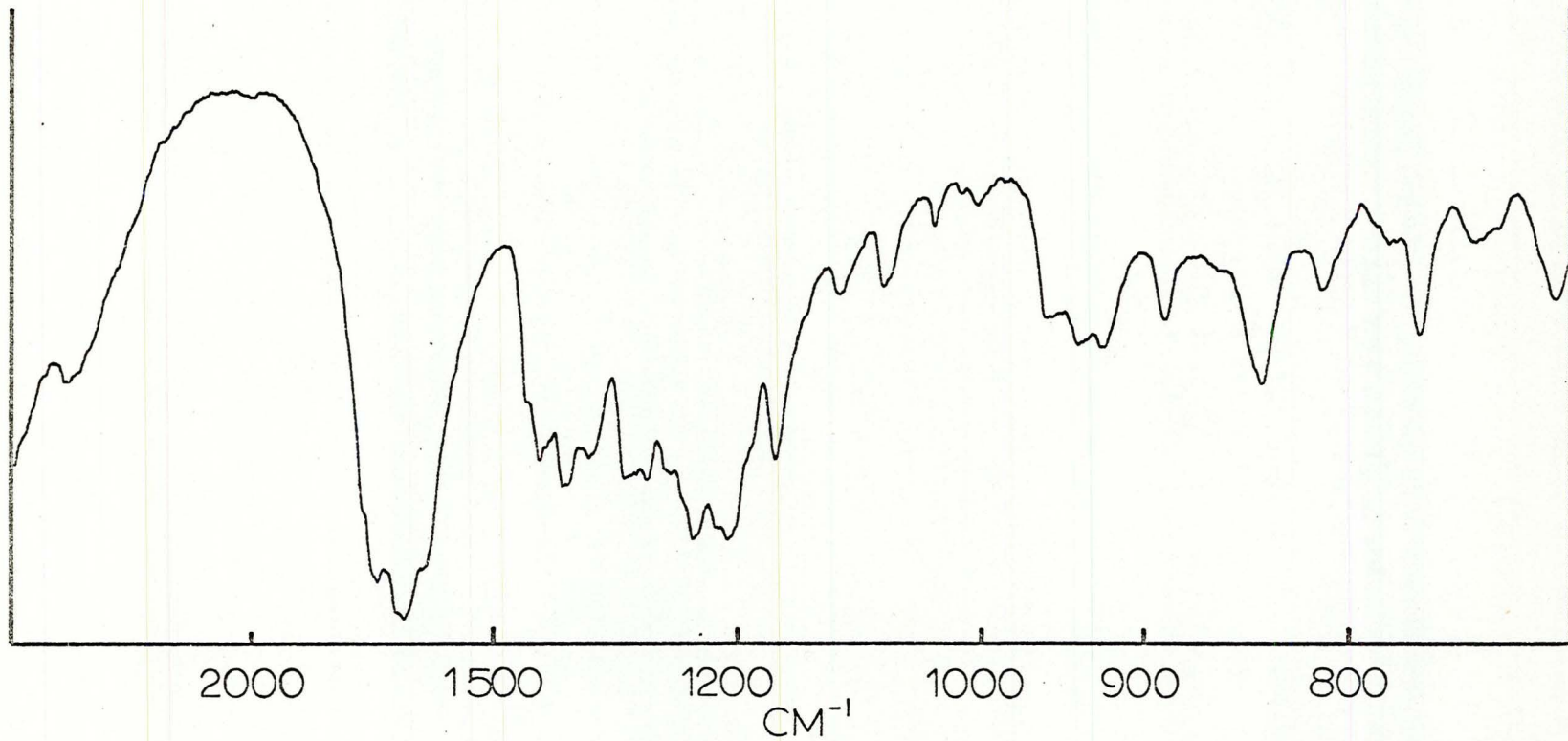
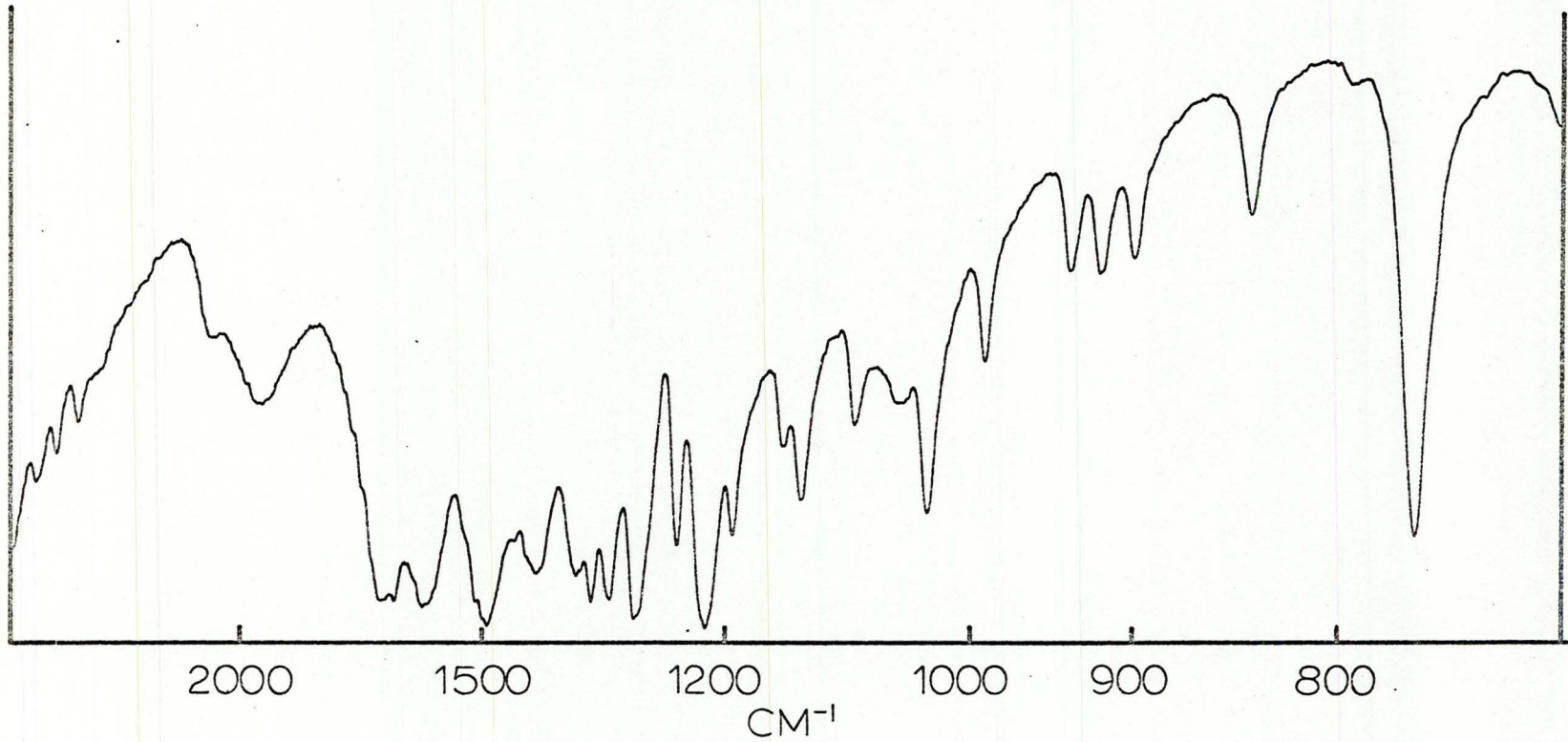Bis hydrogen glutamato platinum (II)

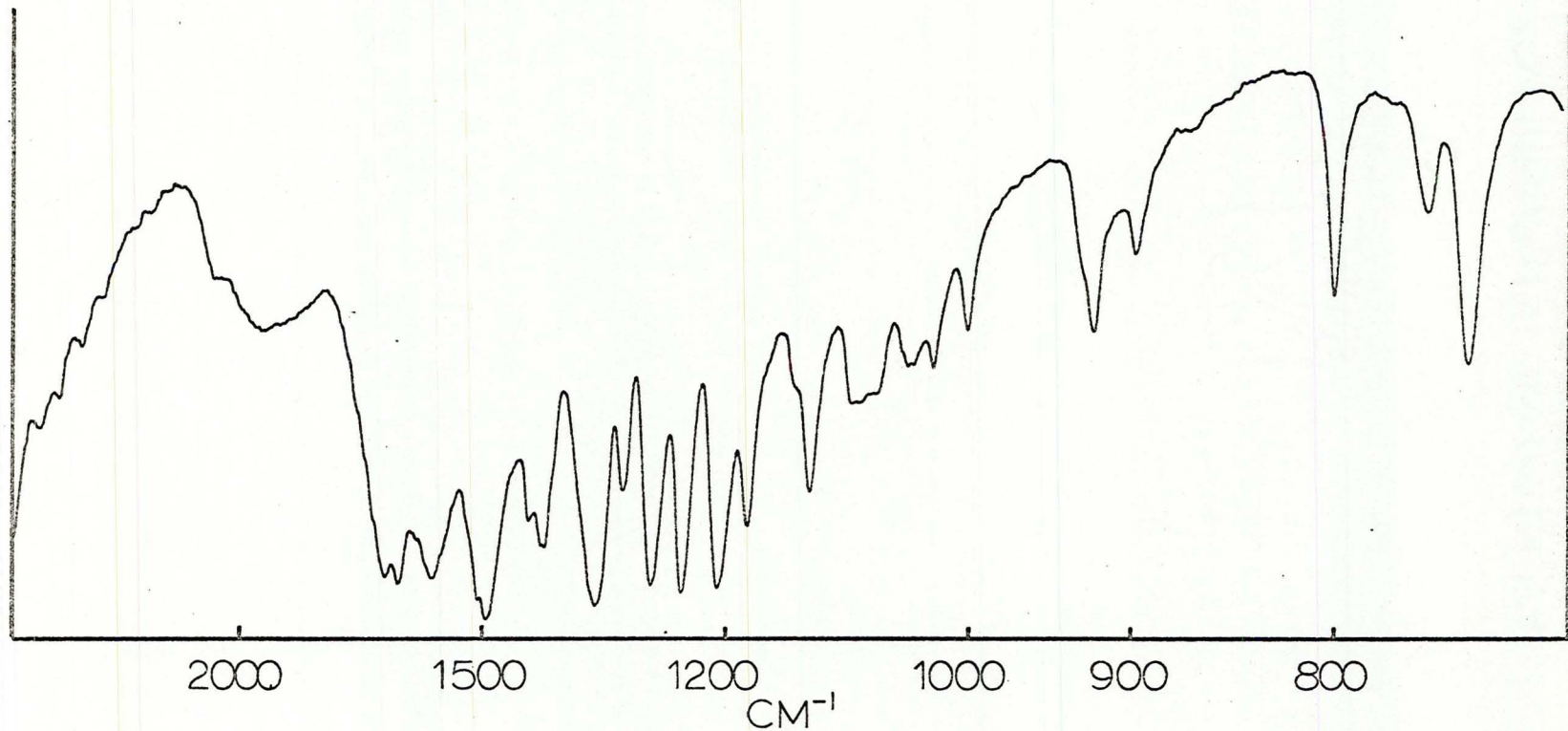Bis hydrogen alpha amino pimelato platinum (II)

77

APPENDIX C

PHOTOMICROGRAPHS
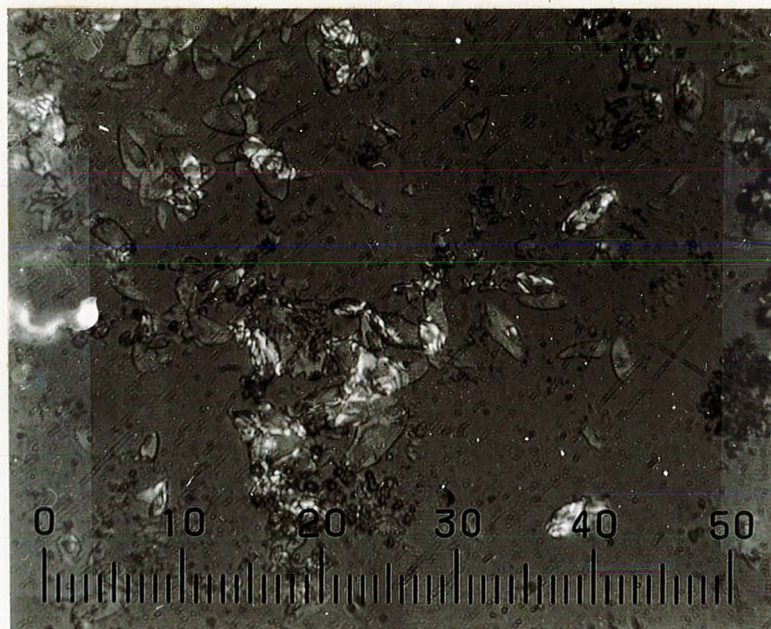
BIS HYDROGEN ALPHA AMINO ADIPATO PLATINUM (II)
1 scale division = 5 microns
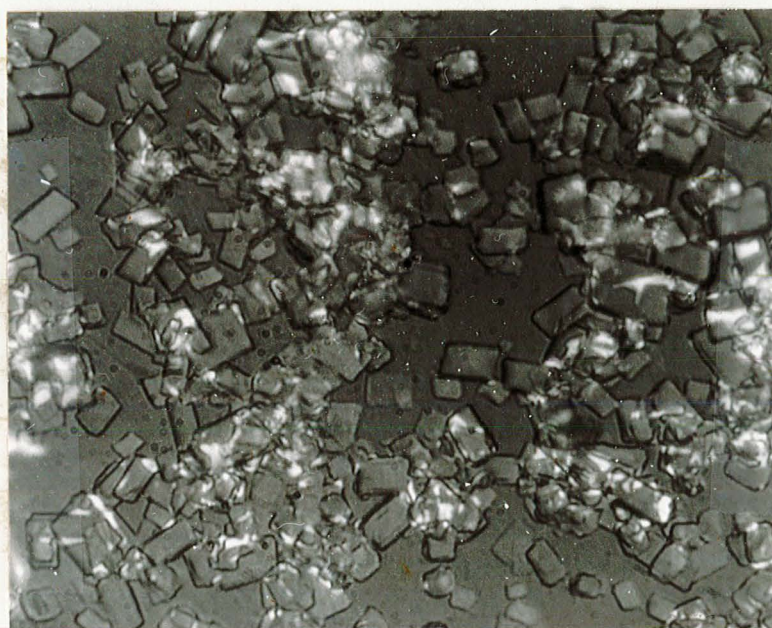


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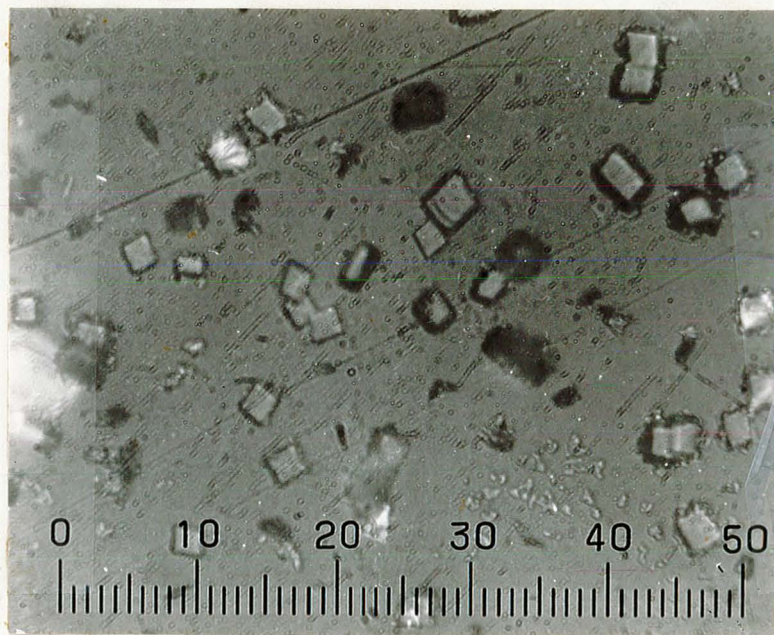
BIS HYDROGEN ALPHA AMINO ADIPATO PALLADIUM (II)
1 scale division = 5 microns
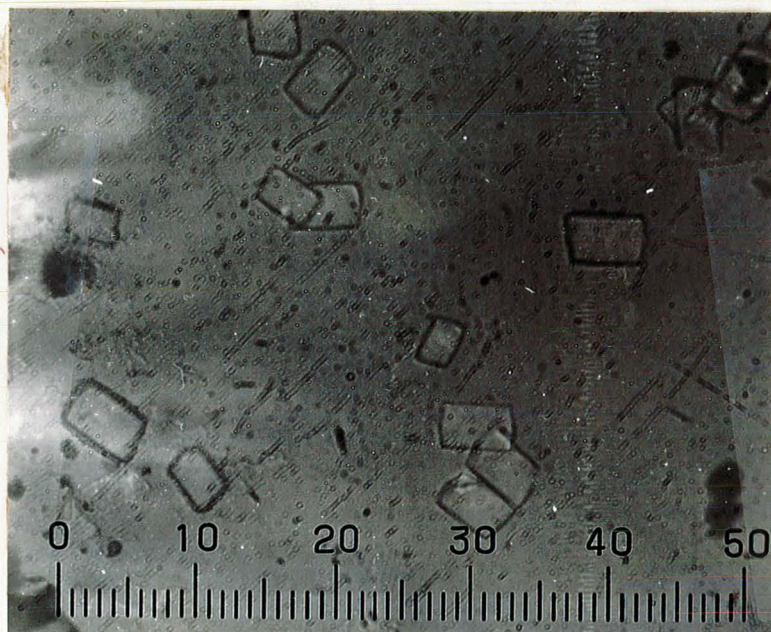


BIS HYDROGEN ALPHA AMINO PIMELATO PALLADIUM (II)

APPENDIX D

FORTRAN COMPUTER PROGRAM

COMPUTER INPUT AND OUTPUT DATA

```
C        DIPROTIC ACID CONSTANT PROGRAM
         TYPE 34
34       FORMAT(43 H SW 3 ON-TYPE NEW VALUE OF N, OFF-USE OLD N)
17       READ 20,VH2O,XMMA,XMB
20       FORMAT(F5.1,F5.3,10H                    )
         PUNCH 20,VH2O,XMMA,XMB
29       IF(SENSE SWITCH 3)30,26
30       TYPE 40
40       FORMAT(47HTYPE NUMBER OF READINGS, PUSH RELEASE AND START)
         ACCEPT 24,I
24       FORMAT(I2)
26       N=0
         T1K=0.0
         T2K=0.0
11       READ 12,VB1,VB2,HCN1,HCN2
12       FORMAT(F5.0,F5.0,E8.0,E8.0)
         C1=XMMA/(VH2O +VB1)
         C2=XMMA/(VH2O+VB2)
         B1=(VB1*XMB)/(VH2O+VB1)
         B2=(VB2*XMB)/(VH2O+VB2)
         X1=HCN1*(B1-C1+HCN1)
         X2=HCN2*(B2-C2+HCN2)
         Y1=2.0*C1-(B1+HCN1)
         Y2=2.0*C2-(B2+HCN2)
         Z1=(HCN1**2)*(B1+HCN1)
         Z2=(HCN2**2)*(B2+HCN2)
         AK1=(Y1*Z2-Y2*Z1)/(X1*Y2-X2*Y1)
         AK2=(X1*Z2-X2*Z1)/( Y1*Z2-Y2*Z1)
         T1K=T1K+AK1
         T2K=T2K+AK2
         N=N+1
         PUNCH 19,AK1,AK2
19       FORMAT(E11.4,2X,E11.4)
         IF(I-N)11,14,11
14       G=I
         T1K=T1K/G
         T2K=T2K/G
         PUNCH 16,T1K,T2K
16       FORMAT(5H K1= E11.4,6H  K2=  E11.4)
         T1K =(-1.0/2.3)*(LOGF(T1K))
         T2K =(-1.0/2.3)*(LOGF(T1K))
         PUNCH 21,T1K,T2K
21       FORMAT(5X,F6.3,12X,F7.3)
         GO TO 17
         END
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50.00.6520.146ASP10 P117

0.86407.773.64E-042.24E-11
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1.72806.921.82E-045.13E-11
02.1606.481.45E-047.24E-11
02.5906.059.65E-051.00E-10
03.0605.625.75E-051.48E-10
03.4505.183.38E-052.52E-10
03.8904.761.41E-056.25E-10


 45.0 .480 .101ASP25 P38
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01.4608.262.82E-045.88E-11
01.9407.771.95E-047.95E-11
02.4207.281.38E-041.12E-10
02.9106.809.11E-051.66E-10
03.4006.315.50E-052.00E-10
03.8805.832.75E-053.39E-10
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2.5906.0508.52E-051.26E-09
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03.0805.722.51E-051.95E-10
03.5205.281.48E-053.31E-10
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50.00.6660.146GLU25 P119
00.8807.921.45E-044.07E-11
01.3207.489.78E-056.61E-11
01.7607.046.92E-051.02E-10
02.2006.604.90E-051.51E-10
02.2406.163.47E-052.19E-10
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50.00.6660.146GLU70 P 8B
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02 .2403 .361 .02E-054 .37E-10
02 .5203 .084 .68E-061 .00E-09

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01.850 5.552.24E-054.68E-11
02.220 5.181.59E-056.92E-11
02.590 4.811.05E-051.05E-10
02.960 4.446.31E-061.82E-10
03.330 4.072.75E-063.98E-10

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7.2977E-05      1.5704E-09
7.9550E-05      1.5753E-09
8.2330E-05      1.5752E-09
7.6451E-05      1.4197E-09
6.9559E-05      1.2943E-09
5.7698E-05      9.2022E-10
K1=  7.2703E-05   K2=  1.4619E-09
     4.143                 8.845


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1.4228E-04      5.9486E-11
1.3758E-04      5.4979E-11
1.2792E-04      5.1586E-11
1.1663E-04      4.7978E-11
9.6259E-05      4.4090E-11
K1=  1.2064E-04   K2=  5.5888E-11
     3.922                10.253


45.0  .480  .101ASP25  P38
1.3492E-04      2.4395E-10
1.4174E-04      1.6566E-10
1.4547E-04      1.3827E-10
1.5121E-04      1.2723E-10
1.4952E-04      1.2565E-10
1.4210E-04      9.7499E-11
1.2461E-04      9.9398E-11
1.0540E-04      8.9157E-11
K1=  1.3687E-04   K2=  1.3585E-10
     3.868                 9.878


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9.4266E-05      3.6364E-10
1.1243E-04      3.1486E-10
1.2891E-04      3.0332E-10
1.3456E-04      2.8283E-10
1.3460E-04      2.6058E-10
1.4207E-04      2.6597E-10
1.2930E-04      3.2932E-10
1.1866E-04      2.8638E-10
K1=  1.2435E-04   K2=  3.0086E-10
     3.909                 9.532
```

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4.5200E-05      7.5077E-11
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4.8878E-05      6.9950E-11
5.3284E-05      7.2057E-11
5.2852E-05      6.7963E-11
5.2655E-05      6.6372E-11
5.0351E-05      6.1870E-11
4.1715E-05      4.7129E-11
K1=  4.9060E-05  K2=  6.6587E-11
     4.314            10.177


50.0  .666  .146GLU25  P119
3.7158E-05      1.1359E-10
4.1299E-05      1.1738E-10
4.4466E-05      1.2134E-10
4.6353E-05      1.2198E-10
3.3845E-05      1.1812E-10
4.4832E-05      1.2083E-10
4.0772E-05      1.0991E-10
3.4683E-05      8.7737E-12
K1=  4.0426E-05  K2=  1.0399E-10
     4.398             9.994


50.0  .666  .146GLU40  P120
3.7980E-05      2.6095E-10
4.1299E-05      2.5040E-10
4.2431E-05      2.6648E-10
4.2994E-05      2.5527E-10
4.4981E-05      2.5244E-10
4.1877E-05      2.3555E-10
3.8037E-05      2.2434E-10
3.2354E-05      1.6333E-10
K1=  4.0244E-05  K2=  2.3860E-10
     4.400             9.633


50.0  .666  .146GLU55  P 8A
4.1847E-05      5.1912E-10
4.5337E-05      5.1857E-10
4.6636E-05      4.8419E-10
4.7505E-05      4.8713E-10
4.7085E-05      4.8116E-10
4.3774E-05      4.4934E-10
4.0083E-05      4.0014E-10
1.9254E-05      8.9793E-11
K1=  4.1440E-05  K2=  4.2868E-10
     4.387             9.378
```

```
50.0 .652 .151ASP55 P115
1.0199E-04      6.6190E-10
1.1243E-04      7.0436E-10
1.2292E-04      5.1413E-10
1.3131E-04      4.7941E-10
1.3778E-04      4.4346E-10
1.4309E-04      4.1235E-10
1.3094E-04      4.2413E-10
1.2703E-04      4.2448E-10
K1=   1.2594E-04   K2=   5.0803E-10
      3.904                9.304


50.0 .652 .151ASP70 P116
9.1609E-05      1.1483E-09
1.0182E-04      1.0425E-09
1.1696E-04      9.7973E-10
1.2806E-04      8.9264E-10
1.3142E-04      8.4406E-10
1.2734E-04      8.0314E-10
1.1903E-04      8.2589E-10
1.0551E-04      1.5078E-09
K1=   1.1522E-04   K2=   1.0055E-09
      3.942                9.007

50.0 .409 .146ADIP 10 11
4.6935E-05      1.3803E-10
4.7817E-05      1.2201E-10
4.7781E-05      1.1348E-10
4.5670E-05      1.0469E-10
4.7053E-05      9.8386E-11
4.5011E-05      9.7848E-11
4.1030E-05      1.0885E-10
4.2184E-05      1.1047E-10
K1=   4.5435E-05   K2=   1.1172E-10
      4.347                9.963


50.0 .409 .146ADIP 2510B
4.9481E-05      2.8164E-10
4.8784E-05      2.5565E-10
4.7781E-05      2.2127E-10
4.4626E-05      2.0839E-10
4.0875E-05      2.1539E-10
4.1913E-05      2.1920E-10
4.0216E-05      2.3815E-10
4.0262E-05      2.7188E-10
K1=   4.4242E-05   K2=   2.3895E-10
      4.359                9.632
```

```
50.0  .409  .146ADIP 40  10
3.9152E-05    6.7628E-10
3.8309E-05    5.5779E-10
3.7697E-05    5.0685E-10
4.6714E-05    4.6664E-10
3.5489E-05    4.6005E-10
3.5997E-05    4.7006E-10
3.4985E-05    4.9833E-10
1.2606E-05    4.8450E-10
K1=   3.5119E-05  K2=   5.1506E-10
       4.459                9.298


50.0  .409  .146ADIP 55  9B
3.6413E-05    1.3486E-09
3.6517E-05    1.1388E-09
3.5936E-05    1.0825E-09
3.3619E-05    1.0470E-09
3.3185E-05    9.6406E-10
3.3540E-05    8.7187E-10
3.1136E-05    8.2499E-10
3.0434E-05    7.4846E-10
K1=   3.3848E-05  K2=   1.0032E-09
       4.475                9.008


50.0  .414  .146ADIP 70  9A
3.0028E-05    2.3389E-09
3.0094E-05    1.9969E-09
2.9606E-05    1.8709E-09
2.8889E-05    1.8115E-09
2.9479E-05    1.7286E-09
2.7952E-05    1.6505E-09
2.6643E-05    1.6449E-09
2.8435E-05    1.4540E-09
K1=   2.8891E-05  K2=   1.8120E-09
       4.544                8.751


50.0  .543  .146PIM 10  11B
2.1165E-05    5.5918E-11
2.2330E-05    4.7908E-11
2.2165E-05    4.5803E-11
2.2360E-05    4.5374E-11
2.3694E-05    4.4762E-11
2.4199E-05    4.3577E-11
2.4694E-05    4.3755E-11
2.3594E-05    4.1460E-11
K1=   2.3025E-05  K2=   4.6070E-11
       4.642                10.718
```

```
50.0  .543  .146PIM 25 12A
2.6312E-05    2.3311E-10
2.8963E-05    2.0417E-10
3.0070E-05    1.9568E-10
3.0236E-05    1.9391E-10
3.1207E-05    1.9082E-10
3.2549E-05    1.8552E-10
3.4134E-05    1.6517E-10
3.2629E-05    1.6152E-10
K1=   3.0763E-05   K2=   1.9124E-10
      4.517                9.729


50.0  .543  .146PIM 40 12B
1.6658E-05    3.2153E-10
1.8074E-05    2.8208E-10
1.9253E-05    2.6381E-10
1.9945E-05    2.3269E-10
2.0996E-05    2.1929E-10
2.2021E-05    2.2289E-10
2.3590E-05    2.2988E-10
2.4692E-05    2.7425E-10
K1=   2.0654E-05   K2=   2.5580E-10
      4.690                9.602


50.0  .543  .146PIM 55 13A
1.4766E-05    6.8766E-10
1.7632E-05    6.0223E-10
1.8846E-05    5.5083E-10
1.8538E-05    5.0904E-10
1.8750E-05    4.6838E-10
1.7465E-05    4.7741E-10
1.8287E-05    4.6909E-10
1.7107E-05    4.5649E-10
K1=   1.7674E-05   K2=   5.2764E-10
      4.757                9.288


50.0  .543  .146PIM 70 13B
1.4766E-05    1.3413E-09
1.5694E-05    1.1485E-09
1.5608E-05    1.0495E-09
1.6531E-05    9.2703E-10
1.7850E-05    8.7348E-10
1.7853E-05    8.6784E-10
1.8279E-05    8.1590E-10
1.7852E-05    7.7549E-10
K1=   1.6804E-05   K2=   9.7490E-10
      4.779                9.021
```

```
 50.00.4310.151PT-ASP 18A
00.5705.135.13E-041.29E-05
00.8604.854.17E-042.19E-05
01.1404.563.72E-043.16E-05
01.4304.282.75E-044.07E-05
01.7103.992.34E-045.25E-05
02.0003.711.91E-046.61E-05
02.2803.421.66E-048.32E-05
02.5703.141.38E-041.00E-04


 25.0.0222.0085PT-GLU 17B
00.5204.729.56E-051.51E-06
00.7904.457.76E-052.75E-06
01.0504.196.46E-054.27E-06
01.3103.935.25E-055.89E-06
01.5703.674.37E-058.13E-06
01.8303.413.55E-051.07E-05
02.1003.142.88E-051.32E-05
02.3502.882.34E-051.62E-05


 50.0.0114.0085PT-ADIP17A
0.2692.4214.47E-054.57E-07
0.5382.1523.16E-051.59E-06
0.6732.0182.63E-052.40E-06
0.8071.8832.19E-053.80E-06
0.9421.7491.82E-054.57E-06
0.4042.2873.72E-059.34E-07
1.0761.6141.51E-056.03E-06
1.2111.4801.23E-057.76E-06


 50.0.0096.0085PT-PIM 16B
0.2272.0433.55E-056.46E-07
0.3411.9292.88E-051.23E-06
0.4541.8162.40E-051.91E-06
0.5681.7032.00E-052.75E-06
0.6811.5891.70E-053.72E-06
0.7951.4761.41E-054.68E-06
0.9081.3621.18E-055.75E-06
1.0221.2491.02E-056.92E-06
```

```
  24.8.0411.0257PD-ASP P73
0.3192.8713.02E-048.32E-06
0.4792.7122.63E-041.20E-05
0.6392.5522.14E-041.66E-05
0.7982.3931.86E-042.14E-05
0.9572.2331.66E-042.82E-05
1.1172.0741.45E-043.89E-05
1.2761.9141.18E-044.79E-05
1.4361.7559.56E-055.89E-05

 100..1431.0856 PD-GLU-L9
0.3322.9881.95E-043.99E-06
0.4982.8221.66E-046.32E-06
0.6642.6561.35E-049.56E-06
0.8302.4901.12E-041.23E-05
0.9962.3248.33E-051.59E-05
1.1622.1587.09E-052.04E-05
1.3281.9925.63E-052.58E-05
1.4941.8264.58E-053.24E-05
 50.0.0425.0952PDADIP 40A
.0892.80282.19E-042.95E-06
.1338.75821.78E-045.89E-06
.1784.71361.48E-048.71E-06
.2230.66901.18E-041.29E-05
.2676.62449.77E-051.66E-05
.3122.57987.76E-052.19E-05
.3568.53526.03E-052.75E-05
.4014.49064.90E-053.39E-05

 50.0.0241.0085PDPIM 15B
0.5705.1305.63E-058.33E-07
0.8554.8454.47E-051.51E-06
1.1404.5603.72E-052.40E-06
1.4254.2753.09E-053.32E-06
1.7103.9902.57E-054.37E-06
1.9953.7052.09E-055.76E-06
2.2803.4201.74E-057.32E-06
2.5653.1351.44E-059.56E-06

 50.0.0961.0085 5HP 14B
02.2720.452.88E-053.55E-07
03.4119.312.14E-056.17E-07
04.5418.181.70E-051.02E-06
05.6817.041.32E-051.45E-06
06.8215.901.05E-051.95E-06
07.9514.778.32E-062.46E-06
09.0313.636.76E-063.16E-06
10.2212.505.50E-063.72E-06
```

```
50.0  .431  .151PT-ASP 18A
1.4034E-04      6.1867E-05
1.5854E-04      6.8859E-05
1.9600E-04      6.8194E-05
1.7457E-04      7.0277E-05
1.8663E-04      7.0484E-05
1.7562E-04      7.6451E-05
1.8024E-04      8.0556E-05
1.5502E-04      9.3510E-05
K1=  1.7087E-04   K2=  7.3775E-05
      3.771                 4.136


25.0  .022  .008PT-GLU 17B
3.6251E-05      7.0017E-06
3.9661E-05      7.7639E-06
4.2819E-05      8.4329E-06
4.4020E-05      8.6341E-06
4.5009E-05      9.3414E-06
4.2718E-05      1.0214E-05
4.2612E-05      1.0082E-05
3.6137E-05      1.1573E-05
K1=  4.1154E-05   K2=  9.1306E-06
      4.390                 5.045


50.0  .011  .008PT-ADIP17A
2.6390E-05      1.9879E-06
2.8928E-05      2.8690E-06
2.9730E-05      3.1607E-06
2.8406E-05      4.0146E-06
3.1727E-05      3.4902E-06
2.7232E-05      2.4696E-06
3.3089E-05      3.5665E-06
3.4196E-05      3.5754E-06
K1=  2.9962E-05   K2=  3.1417E-06
      4.528                 5.509


50.0  .009  .008PT-PIM 16B
1.8294E-05      3.0180E-06
1.7623E-05      3.5958E-06
1.7725E-05      3.9653E-06
1.7440E-05      4.3945E-06
1.7537E-05      4.7358E-06
1.7008E-05      4.8933E-06
1.6668E-05      4.9968E-06
2.0608E-05      4.2510E-06
K1=  1.7863E-05   K2=  4.2313E-06
      4.753                 5.379
```

```
50.0  .032  .151PDASP  24B
1.6598E-04     7.8880E-06
1.8103E-04     1.0502E-05
1.7287E-04     1.2232E-05
2.0409E-04     1.1767E-05
2.2913E-04     1.2349E-05
2.0006E-04     1.4680E-05
1.9088E-04     1.7045E-05
1.9108E-04     1.8263E-05
K1=  1.9189E-04  K2=   1.3091E-05
        3.721                4.888


50.0  .077  .151PD ASP  24A
2.6870E-05     1.4190E-05
3.3417E-05     1.5146E-05
4.2680E-05     1.6390E-05
4.7419E-05     1.9015E-05
4.4956E-05     2.3367E-05
4.8444E-05     2.4794E-05
4.3217E-05     3.0658E-05
5.1175E-05     2.7882E-05
K1=  4.2272E-05  K2=   2.1430E-05
        4.378                4.674


24.8  .041  .025PD-ASP  P73
1.4167E-04     3.7875E-05
1.6506E-04     3.3540E-05
1.6486E-04     3.2450E-05
1.8832E-04     2.9823E-05
2.2381E-04     2.8584E-05
2.4662E-04     3.0473E-05
2.5965E-04     2.8198E-05
2.9716E-04     2.4561E-05
K1=  2.1089E-04  K2=   3.0688E-05
        3.680                4.518


40.0  .073  .146PD-GLU  P93
5.2756E-06     2.0940E-06
6.9579E-06     3.1546E-06
7.9639E-06     4.3593E-06
8.6017E-06     5.1652E-06
9.2593E-06     5.4550E-06
9.5833E-06     5.9220E-06
1.0834E-05     5.4481E-06
1.4593E-05     3.9851E-06
K1=  9.1336E-06  K2=   4.4479E-06
        5.045                5.357
```

50.0 .068 .151 PD ADIP23

| | |
|---|---|
| 2.3706E-05 | 8.3975E-06 |
| 2.8982E-05 | 9.2246E-06 |
| 3.2764E-05 | 1.0128E-05 |
| 3.7460E-05 | 9.6988E-06 |
| 3.6542E-05 | 9.8413E-06 |
| 4.1780E-05 | 8.9921E-06 |
| 4.2729E-05 | 8.6659E-06 |
| 4.5040E-05 | 9.0640E-06 |

K1= 3.6125E-05   K2= 9.2516E-06
4.447                 5.039

50.0 .042 .095PDADIP 40A

| | |
|---|---|
| 1.5927E-04 | 1.2430E-05 |
| 1.4635E-04 | 1.5475E-05 |
| 1.4741E-04 | 1.5674E-05 |
| 1.3392E-04 | 1.7510E-05 |
| 1.3800E-04 | 1.6813E-05 |
| 1.2532E-04 | 1.8044E-05 |
| 1.0475E-04 | 1.9856E-05 |
| 9.1188E-05 | 2.2161E-05 |

K1= 1.3078E-04   K2= 1.7245E-05
3.887                 4.768

50.0 .024 .008PDPIM 15B

| | |
|---|---|
| 2.2560E-05 | 3.8751E-06 |
| 2.3310E-05 | 4.3197E-06 |
| 2.5064E-05 | 4.7733E-06 |
| 2.6844E-05 | 4.8124E-06 |
| 2.8702E-05 | 4.7437E-06 |
| 2.8544E-05 | 4.9594E-06 |
| 3.0394E-05 | 4.8657E-06 |
| 2.8630E-05 | 5.5072E-06 |

K1= 2.6756E-05   K2= 4.7321E-06
4.577                 5.330

APPENDIX E

POLAROGRAPHIC TRACINGS

+.4  0 -.4 -.8 -1.2 -1.6 R -1.6 -1.2 -.8 -.4  0
VOLTS
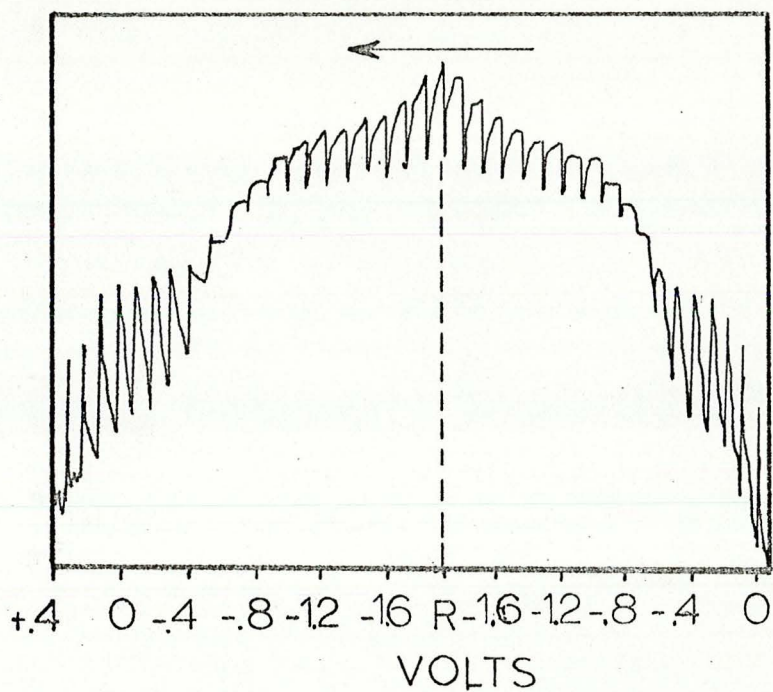
Potassium tetra chloro palladate(II)
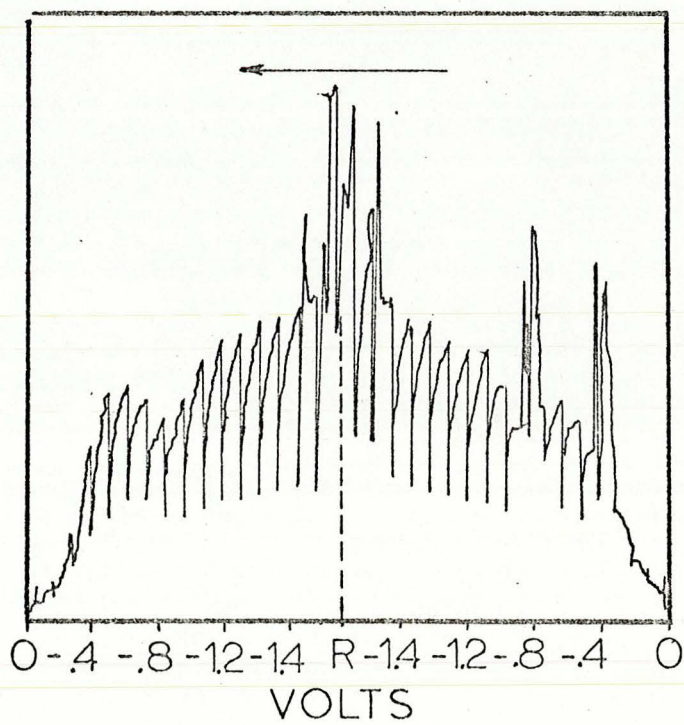


0 -.4 -.8 -1.2 -1.4 R -1.4 -1.2 -.8 -.4  0
VOLTS

Bis hydrogen alpha amino adipato palladium (II)

O     -.4     -.8     -1.2     -1.6 -1.6     -1.2     -.8     -.4     O

**VOLTS**

Bis hydrogen aspartato platinum (II)



O     -.4     -.8     -1.2     -1.2     -.8     -.4     O

**VOLTS**
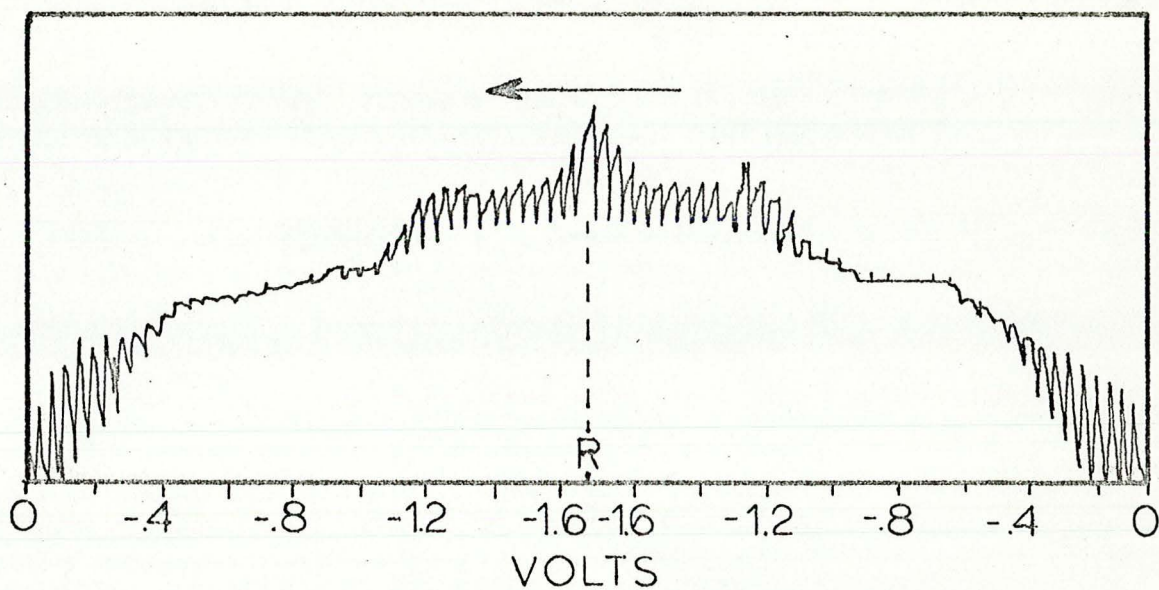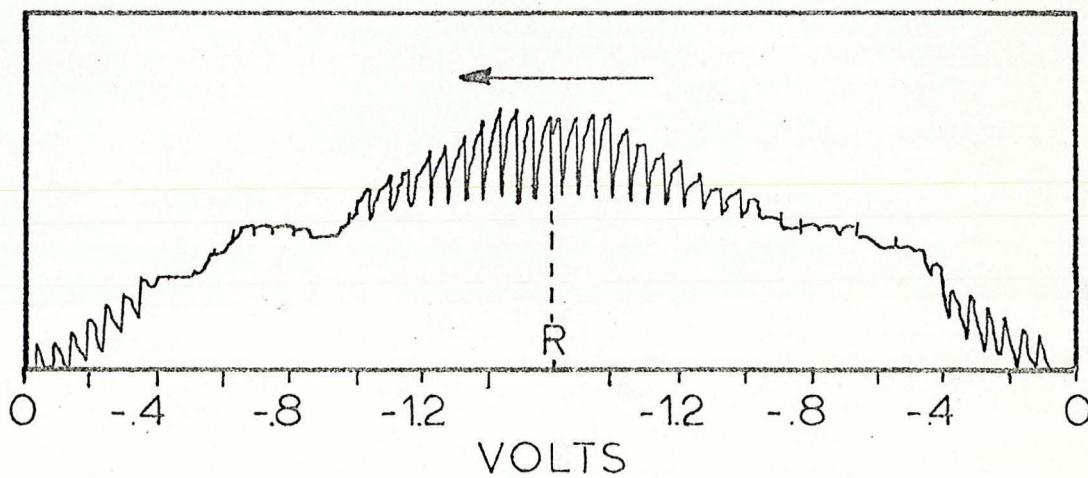
Bis hydrogen alpha amino adipato palladium (II)

APPENDIX F·

TITRATION DATA FOR STABILITY CONSTANTS

0.0817 g $K_2PdCl_4$

0.0679 g Aspartic Acid

0.0933 g K Cl

Volume - 50.0 ml.

0.0952 M  KOH

| Volume | pH |
|---|---|
| 0.00 | 2.29 |
| 1.00 | 2.40 |
| 2.00 | 2.56 |
| 3.25 | 2.74 |
| 4.50 | 3.05 |
| 5.75 | 3.38 |
| 7.00 | 3.72 |
| 8.01 | 4.02 |
| 9.00 | 4.42 |
| 10.00 | 5.43 |
| 10.07 | 5.59 |
| 10.18 | 6.29 |
| 10.20 | 6.83 |
| 10.24 | 7.62 |
| 10.27 | 8.20 |
| 10.30 | 8.57 |
| 10.50 | 9.59 |
| 10.75 | 10.15 |
| 11.00 | 10.48 |

0.0817 g $K_2PdCl_4$
0.0883 g Glutamic Acid
Volume - 50.0 ml.
0.0952 M KOH

| Volume | pH |
| --- | --- |
| 0.00 | 2.35 |
| 1.00 | 2.43 |
| 2.00 | 2.61 |
| 3.00 | 2.80 |
| 4.00 | 3.03 |
| 5.00 | 3.32 |
| 6.00 | 3.66 |
| 7.00 | 3.97 |
| 8.00 | 4.27 |
| 9.00 | 4.53 |
| 10.00 | 4.88 |
| 10.50 | 5.12 |
| 11.00 | 5.48 |
| 11.25 | 5.77 |
| 11.50 | 6.84 |
| 11.57 | 7.81 |
| 11.61 | 8.20 |
| 11.67 | 8.49 |
| 11.75 | 8.75 |
| 12.00 | 9.19 |

0.0817 g $K_2PdCl_4$

0.0821 g a-Amino Adipic Acid

0.0933 g K Cl

Volume - 50.0 ml.

0.0952 M KOH

| Volume | pH |
|--------|------|
| 0.00 | 2.53 |
| 1.00 | 2.64 |
| 2.00 | 2.82 |
| 3.00 | 3.11 |
| 4.00 | 3.53 |
| 5.00 | 3.88 |
| 6.00 | 4.13 |
| 7.00 | 4.40 |
| 8.00 | 4.67 |
| 9.00 | 5.03 |
| 9.50 | 5.33 |
| 10.00 | 5.80 |
| 10.25 | 6.70 |
| 10.50 | 7.96 |
| 11.02 | 9.50 |

0.0817 g $K_2PdCl_4$

0.0893 g a-Amino Pimelic Acid

0.0933 g K Cl

Volume - 50.0 ml

0.0952 M KOH

| Volume | pH |
|--------|------|
| 0.00 | 2.43 |
| 1.00 | 2.62 |
| 2.00 | 2.90 |
| 3.00 | 3.33 |
| 4.00 | 3.78 |
| 5.02 | 4.11 |
| 6.00 | 4.40 |
| 7.00 | 4.70 |
| 8.00 | 5.09 |
| 9.00 | 5.69 |
| 9.25 | 6.01 |
| 9.50 | 6.92 |
| 9.60 | 7.47 |
| 9.65 | 7.64 |
| 9.70 | 7.87 |
| 9.75 | 8.05 |
| 9.90 | 8.82 |
| 10.00 | 9.33 |

0.1038 g $K_2PtCl_4$

0.0729 g Aspartic Acid

Volume - 50.0 ml.

0.0952 M KOH

| Volume | pH |
|--------|------|
| 0.00 | 2.69 |
| 1.00 | 2.93 |
| 2.00 | 3.22 |
| 3.00 | 3.52 |
| 4.00 | 3.81 |
| 5.00 | 4.13 |
| 6.00 | 4.61 |
| 6.50 | 5.18 |
| 6.75 | 5.87 |
| 6.85 | 6.23 |
| 6.95 | 6.56 |
| 7.00 | 6.68 |
| 7.05 | 6.78 |
| 7.10 | 6.88 |
| 7.15 | 6.98 |
| 7.20 | 7.07 |
| 7.25 | 7.14 |
| 7.30 | 7.22 |
| 7.40 | 7.39 |
| 7.50 | 7.55 |
| 7.70 | 7.90 |
| 8.00 | 8.42 |
| 8.25 | 8.72 |
| 8.50 | 8.98 |

0.1038 g $K_2PtCl_4$

0.0833 g Glutamic Acid

0.0933 g K Cl

Volume - 50.0 ml.

0.0952 M   KOH

| Volume | pH |
|--------|------|
| 0.00 | 2.93 |
| 1.00 | 3.28 |
| 2.00 | 3.61 |
| 3.00 | 3.90 |
| 4.00 | 4.16 |
| 5.00 | 4.43 |
| 6.00 | 4.79 |
| 6.50 | 5.03 |
| 6.75 | 5.21 |
| 7.00 | 5.51 |
| 7.26 | 6.11 |
| 7.28 | 6.21 |
| 7.38 | 6.61 |
| 7.41 | 6.79 |
| 7.50 | 6.98 |
| 7.54 | 7.08 |
| 7.62 | 7.29 |
| 7.67 | 7.41 |
| 7.75 | 7.62 |
| 8.00 | 8.16 |
| 8.50 | 8.71 |
| 9.00 | 9.00 |

0.1038 g $K_2PtCl_4$

0.0821 g a-Amino Adipic Acid

0.0933 g K Cl

Volume - 50.0 ml.

0.0952 M KOH

| Volume | pH |
|--------|------|
| 0.00 | 2.44 |
| 1.00 | 2.63 |
| 2.00 | 2.90 |
| 3.00 | 3.30 |
| 4.00 | 3.72 |
| 5.00 | 4.05 |
| 6.20 | 4.42 |
| 7.26 | 4.76 |
| 8.25 | 5.10 |
| 8.65 | 5.30 |
| 9.02 | 5.52 |
| 9.25 | 5.68 |
| 9.50 | 6.00 |
| 9.70 | 6.45 |
| 9.80 | 6.89 |
| 9.90 | 7.51 |
| 10.00 | 8.02 |
| 10.05 | 8.45 |

0.1038 g $K_2PtCl_4$
0.0893 g a-Amino Pimelic Acid
0.1093 g K Cl
Volume - 50.0 ml.
0.0952 M KOH

| Volume | pH |
|--------|------|
| 0.00 | 3.60 |
| 1.00 | 3.96 |
| 2.00 | 4.30 |
| 3.00 | 4.57 |
| 4.00 | 4.87 |
| 5.00 | 5.42 |
| 5.50 | 6.20 |
| 5.75 | 6.70 |
| 6.00 | 7.03 |
| 6.10 | 7.18 |
| 6.20 | 7.30 |
| 6.30 | 7.44 |
| 6.40 | 7.59 |
| 6.52 | 7.78 |
| 6.60 | 7.92 |
| 6.70 | 8.07 |
| 7.00 | 8.43 |
| 7.50 | 8.79 |