

RECEIVED BY DTIE FEB 13 1970

IS-T-329

AMES LABORATORY

Iowa State University

Ames, Iowa

MASTER

AEC Contract No. W-7405-eng-82

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

SUBSTITUTION REACTIONS OF DICHLORO (ETHYLENEDIAMINE)
PLATINUM (II)

by

Ronald Frank Coley

Ph. D. Thesis, November 1969

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

feg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SUBSTITUTION REACTIONS OF DICHLORO(ETHYLENEDIAMINE)PLATINUM(II)

by

Ronald Frank Coley

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subjects: Inorganic Chemistry
Physical Chemistry

Approved:

Don S. Martin

Don S. Martin

In Charge of Major Work

J D Corbett/PAK

J D Corbett by JHespenson

Heads of Major Departments

J B. Page

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

November 1969

TABLE OF CONTENTS

	Page
ABSTRACT	v
I. INTRODUCTION	1
A. Nature and Purpose of the Research	1
B. Background Pertaining to Spectra	1
C. Background Pertaining to Kinetics and Equilibria	7
II. MATERIALS AND EQUIPMENT	11
III. EXPERIMENTAL APPARATUS AND TECHNIQUES	16
A. Aquation Equilibria	16
B. Aquation Kinetics	18
C. Anation Kinetics for the Diaquo Species	23
D. Anation Kinetics for the Monoaquo Species	25
IV. TREATMENT OF EXPERIMENTAL DATA	28
A. Aquation Equilibria	28
B. Aquation Kinetics	35
C. Anation Kinetics for the Diaquo Species	40
D. Anation Kinetics for the Monoaquo Species	45
V. RESULTS	49
A. Aquation Equilibria	49
B. Aquation Kinetics	55
C. Anation Kinetics for the Diaquo Species	60
D. Anation Kinetics for the Monoaquo Species	64
VI. DISCUSSION	73
A. Spectra	73
B. Kinetics and Equilibria	77
VII. LITERATURE CITED	89

TABLE OF CONTENTS (Continued)

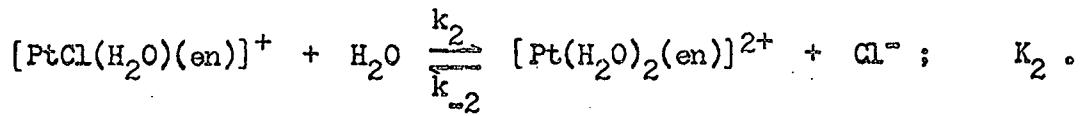
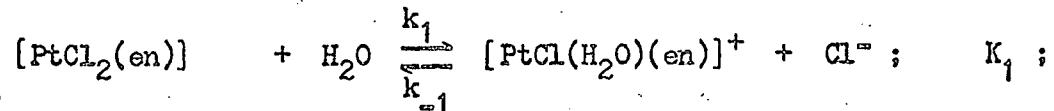
	Page
VIII. ACKNOWLEDGMENTS	93
IX. APPENDIX	94

SUBSTITUTION REACTIONS OF DICHLORO(ETHYLENEDIAMINE)PLATINUM(II)*

Ronald Frank Coley

Under the supervision of Don S. Martin, Jr.
 From the Department of Chemistry
 Iowa State University of Science and Technology

Kinetics and equilibria for the successive aquation reactions of dichloro(ethylenediamine)platinum(II) have been studied spectrophotometrically and by means of titrations of the acidic protons on the H_2O ligands formed according to the reactions:



Titrations of equilibrium solutions were performed over the range of 10^{-4} M to 10^{-3} M total complex concentration at an ionic strength of 0.318 M for $25^\circ C$, $30^\circ C$ and $35^\circ C$. For $25^\circ C$: $K_1 = 2.19 \pm 0.11 \times 10^{-3}$ M; $\Delta H^\circ_1 = 4$ kcal mole $^{-1}$ and $K_2 = 1.43 \pm 0.11 \times 10^{-4}$ M; $\Delta H^\circ_2 = -1$ kcal mole $^{-1}$. Values for k_{-1} and k_{-2} were determined spectrophotometrically from the relaxation periods when high chloride concentrations were added to equilibrium solutions. At $25^\circ C$: $k_{-1} = 1.54 \pm 0.03 \times 10^{-2}$ sec $^{-1}$ M $^{-1}$; $k_{-2} = 3.11 \pm 0.35 \times 10^{-1}$ sec $^{-1}$ M $^{-1}$. Values for k_1 were determined spectrophotometrically and from pH-stat studies in basic solutions. From the values for the concentration equilibrium quotient and the specific rate constant for anation of

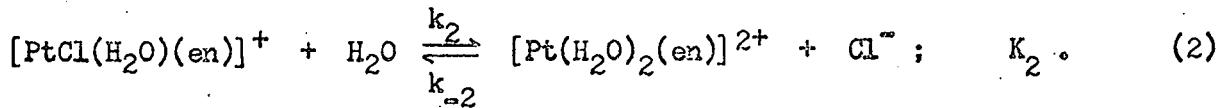
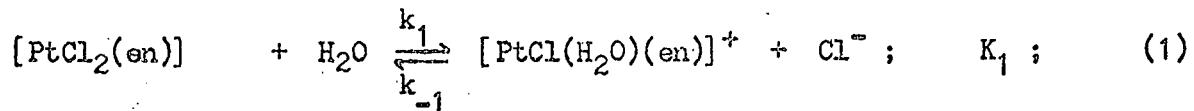
* USAEC Report IS-T-329. This work was performed under Contract W-7405-eng-82 with the Atomic Energy Commission.

the diaquo species, the rate constant k_2 was evaluated. At 25°C: $k_1 = 3.4 \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$; $k_2 = 4.45 \pm 0.61 \times 10^{-5} \text{ sec}^{-1}$ with the associated activation parameters: $\Delta H^{\ddagger}_1 = 21 \text{ kcal mole}^{-1}$; $\Delta H^{\ddagger}_2 = 8 \text{ kcal mole}^{-1}$; $\Delta S^{\ddagger}_1 = -16 \text{ eu}$; $\Delta S^{\ddagger}_2 = -51 \text{ eu}$.

I. INTRODUCTION

A. Nature and Purpose of the Research

The subject of this investigation is the successive aquation reactions of dichloro(ethylenediamine)platinum(II), $[\text{PtCl}_2(\text{en})]$, and the chloride aquation of the resultant aquo complexes. The chemical system of interest may be described by the reversible reaction sequence:



This research has as its main objective the determination of the specific rate constants, k_1 , k_{-1} , k_2 , and k_{-2} , and of the related concentration equilibrium quotients, K_1 and K_2 .

B. Background Pertaining to Spectra

Since many of the kinetic studies which were conducted during the course of this work involved utilization of the electronic absorption spectra of the complex species, and since certain fascinating spectral phenomena were observed by this worker, it seems pertinent, and interesting in itself, to briefly outline the development of the theory of such spectra as related to square-planar complexes of platinum(II). Such complexes have been known to exist at least since 1828 when Magnus (1) prepared the deeply colored, green salt which is now known to be $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$. The possibility of the square-planar configuration, as an alternative for the tetrahedral configuration, was first proposed by Alfred Werner (2) in 1893.

One of the first steps towards the description of electronic absorption

spectra was an electrostatic or Crystal Field Theory (CFT) such as that which was utilized by Bethe (3). Ilse and Hartmann (4), and others, applied CFT to coordination compounds. In its original form, CFT considered that the ligands seemed to provide an electrostatic field which perturbed the orbitals of a central metal ion. Consequently, bonding, especially the covalent contribution to the bonds, was ignored. When applied to coordination complexes in solution, the theory is usually termed Ligand Field Theory (LFT).

An alternative treatment utilized techniques developed by Hückel (5) for conjugated organic systems to provide a molecular orbital (MO) description for coordination compounds. This method involves linear combinations of atomic orbitals (LCAO). Wolfsberg and Helmholz (6) used such an extended Hückel model in applications to some tetrahedral ions. Their approach is sometimes referred to as the Mulliken-Wolfsberg-Helmholz (MWH) method. The MWH method has been modified by Ballhausen and Gray (7) and subsequently applied to a number of transition metal complexes. Some authors have questioned the reliability of the MWH method in such applications, and considerable controversy has appeared in the literature among the opinions of Gray, Ballhausen, et al. (7-10); Cotton, Harris, et al. (11-13); and, Fenske, et al. (14-16).

Utilizing either MO or LFT one can attempt to explain the electronic absorption spectra of square-planar complexes, such as $[\text{PtCl}_4]^{2-}$. For purposes of the following discussion, the ligands have been chosen to lie along the x and y axes of a right-handed Cartesian coordinate system with the platinum atom located at the origin. Such square-planar complexes, with four equivalent ligands, belong to the point group D_{4h} . Considering

the MO approach, if one used as a basis set the $(n-1)d$, ns, and np metal atomic orbitals (AO), and the ns and np ligand AO, using group theoretical principles (17), one can obtain the "symmetry-adapted" ligand molecular orbitals (LMO) and the "symmetry-adapted" metal atomic orbitals (MAO). The one-electron MO's for the complex are then constructed as linear combinations of the LMO's and the MAO's, wherein symmetry considerations prohibit combination of components which belong to different irreducible representations of the group.

In terms of LFT, the absorption spectra result from transitions within the metal d-orbital levels. According to MO theory, these transitions occur among the MO levels which are predominantly metal d-orbital in character. Thus, it is qualitatively correct to correlate the MO levels with the LFT d-orbital levels.

Again, in terms of LFT, the actual ordering of the d-orbital levels in such complexes can be approximated from a simple electrostatic approach. Thus, if one considers forming a square-planar electrostatic field by removing the charges from along the z-axis of an octahedral field, one expects a progressive shift in the d-orbital energy levels as indicated in Figure 1. In this figure, the effect has been indicated at three stages. The question remains for experiment and theoretical calculations to determine which configuration of Figure 1 applies to square-planar complexes. The state of the theory is such that it is not possible to provide a distinction between the possible orderings of Figure 1.

In the past, various workers have proposed ordering A (18). Others have proposed configuration B (8, 19). Still others have suggested that configuration C best represents the physical situation in square-planar

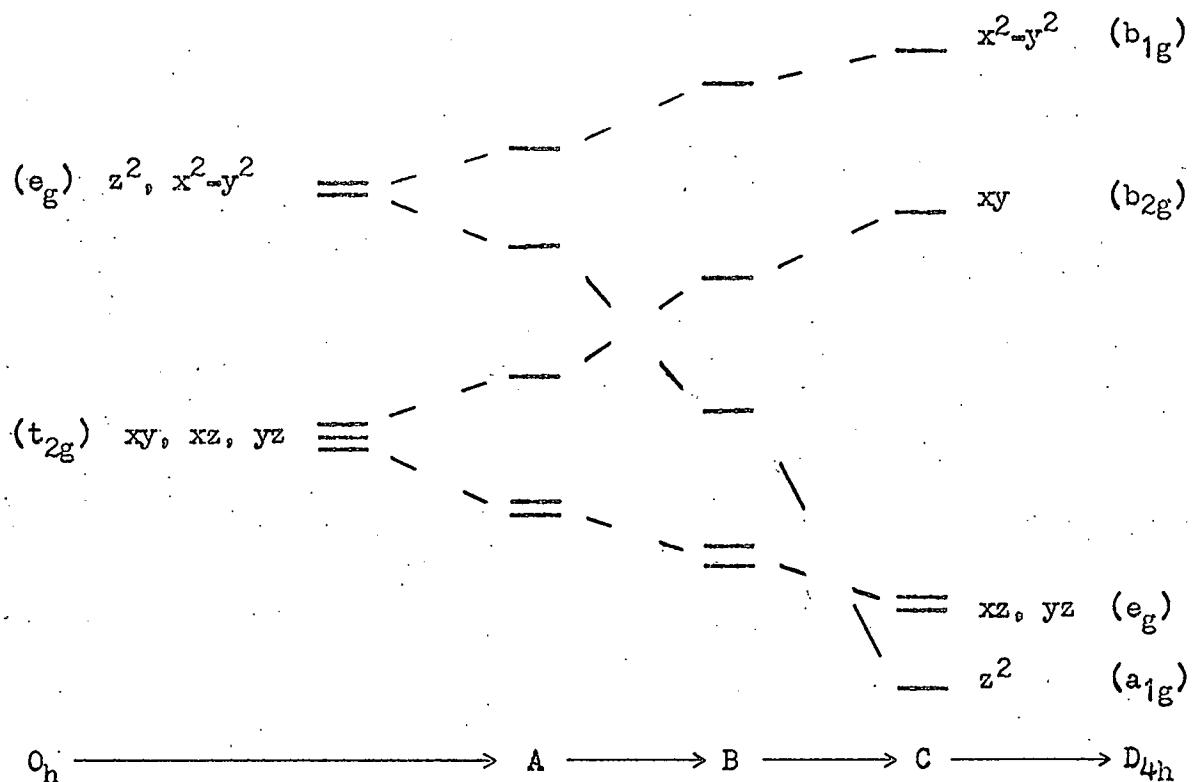


Figure 1. Qualitative effect on the d orbitals at various stages of removing the charges from along the z-axis of an octahedral field

complexes (10, 12, 20). The question of energy level ordering for the $[\text{PtCl}_4]^{2-}$ ion was not resolved until low temperature spectra using polarized light were analyzed for single crystals of $\text{K}_2[\text{PtCl}_4]$ (21). Such spectra, when considered in conjunction with the magnetic circular dichroism studies of Martin, *et al.* (22), later corroborated by McCaffery, Schatz and Stephens (23), have provided rather decisive support for the ordering C of Figure 1. Mason and Gray (24) have recently reported results of spectra for square-planar complexes recorded in non-aqueous media which they interpreted according to ordering C. It now seems that the latter ordering of Figure 1 is commonly accepted as the best approximation to the physical reality for $[\text{PtCl}_4]^{2-}$.

A Gaussian analysis of the spectrum of $[\text{PtCl}_4]^{2-}$ in aqueous solution shows two moderately intense bands which are associated with the singlet-singlet $\text{xy} \rightarrow \text{x}^2-\text{y}^2$ and $(\text{xz}, \text{yz}) \rightarrow \text{x}^2-\text{y}^2$ transitions. The two corresponding spin-forbidden transitions are assigned to the two less intense peaks at longer wavelengths. Presumably, the spin-allowed $\text{z}^2 \rightarrow \text{x}^2-\text{y}^2$ transition energy is such that the associated band is masked by the intensity of the charge transfer band. Mason and Gray (24), for example, on the basis of their work in non-aqueous media, have assigned the $\text{z}^2 \rightarrow \text{x}^2-\text{y}^2$ band in the region of the charge transfer band.

Chatt, Gamen and Orgel (20) state that since the positions of the absorption bands for the entire series of Pt(II) chloro-ammine complexes show regular shifts to shorter wavelengths as the chloride ligands are successively replaced by ammonia ligands, one can generalize the description used for $[\text{PtCl}_4]^{2-}$ onto the entire series. These workers continue by stating that the lower symmetry of some of the complexes is expected to only slightly modify the character of the orbitals involved. Thus, they conclude, the approximate description of the $\text{d} \rightarrow \text{d}$ transitions retains its meaning. In fact, however, the differences may not be as subtle as the above statement implies. Consider, for example, $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$, which has C_{2v} symmetry. For such a complex, the coordinate system of Figure 2 is acceptably consistent with the convention of taking the z -axis as the major rotational axis. Such a choice of axes results in a correlation between the d orbitals in D_{4h} and C_{2v} symmetries as indicated by the diagram of Table 1. As one can see, the description of transitions in C_{2v} symmetry in terms of the related $\text{d} \rightarrow \text{d}$ transitions in D_{4h} symmetry is indeed approximate. It also seems pertinent to note that the metal p_x , p_y and p_z or-

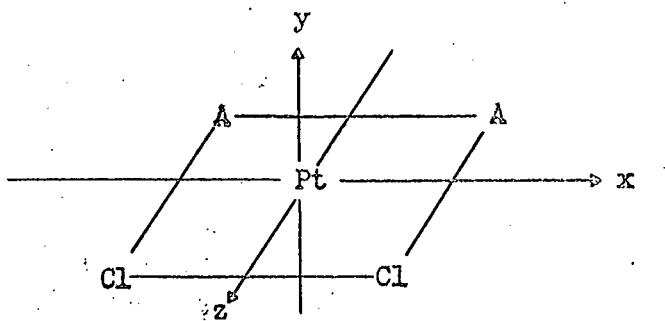


Figure 2. Coordinate system for square-planar Pt(II) complex with C_{2v} symmetry. For the discussion herein presented, $A = NH_3$

Table 1. Correlation between d orbitals in D_{4h} and C_{2v} symmetries

D_{4h} representations and orbitals	C_{2v} representations and orbitals
b_{1g}	x^2-y^2
b_{2g}	xy
e_g	xz, yz
a_{1g}	z^2

bitals transform as b_1 , b_2 and a_1 , respectively, in C_{2v} symmetry. This results in some mixing of p and d orbitals which should provide a mechanism for band intensification even without invoking vibronic coupling. In fact, the intensities of the bands for cis- $[PtCl_2(NH_3)_2]$ are somewhat greater than the observed intensities of the $[PtCl_4]^{2-}$ bands (20). Furthermore, one can predict the polarization of electric dipole transitions under C_{2v} symmetry. Using the two hole formalism for Pt(II), one can easily derive the selection rules of Table 2. Thus, if one were fortunate enough to have available single crystals in which the molecular plane was oriented perpendicular to the crystal surface, studies of absorption spectra using polar-

Table 2. Selection rules for electric dipole transitions for Pt(II) complexes of C_{2v} symmetry

Transition	x	y	z
$B_1 \rightarrow A_1$	allowed	forbidden	forbidden
$A_2 \rightarrow A_1$	forbidden	forbidden	forbidden
$B_2 \rightarrow A_1$	forbidden	allowed	forbidden

ized light could provide valuable information pertinent to the assignment of absorption bands.

C. Background Pertaining to Kinetics and Equilibria

A very large number of kinetic studies of substitution reactions of square-planar Pt(II) complexes has been reported in the literature. The development of such work has been presented in review articles and texts (25-28). In a recent review article, Martin (29) has outlined the development of theories related to ligand substitution reactions of square-planar complexes of platinum(II).

It is now generally accepted that Pt(II) complexes undergo ligand substitution by an associative nucleophilic displacement process involving a five-coordinated transition state of roughly trigonal bipyramidal configuration. As indicated by the reactions of Equations 1 and 2, such ligand substitution processes may be reversible, resulting in the establishment of equilibria. To simplify the treatment of the kinetics, it is common to study such ligand substitution reactions under pseudo first-order conditions. Such utilization of a large excess of the nucleophile may drive the ligand exchange near enough to completion to permit the neglecting of the

reversibility. Then, if the rate of replacement of a solvent ligand by the nucleophile is sufficiently rapid, the concentration of solvent-containing species may be held insignificant. Under such conditions, one obtains the rate law for what is considered to be the normal mode of ligand substitution reactions for Pt(II) complexes, namely: Rate = complex ($k_1 + k_y Y$). The constant k_1 is the specific rate constant for ligand substitution by solvent which is then rapidly replaced by the nucleophile; the constant k_y refers to the direct substitution by the nucleophile.

The question of whether or not substitution reactions of square-planar complexes of platinum(II) involve a trigonal bipyramidal intermediate has been discussed by Langford and Gray (28). These authors propose the existence of such an intermediate since the resultant mechanism is able to account for all available data.

Seeking an ordering of nucleophiles in terms of their reactivities, and desiring to observe the effect of changing the substrate platinum complex on reactivities, Belluco, *et al.* (30) defined a nucleophilic reactivity, n_{Pt} , as $\log(k_y/k_1)$ for trans-[PtCl₂(py)₂] (py = pyridine) in methanol at 30.0°C. They noted that for several other neutral substrates the data was well represented by the expression: $\log(k_y/k_1)_i = s_i n_{Pt} + \log(k_1)_i$, where s_i was called the nucleophilic discrimination factor for the *i*th substrate. Their ordering of nucleophiles was in agreement with the "hard and soft" concept of acid and bases which had been proposed by Pearson (31). For example, ligand replacement by hydroxide, which is normally considered to be a strong nucleophile, is immeasurably slow for the "soft" Pt(II) complexes when compared with the solvation process in aqueous media.

Finally, it must be noted that several exceptions to the "normal"

ligand replacement behavior have been observed in isotopic exchange studies. Isotopic exchange of ligands is usually considered to be only a special case of ligand exchange; however, investigations outside the pseudo first-order regions have demonstrated processes involving dimer transition states (32-34).

Concentration equilibrium quotients associated with ligand substitution reactions which form aquo species have been determined by a variety of methods. Grinberg and Shagisultanova (35) utilized titration of the aquo complexes with hydroxide, as did Nikolaeva and Pastukhova (36). In the application of a titrimetric method, Grantham, Elleman and Martin (37) found that it was necessary to correct titration data for the amount of hydrolysis which had occurred during the titration. Martin *et al.* (37-42) have used this method for the entire chloroammine series of Pt(II) complexes, as well as for some bromo complexes (33, 43). A radiochemical technique provided Martin and Bahn (44) with a direct measurement of the equilibrium quotient for the aquation reaction of $[\text{PtBr}(\text{dien})]^+$ (dien = diethylenetri-amine). Elding and Leden (45) have utilized spectrophotometric measurements with the subsequent application of the method of corresponding solutions (46) to determine the concentration equilibrium quotients for the aquation reactions of $[\text{PtCl}_4]^{2-}$. They also determined the constant for the second step from spectrophotometric measurements following anion exchange separation of negatively charged species from uncharged species. Their value for the concentration equilibrium quotient for the first aquation reaction agreed well with the ratio of the forward and reverse rate constants which they independently measured. Typically, such determinations have yielded values for concentration equilibrium quotients with errors of the order of

ten percent. Possibly the spectrophotometric method of determining successive formation constants described by Newman and Hume (47) deserves some attention.

II. MATERIALS AND EQUIPMENT

The method described by Basolo, Bailer and Tarr (48) was used, in a slightly modified form, to prepare $[\text{PtCl}_2(\text{en})]$. One modification consisted of dissolving the starting material, $\text{K}_2[\text{PtCl}_4]$, in 0.05 M HCl, rather than in water, and adding enough 5% aqueous ethylenediamine to both neutralize the acid and effect 80% conversion. Instead of adding portions of the ethylenediamine and occasionally stirring, the ethylenediamine was allowed to slowly drip from a burette into the $\text{K}_2[\text{PtCl}_4]$ solution over a period of several hours with constant stirring. The process was interrupted every hour or so and the product was collected. Usually, the last fraction contained the coordination polymer, $[\text{Pt}(\text{en})_2][\text{PtCl}_4]$, and was therefore discarded. The yield of small, yellow-green crystals was typically about 60%.

The product from such preparations was recrystallized, in small portions, from water to which chloride had been added. A satisfactory, although slow, recrystallization procedure consisted of adding about 0.5 gram of the compound to a beaker containing 200 ml of 0.05 M HCl and warming to 65°C in a water bath with constant stirring. (Temperatures much greater than 75°C resulted in decomposition, as evidenced by the deposition of a platinum mirror on the beaker.) After one or two hours, the solution was rapidly filtered through a steam-heated Büchner funnel, poured into a petri dish and covered. Crystallization proceeded rapidly at first, then more slowly for the next several days. The resultant bright yellow needles were collected by filtration, washed with 0.05 M HCl, alcohol and ether, respectively. The recrystallization yield was also about 60%.

The $[\text{PtCl}_2(\text{en})]$ which was used for the studies described in this work

came from two preparations. The analyses for these preparations are given in Table 3.

Table 3. Results of elemental analyses for the two preparations of the complex, $[\text{PtCl}_2(\text{en})]$, used for studies described in this work. Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois. The listed analytical results for the recrystallized product of the first preparation are average values for two determinations of each element

Element	% analytical (crude product)	% analytical (recrystallized)	% calculated
Platinum	59.44	59.41	59.82
Carbon	7.54	7.38	7.37
Hydrogen	2.57	2.48	2.47
Nitrogen	8.22	8.28	8.59
Chlorine	21.99	21.89	21.74
Platinum	60.16	59.35	59.82
Carbon	7.53	7.42	7.37
Hydrogen	2.43	2.49	2.47
Nitrogen	8.66	8.89	8.59
Chlorine	21.83	22.06	21.74

Although, to within the accuracy of such analyses, one could say that the complex was recrystallized to constant composition, it is recognized that one main impurity is a coordination polymer and therefore would be undetectable by elemental analysis. In cases such as this, perhaps the uv absorption spectrum provides a better criterion of purity than does the elemental analysis. Since the absorption at a valley in such spectra is highly sensitive to impurities, it is customary to use the ratio of absorbances, measured at a maximum and at a minimum (the peak to valley ratio), as a criterion of purity. For $[\text{PtCl}_2(\text{en})]$, the peak (300 nm) to valley

(245 nm) ratio increases markedly upon recrystallization. In some cases this increase amounted to a factor of two or three. A peak to valley ratio of approximately seven has been accepted by this worker as representative of pure $[\text{PtCl}_2(\text{en})]$ (>99%).

The ethylenediamine which was used in the preparations of the complex had been freshly distilled using a fractionating column packed with 1/8 inch glass helices. The boiling point range of the organic fraction which was collected from such distillations was 116.5-117.0°C. The 5% aqueous ethylenediamine solutions were prepared as soon as possible after distillation since such dilute solutions were more resistant toward decomposition than was the pure organic.

The $\text{K}_2[\text{PtCl}_4]$ was prepared from iridium-free $\text{K}_2[\text{PtCl}_6]$ (39) by reduction with freshly prepared SO_2 solution according to the method of Keller (49).

All other reagents were analytical reagent grade chemicals which were certified to meet A. C. S. standards. All water was drawn from the laboratory distilled water tap, redistilled from alkaline permanganate and again distilled through a fractionating column.

Weighings of salts used for ionic strength adjustment were performed on an Ohaus "Cent-O-Gram" triple beam balance, Model 311. This is a 311 gram capacity balance calibrated to 0.01 gram units. When precise weighings of small quantities were desired, such as weighings of the complex, a Sartorius single pan analytical balance, Model 2404, was used. This device is a 100 gram capacity, five place, digital read-out balance with a precision (standard deviation) of ± 0.01 mg.

The acid-base titrations and the pH-stat studies were conducted using

a Radiometer SBR2c/ABU1c/TTA3 automatic recording titration apparatus in conjunction with either a 2.500 ml burette with an accuracy of $2.5 \mu\text{l} \pm 0.5\%$ or a 0.2500 ml burette with an accuracy of $1 \mu\text{l} \pm 0.7\%$. The titration vessel was equipped with a water jacket for temperature control and with a gas inlet tube for atmosphere control. In all such studies, a slight positive pressure was maintained in the vessel by bubbling grade "A" purified nitrogen through the solution and allowing the gas to escape through the electrode and gas inlet fittings. Prior to admission into the vessel, the nitrogen was passed through a tower containing Ascarite.

The constant temperature baths were Sargent water baths controlled by Sargent micro-set thermoregulators, relays and combination circulating-heating towers. For 25.0°C and 30.0°C a cold tap water cooling coil was also employed. The desired temperature was set to match the corrected reading on a 0.1°C thermometer which had been calibrated by the National Bureau of Standards. At 25.0°C and 30.0°C , the temperature variations in the baths were less than $\pm 0.05^\circ\text{C}$, as measured by a Beckman six degree differential thermometer which was calibrated in 0.01°C units. At 35.0°C , the temperature was controlled to within $\pm 0.08^\circ\text{C}$, as measured by a 0.1°C thermometer.

Spectra and absorbance measurements were recorded using a Cary 14 spectrophotometer with the hydrogen lamp light source. All spectrophotometric cells had silica optical windows and known path lengths. Reference solutions contained all electrolytes and reagents, except the complex, in the same concentrations as the sample solutions. Absorbance data were always made relative to base line which had been recorded using the appropriate reference solution in both the sample and the reference cells.

Stopped-flow experiments utilized a Durram-Gibson stopped-flow spectrophotometer in conjunction with a Tetrox, type 564, storage oscilloscope. Photographs of oscilloscope traces were made with a Polaroid Land camera.

III. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Aquation Equilibria

The aquation concentration equilibrium quotients were determined via potentiometric titrations of equilibrium solutions. At each temperature studied, solutions of six different total complex concentrations were titrated. The ionic strength was maintained at 0.318 M by the addition of NaClO_4 ; the contribution to the ionic strength of the various complex species was neglected. Having been prepared by the concentrated sodium hydroxide method (50), the NaOH titrant was carbonate-free. The titrant was stored under nitrogen, and all titrations were performed under a nitrogen atmosphere. Standardization of the NaOH was accomplished by titrating solutions of primary standard potassium acid phthalate (KHP) of concentration similar to the acid concentration of the most concentrated equilibrium complex solution, that is, about 1×10^{-3} M. The standard KHP solutions were prepared by dissolving a weighed quantity of the solid, primary standard KHP in the same 0.318 M NaClO_4 solution which was used to prepare the complex solutions.

The complex solutions were prepared as follows: The solution of maximum concentration, 1×10^{-3} M, was prepared by placing a weighed quantity of solid $[\text{PtCl}_2(\text{en})]$ in a one liter volumetric flask and filling to the mark with 0.318 M NaClO_4 solution. A teflon-coated, magnetic stirring bar was introduced, and the flask was covered with opaque tape to exclude light. The flask was then sealed with tape and placed on a mechanical-magnetic stirrer at room temperature. To minimize heating from the electric stirring motor, two layers of 1/16 inch asbestos sheet were placed

between the flask and the stirrer plate. Solutions were stirred for at least 12 hours. (Solubility studies had indicated that this amount of time was at least one and one-half times that required to dissolve all the complex present at room temperature.) After dissolution, the solution was removed from the stirrer and allowed to cool for at least one hour. The solutions of lower total complex concentrations were then prepared by placing aliquots of the 1×10^{-3} M complex solution in 250 ml volumetric flasks and diluting to the mark with the 0.318 M NaClO_4 solution which had been used to dissolve the complex. The six flasks containing the complex solutions were then covered with opaque tape, sealed, placed in a constant temperature bath, and allowed to equilibrate for 18 to 24 hours.

Six complex solutions, together with a standard KHP solution, were titrated in sets. A set of titrations consisted of two or three standardization titrations and two titrations of each complex solution. Such sets of titrations were repeated periodically over a 25 to 30 hour period until each complex solution had been titrated about ten times, or until samples were exhausted. The technique of simultaneous standardization at the temperature of measurement (the standard KHP having been kept in the constant temperature bath also) served to compensate for minor changes in NaOH concentration, for instrumental drift, and for small volume errors resulting from the different temperatures which were studied. All such small errors were neglected, as were the changes resulting from any temperature deviation during the time interval between sample removal and the end-point of the titration. The small errors resulting from hydrolysis during the titration were also ignored. The latter errors were, if fact, made negligible by performing the titrations as rapidly as possible in the thermo-

stated titration vessel. The total time from sample removal to the end-point of the titration was less than three minutes. The actual titration time required to reach the end-point was less than one minute in all cases.

Since, in the past, workers in this laboratory had observed the effect of hydrolysis during slower titrations (37), it seemed advisable to demonstrate that the titrations performed by this worker were indeed rapid enough to make such a correction unnecessary. As a check, therefore, some titrations were performed at a total titration time of approximately twice that mentioned previously. The end-points of these slower titrations were in agreement with the rapid titrations to well within one standard deviation in all cases. Thus, the error introduced by hydrolysis during the titrations performed by this worker has been shown to be negligible.

B. Aquation Kinetics

The aquation of $[\text{PtCl}_2(\text{en})]$ was studied by two methods, both being subject to the same difficulty - dissolution of the compound. Even when ground to a fine powder, the compound is difficult to dissolve. A solubility study indicated that, at room temperature, the maximum solubility of the complex is $< 1.5 \times 10^{-3}$ M. Although 2×10^{-3} M solutions are preparable with vigorous stirring for several hours, such is the result of the greater solubility of the aquo complexes formed by the hydrolysis. Addition of chloride to such solutions, with the subsequent reversal of the aquation reactions, results in precipitation of the dichloro complex. Solubility studies also indicated that 1×10^{-3} M solutions were attainable within minutes, however, this did the experimentor no good since the larger particles of solid complex remained undissolved. Apparently, the solid, powdered $[\text{PtCl}_2(\text{en})]$ is very resistant to wetting and the unavoidable lumps

which form in the powder require several hours of stirring for dissolution. It was, therefore, impossible to weigh a specific amount of the complex, rapidly dissolve it, and study the subsequent aquation.

For the above reason, a rapid dissolution technique was employed for the aquation studies. This technique consisted of adding excess solid $[\text{PtCl}_2(\text{en})]$ to a solution of inert electrolyte, 0.318 M NaClO_4 , shaking for about 15 seconds, and filtering. A sample of the filtrate from such preparations was rapidly withdrawn using a pipet and placed in the spectrophotometric cell or in the titration vessel, depending upon the experiment to be conducted. Such a method requires, of course, a means of determining the complex concentration. To accomplish this end, solutions of various $[\text{PtCl}_2(\text{en})]$ concentrations were prepared in 0.318 M KCl and their spectra recorded. The high chloride concentration employed for these solutions essentially suppressed the aquation reactions of Equations 1 and 2. Thus, such solutions provided a basis for the spectrophotometric determination of the concentration of the complex. The spectra of solutions varying in $[\text{PtCl}_2(\text{en})]$ concentration in 0.318 M KCl are shown in Figure 3. A plot of the absorbance at 300 nm exhibited by these solutions, versus the concentration of the complex, is shown in Figure 4. From such data, was calculated a value of $230 \text{ M}^{-1} \text{ cm}^{-1}$ for the molar extinction coefficient of $[\text{PtCl}_2(\text{en})]$ at 300 nm. This value was used for the spectrophotometric determination of the complex concentration in solutions which were prepared by the rapid dissolution technique.

In the spectrophotometric method for studying the aquation, a sample prepared by the rapid dissolution technique was placed in the water-jacketed spectrophotometric cell, and the spectrum was recorded periodically. Since

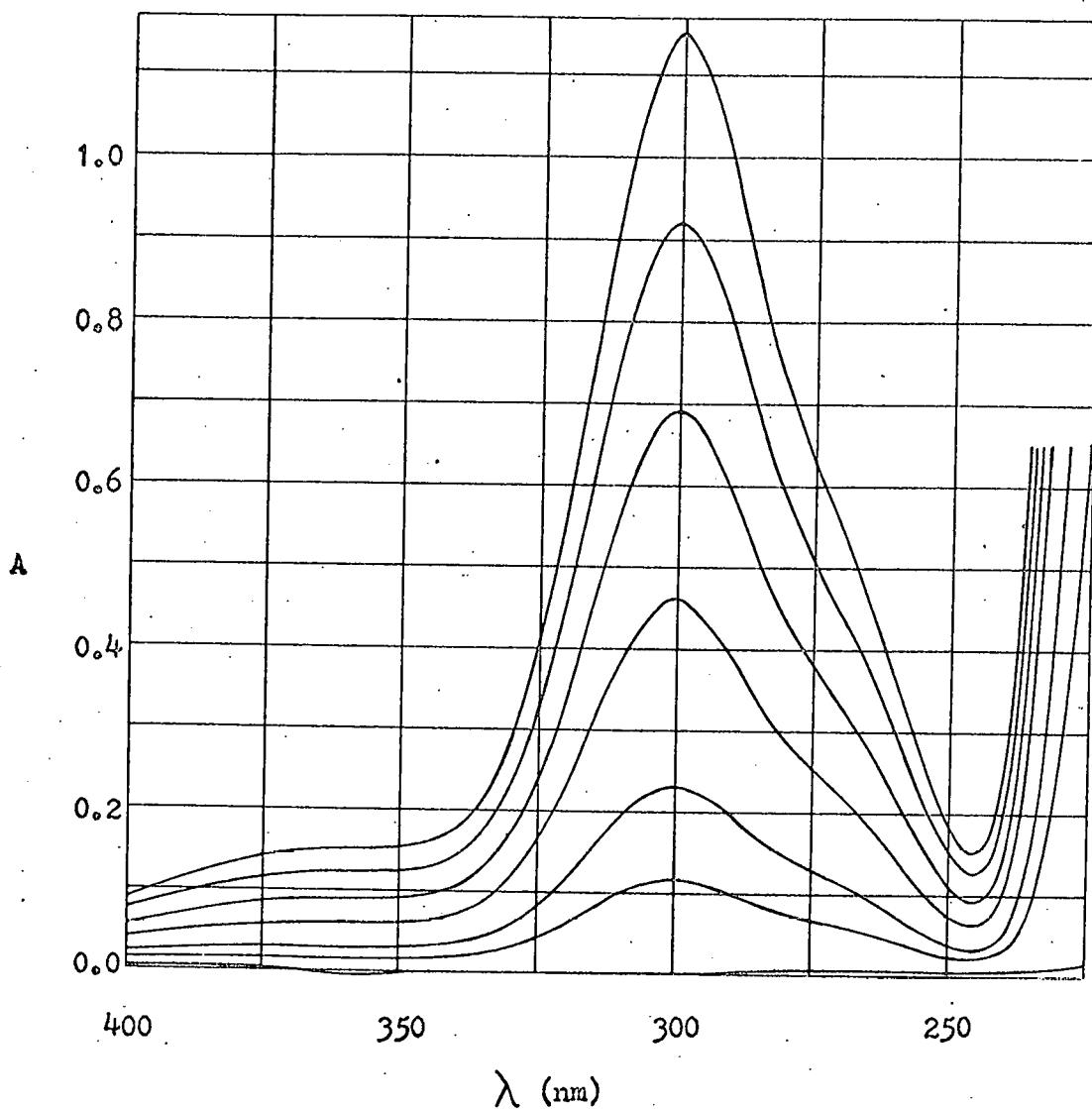


Figure 3. Absorption spectra of solutions of $[\text{PtCl}_2(\text{en})]$ in 0.318 M KCl . The spectra were recorded at 25.0°C using 5.00 cm cells. The base line was recorded with the 0.318 M KCl solution in both reference and sample cells

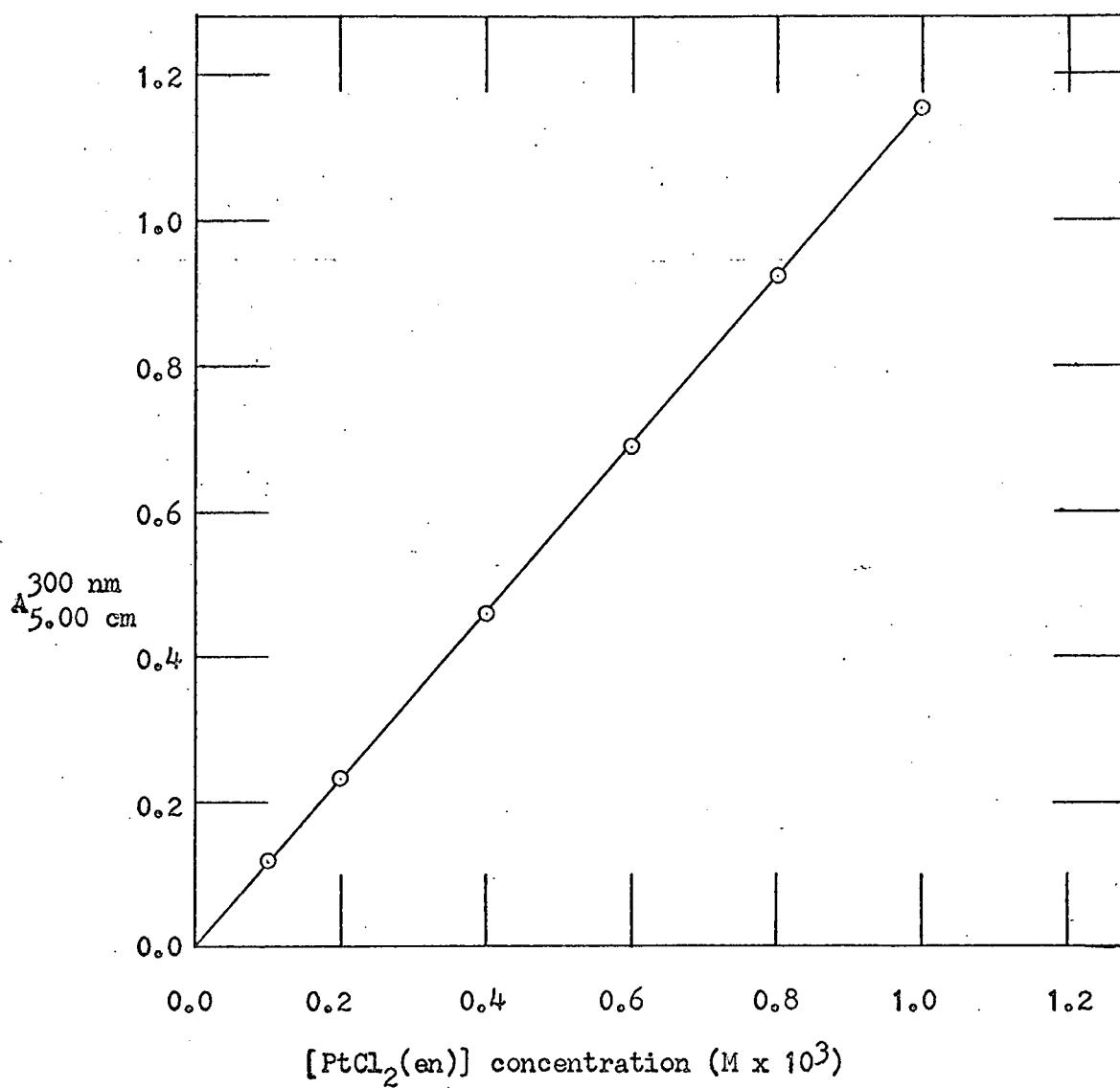


Figure 4. Absorbance at 300 nm versus [PtCl₂(en)] concentration. Data taken from the spectra of Figure 3. Note the excellent adherence to Beer's law, whence: $\epsilon_0 = 230 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$

the decrease in absorbance at 300 nm during the aquation was linear with time for approximately the first hour of reaction, extrapolation to "zero" time and determination of an initial slope were not difficult. It was possible to begin the first spectral recording within six minutes after dissolution of the complex. The circulation of water from the thermostatic bath through the cell jacket established temperature equilibration of the sample within fifteen minutes and kept the temperature deviations during reactions to less than 0.1°C .

The other method for studying the aquation utilized a pH-stat technique. In these experiments, a sample which had been prepared by the rapid dissolution technique was placed in the water-jacketed titration vessel within three minutes after dissolution and was allowed to thermally equilibrate for ten minutes. The vessel was pre-heated by immersion in the water bath, and the ten minute equilibration period was shown to be quite adequate. The pH-stat control was then begun by simply turning on the instrument which had been set to maintain the desired pH. The titrator then effected the addition of NaOH to neutralize the weakly acidic aquo species, as they were formed, in order to maintain the pH at the pre-selected value. It was found that, at a pH of 8, both chloride ligands would not be completely replaced by hydroxide. At pH values of 11 or 12, apparently more than two equivalents of hydroxide per platinum were consumed. The latter fact can only be explained in terms of hydroxide reaction with the ethylenediamine ligand since no apparent decomposition was observed. At a pH of 9, two hydroxides per platinum were quantitatively consumed. Independent of the final state of such pH-stat studies, one can obtain a value for the specific rate constant for the first aquation reaction of $[\text{PtCl}_2(\text{en})]$ if

the initial complex concentration is known. For the experiments which proceeded to an unknown equilibrium condition, the complex concentration was determined spectrophotometrically, as described earlier, by simultaneously performing a spectrophotometric determination for the same sample. This was, in fact, the method which was used to verify that the reaction proceeded quantitatively to the dihydroxo species at a pH of 9. That is, by assuming that two hydroxides per platinum had been consumed at pH 9, one could calculate the complex concentration from the final volume and concentration of the consumed NaOH. Such calculated complex concentrations agreed with the spectrophotometrically determined concentration, at a pH of 9, to within five percent.

Conducting two independent measurements of the specific rate constant for the first aquation reaction on the same sample and obtaining congruous values for both the complex concentration and the rate constant is, of course, gratifying. More such experiments would have been performed were it not for the fact that one can actually predict the value for the rate constant for the aquation reaction from the concentration equilibrium quotient and the reverse rate constant to well within the experimental accuracy involved in such studies.

C. Aquation Kinetics for the Diaquo Species

The rapidity of these reactions made conventional spectrophotometric methods inapplicable; therefore stopped-flow spectrophotometry was employed. The changes in absorbance during reactions, having been recorded as voltage changes on the oscilloscope screen, were subsequently photographically recorded. By utilizing water from a constant temperature bath, it was possible to control the temperature of the mixing chamber, which includes the

two driving syringes, mixing jet, and cuvette, to within 0.1°C of the desired temperature.

All of these reactions were conducted at an ionic strength of 0.32 M. The ionic strength was adjusted with HClO_4 , that is, the complex was originally dissolved in the 0.32 M HClO_4 . Employment of either 0.318 M NaCl or of a 50/50 volume mixture of the 0.318 M NaCl and the 0.32 M HClO_4 provided the constant ionic strength during the reactions. Reaction initiation was accomplished by the simultaneous injection into the cuvette of equal volumes of a complex solution and a chloride solution.

For each experiment, two sweeps of the ten centimeter oscilloscope scale were recorded. The sweep rate, in all cases, was two seconds per centimeter. The absorbance was recorded at 285 nm to avoid any contribution from the successive anation reaction. At this wavelength, the mono-aquo and diaquo species exhibit an isosbestic point.

Having obtained values for the specific rate constant for anation of the diaquo species based on a large number of similar experiments, it seemed advisable that one provide a verifying experiment which was based upon a different technique. After all, it would indeed be distressful if the stopped-flow studies had actually been conducted on some reaction other than the assumed anation of the diaquo species. To appease the pessimism of this worker, a corroborating experiment was conducted under second-order conditions. This experiment utilized a solution of the dihydroxo species, $[\text{Pt}(\text{OH})_2(\text{en})]$, which was the result of a pH-stat study of the rate of aquation. By the addition of a minute volume of concentrated HClO_4 to this solution, rapid and complete conversion to the diaquo species was effected. The resultant solution contained $[\text{Pt}(\text{H}_2\text{O})_2(\text{en})]^{2+}$ as the predominant complex

species. The return to an equilibrium condition with respect to the reactions of Equation 1 and 2 was observed spectrophotometrically with the sample in the water-jacketed spectrophotometric cell. Experimentally, the technique which was employed was essentially the same as that used for spectrophotometric studies of the anation of the monoquo species.

D. Anation Kinetics for the Monoquo Species

These reactions were studied spectrophotometrically when chloride was added to solutions which were at equilibrium with respect to the reactions of Equations 1 and 2. Prior to the start of a reaction, a 15.00 ml sample of a complex solution (in 0.318 M NaClO_4) was placed in a small polyethylene bottle and the bottle was placed in a constant temperature bath. A 15.00 ml sample of 0.318 M NaCl, or of a 50/50 volume mixture of the 0.318 M NaCl and the 0.318 M NaClO_4 , was placed in a similar bottle and this bottle was also placed in the water bath. The water-jacketed spectrophotometric cell was placed in the Cary spectrophotometer and water from the bath was pumped through the cell jacket.

To begin a reaction, one removed the two bottles from the bath and, at "zero" time, the contents of one was poured into the other while simultaneously starting a timer. The resultant solution was poured from one bottle to the other two more times with swirling between pours. A spout was quickly fitted on the bottle containing the solution; the bottle was inverted; the first few milliliters of solution were discharged into a waste beaker; the cell was filled; and the spectrophotometer was turned on. The interval between time "zero" and the first spectral recording varied from 0.45 to 0.75 minutes. For the first ten minutes of reaction the absorbance at 300 nm was recorded as a function of time. After ten minutes, the

entire uv spectrum was periodically recorded until approximately ten reaction half-times had elapsed.

The half-times of such reactions ranged from two to ten minutes depending upon the temperature and chloride concentration. Under similar conditions, the anation of the diaquo species proceeded with reaction half-times from seven to twenty-nine seconds, respectively. The first data point for anation of the mono aquo species was taken at one minute after mixing; thus conversion of the diaquo species to the mono aquo species was essentially completed prior to this time. The high chloride to complex ratios which were employed during these studies assured one of essentially complete conversion to the dichloro complex. It should be noted, however, that definite and reproducible evidence of a minor (<1%) reaction was observed during these studies. Thus, one could continue to observe slow increases in absorbance at 300 nm for several days, at which time the spectra of such solutions agreed with those of solutions of $[\text{PtCl}_2(\text{en})]$ which had been dissolved in 0.318 M KCl, to within the accuracy of spectrophotometric measurements. It was partially for this reason, and partially for convenience, that the "infinite" time readings for these studies of the anation of the mono aquo species were taken at approximately ten reaction half-times.

A corroborating set of experiments was performed using complex solutions which were prepared in 0.32 M HClO_4 rather than in 0.318 M NaClO_4 . Such experiments served to establish the pH independence of these reactions over the pH range of 1 to 5. The results of these four experiments were not used in the calculation of the specific rate constant for anation of the mono aquo species, but such results are listed with the others in Table

23 for comparison purposes. As can be seen from the values listed in that table, these four experiments provided an average value for $k_{\text{obsd.}}$ which agreed with the average value from twelve independent experiments to within three percent, that is, to within one standard deviation.

IV. TREATMENT OF EXPERIMENTAL DATA

A. Aquation Equilibria

The results of titrations of equilibrium solutions of $[\text{PtCl}_2(\text{en})]$ in water at a constant ionic strength are used to calculate the concentration equilibrium quotients for both the first and the second successive aquation reactions. At the outset, it is assumed that the dissolution of the complex in water results in the establishment of the simultaneous equilibria of Equations 1 and 2.

It has been shown that the products of such aquation reactions involving similar platinum(II) complexes are weak acids, titratable with NaOH (35-43). The existence of the specific product species indicated in Equations 1 and 2 has been demonstrated by other workers (51).

For the purpose of further development, the following symbols are defined:

a = total complex concentration in mM units;

x_e = equilibrium concentration of the monoquo species in mM units;

y_e = equilibrium concentration of the diaquo species in mM units.

Assuming that one hydrogen of each water ligand is titratable with NaOH, an additional symbol, called the equilibrium titre, is defined by:

T = equilibrium acid concentration in mM units.

If the activities of the various species are given by the symbols:

a_0 = activity of $[\text{PtCl}_2(\text{en})]$;

a_+ = activity of $[\text{PtCl}(\text{H}_2\text{O})(\text{en})]^+$;

a_{2+} = activity of $[\text{Pt}(\text{H}_2\text{O})_2(\text{en})]^{2+}$;

$a_{\text{--}}$ = activity of Cl^- ;

then the thermodynamic equilibrium constants for the reactions depicted in Equations 1 and 2 are respectively given by:

$$K_1^{\circ} = \frac{(a_+)(a_{\text{--}})}{(a_0)}, \quad (3)$$

and

$$K_2^{\circ} = \frac{(a_{2+})(a_{\text{--}})}{(a_+)} . \quad (4)$$

In terms of activity coefficients and concentrations, Equations 3 and 4 become:

$$K_1^{\circ} = \frac{(\gamma_+)(x_e)(\gamma_{\text{--}})(x_e + 2y_e)}{(\gamma_0)(a - x_e - y_e)} , \quad (5)$$

and

$$K_2^{\circ} = \frac{(\gamma_{2+})(y_e)(\gamma_{\text{--}})(x_e + 2y_e)}{(\gamma_+)(x_e)} . \quad (6)$$

The activity coefficients may be isolated, and Equations 5 and 6 may be written as:

$$K_1^{\circ} = \Gamma_1 \frac{(x_e)(x_e + 2y_e)}{(a - x_e - y_e)} , \quad (7)$$

$$K_2^{\circ} = \Gamma_2 \frac{(y_e)(x_e + 2y_e)}{(x_e)} , \quad (8)$$

where the additional symbols are defined by:

$$\Gamma_1 = \frac{(\gamma_+)(\gamma_{\text{--}})}{(\gamma_0)} , \quad (9)$$

and

$$\Gamma_2 = \frac{(\gamma_{2+})(\gamma_{-})}{(\gamma_{+})} . \quad (10)$$

Introduction of the corresponding concentration equilibrium quotients, K_1 and K_2 , into Equations 7 and 8, followed by rearrangement, yields:

$$\begin{aligned} K_1 &= K^o_1 / \Gamma_1 \\ &= \frac{(x_e)(x_e + 2y_e)}{(a - x_e - y_e)} , \end{aligned} \quad (11)$$

and

$$\begin{aligned} K_2 &= K^o_2 / \Gamma_2 \\ &= \frac{(y_e)(x_e + 2y_e)}{(x_e)} . \end{aligned} \quad (12)$$

With the introduction of the definition of the equilibrium titre, T , the product of K_1 and K_2 may be rearranged to yield a cubic equation in T as follows: In terms of the equilibrium titre, Equations 11 and 12 may be written as:

$$K_1 = \frac{(x_e)(T)}{(a - T + y_e)} , \quad (13)$$

and

$$K_2 = \frac{(y_e)(T)}{(x_e)} , \quad (14)$$

the product being:

$$K_1 K_2 = \frac{(y_e)(T)^2}{(a - T + y_e)} . \quad (15)$$

which, upon rearrangement, gives:

$$(a - T)K_1K_2 = (y_e)(T^2 - K_1K_2) . \quad (16)$$

Further use of the definition of the equilibrium titre enables one to write Equation 14 in the form:

$$K_2 = \frac{(y_e)(T)}{(T - 2y_e)} , \quad (17)$$

which, upon rearrangement, yields:

$$K_2T = (y_e)(T + 2K_2) . \quad (18)$$

Solution of Equation 18 for the equilibrium concentration of the diaquo species gives:

$$y_e = \frac{K_2T}{(T + 2K_2)} . \quad (19)$$

Substitution of the right-hand side of Equation 19 into Equation 16 then yields:

$$(a - T)K_1K_2 = \frac{K_2T(T^2 - K_1K_2)}{(T + 2K_2)} . \quad (20)$$

Clearing Equation 20 of fractions and dividing through by K_2 yields:

$$(a - T)K_1(T + 2K_2) = T(T^2 - K_1K_2) , \quad (21)$$

which may be written as:

$$(a - T)TK_1 + (2a - T)K_1K_2 = T^3 . \quad (22)$$

In the past, workers in this laboratory have utilized Equation 22 to evaluate the concentration equilibrium quotients by the determination of the equilibrium titre, T , for two different values of total complex concentra-

tion, a , with the subsequent solution of the resultant pair of simultaneous equations in the two unknowns, K_1 and $K_1 K_2$ (37-43). The values of K_1 and K_2 , so determined, have then been used to predict values of the equilibrium titres for solutions of other total complex concentrations. The agreement between such predicted values and the experimental values for T has been used as an indication of the consistency of the determined values for K_1 and K_2 over the complex concentration ranges which had been studied. Typically, the agreement between such calculated and experimentally determined values for T has been within a few percent of the calculated value.

It seemed to be at least intuitively obvious to this worker that the values for K_1 and K_2 would be better defined if the method of their calculation utilized all experimentally determined (a, T) data points. Equation 22 is a function of the two variables, a and T , and of the two parameters, α and β , that is, Equation 22 may be written in the form:

$$F(a, T, \alpha, \beta) = T^3 + \alpha T^2 + (\beta - a\alpha)T - 2a\beta = 0, \quad (23)$$

where:

$$\alpha = K_1, \quad (24)$$

and

$$\beta = K_1 K_2. \quad (25)$$

The form of Equation 23 suggested that a generalized least squares analysis, such as that described by Wentworth (52), patterned after the treatment of Deming (53), would be applicable. To accomplish this end, a computer program was written to perform the least squares adjustment. The quantity which was minimized was the sum of the weighted squares of the differences between the experimentally determined and the least squares

adjusted values for T. The a values were assumed to be exact, a simplification well justified by the fact that the errors in a values were an order of magnitude smaller than the errors in T values. (A rigorous development of the theory of least squares adjustment as applied to the function of Equation 23 is given in the Appendix.) The program was written to output the values of K_1 and K_2 with their associated standard deviations. Also, by utilization of an Iowa State University Computation Center library subroutine which employs a Newton-Raphson iterative technique, the program solves the cubic Equation 23 for the values of T at each experimental value of a using the least squares values for K_1 and K_2 . The percent differences between such calculated values for T and the experimentally determined T values were less than one percent of the calculated values in essentially all cases. The program also generates a plot of calculated T values versus a values and superimposes the experimentally determined (a,T) data points. The required input information consists of the (a,T) data points, the standard deviation of each T value, and initial estimates for K_1 and K_2 .

The calculation of T from equivalent volume titration data is, of course, trivial and need not be outlined herein. However, certain comments related to the calculation of the standard deviations of the T values are pertinent. The standard deviation of each T was calculated using the usual formula for the propagation of errors ignoring the higher order and covariance terms (53). For a function of three variables, $G(x,y,z)$, the appropriate equation for the standard deviation of the function, σ_G , is:

$$\sigma_G = [(\delta G/\delta x)^2(\sigma_x)^2 + (\delta G/\delta y)^2(\sigma_y)^2 + (\delta G/\delta z)^2(\sigma_z)^2]^{1/2} \quad (26)$$

The titre is a function of the molarity of the base, of the equivalent

volume of the base, and of the sample volume. The standard deviation of the sample volume was taken as the manufacturer's tolerance of the pipet used to withdraw the sample. The standard deviation of the equivalent volume was calculated from the experimental values according to the defining equation:

$$\sigma_{V_e} = [(\sum_i |V_{e_i} - \bar{V}_e|^2)/(N - 1)]^{\frac{1}{2}}, \quad (27)$$

where V_{e_i} is the i th experimental value, \bar{V}_e is the mean value, and N is the number of measurements. The standard deviation of the concentration of the NaOH was calculated from an equation of the form of Equation 26 since, as determined, the concentration of the NaOH was a function of the concentration of the primary standard acid, of the volume of the primary standard acid solution, and of the volume of the base equivalent to the volume of the primary standard acid. Once again, the standard deviation of the volume of the base equivalent to the volume of the primary standard acid was calculated from the experimentally determined values according to the defining equation (Equation 27). The standard deviation of the volume of the primary standard acid solution was taken as the manufacturer's tolerance of the pipet which was used. The standard deviation of the concentration of the primary standard acid solution was calculated from an equation of the form of Equation 26, since this concentration was a function of the measured weight of the acid, of the molecular weight of the acid, and of the volume of the flask which was used to prepare the solution. Finally, the standard deviation of the volume of the flask was taken as the manufacturer's tolerance; the standard deviation of the molecular weight was taken as ± 2 in the last place of the published value (54); the standard deviation

of the measured weight was taken to be the balance manufacturer's published standard deviation.

Thus, the computer technique employed by this worker provided a completely rigorous propagation of errors from first weight and volume measurements through to the experimentally obtained values for the equilibrium titres. The values for the standard deviations of these titres were used to determine weights for the least squares adjustment according to the usual definition which states that weights are inversely proportional to the square of the errors (53). The output errors for the concentration equilibrium quotients were those based on the "goodness of fit" of the data to the theoretical Equation 23 (53).

B. Aquation Kinetics

Spectrophotometric experiments were analysed by an initial slope treatment. Since the reactions were initiated by dissolving pure complex, the initial rate of the reaction is given by:

$$(dx/dt)_0 = k_1 a, \quad (28)$$

where:

x = the molar concentration of the monoquo species;

k_1 = the specific rate constant for the first aquation of the dichloro species in sec^{-1} units;

a = the initial total complex concentration in molar units.

The absorbance, A , of such a solution is given by:

$$A = \epsilon_0 l(a-x) + \epsilon_1 l x = \epsilon_0 l a + (\epsilon_1 - \epsilon_0) l x, \quad (29)$$

where:

ϵ_0 = the molar extinction coefficient of the dichloro species in $\text{M}^{-1} \text{cm}^{-1}$ units;

l = the spectrophotometric cell path length in cm;

ϵ_1 = the molar extinction coefficient of the monoquo species in $M^{-1} \text{ cm}^{-1}$ units.

Differentiation of Equation 29, followed by evaluation at time zero, gives:

$$(dA/dt)_0 = (\epsilon_1 - \epsilon_0)l(dx/dt)_0, \quad (30)$$

which, when combined with Equation 28, yields:

$$\frac{(dA/dt)_0}{(\epsilon_1 - \epsilon_0)l} = k_1 a. \quad (31)$$

Thus, the specific rate constant may be evaluated from spectrophotometric data according to the equation:

$$k_1 = \frac{(dA/dt)_0}{a(\epsilon_1 - \epsilon_0)l}, \quad (32)$$

provided the extinction coefficients of both species are known for the wavelength of measurement.

The value of $230 \pm 2 M^{-1} \text{ cm}^{-1}$ at 300 nm for the extinction coefficient of the dichloro species was, as mentioned earlier, obtained from solutions of the complex in 0.318 M KCl. Knowing this, and the values for the concentration equilibrium quotients, one can evaluate the extinction coefficient for the monoquo species from the spectra of aquo-equilibrium solutions of known total complex concentrations. From the equilibrium studies, several such spectra were available and some of these are shown in Figure 5. The value for the extinction coefficient of the monoquo species at 300 nm was calculated to be $92 \pm 4 M^{-1} \text{ cm}^{-1}$. As a result of such calculations, a value of $87 \pm 18 M^{-1} \text{ cm}^{-1}$ for the extinction coefficient of the diaquo species at 300 nm was also obtained. The similar values for the two aquo

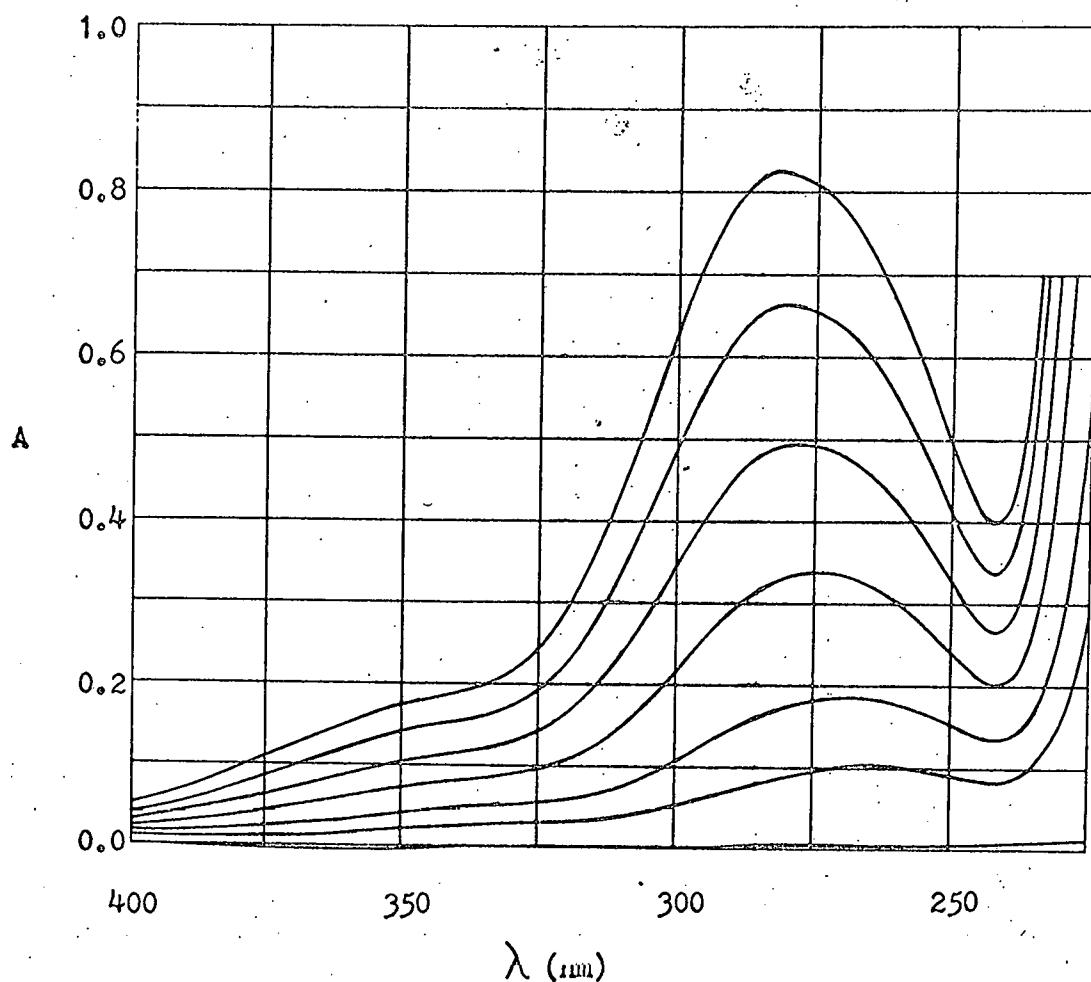
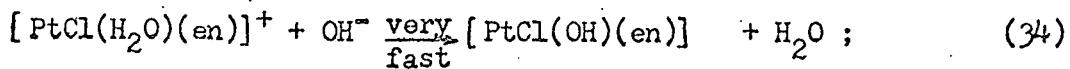
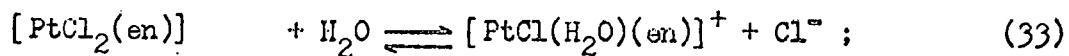
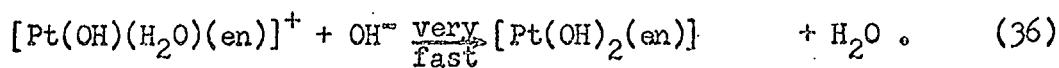
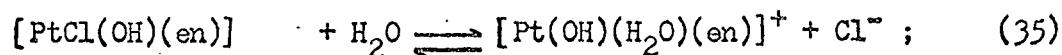


Figure 5. Absorption spectra of solutions of $[\text{PtCl}_2(\text{en})]$ in 0.318 M NaClO_4 . The spectra were recorded at 25.0°C using 5.00 cm cells. The base line was recorded with the 0.318 M NaClO_4 solution in both reference and sample cells. Notice the effect of the greater amount of aquation in the more dilute samples

species is of benefit in the spectrophotometric study of the aquation at 300 nm because small amounts of the successive aquation of the monoquo species in the early part of the study will cause an undetectable effect. It is also very convenient, of course, that the magnitude of the quantity $(\epsilon_1 - \epsilon_0)$ is as large as it is ($138 \text{ M}^{-1} \text{ cm}^{-1}$) because the inherent error in the difference becomes less important as the magnitude of the difference increases. Nevertheless, the resultant value for k_1 does rely on the value of this difference in extinction coefficients which, in turn, is dependent on the values of the concentration equilibrium quotients. Even though this worker believes that K_1 and K_2 are rather well defined, it is recognized that calculations of equilibrium concentrations of three species from such concentration equilibrium quotients is not very precise. Consideration of this, together with the fact that the absorbance changes during the linear-change portions of such reactions were typically only about two tenths of an absorbance unit, leads one to the expectation that the resultant k_1 will not be well defined. Such expectation is, in fact, borne out by the observed experimental scatter.

The pH-stat experiments were also begun with a solution of pure $[\text{PtCl}_2(\text{en})]$. Any initial aquo species formed during the sample preparation and thermal equilibration period have no influence on the observed rate of hydroxide consumption. Assuming the acid-base neutralization involved to be effectively instantaneous, one observes the reaction sequence:





The above reaction sequence is based on the known fact that the substitution of chloride by hydroxide in aqueous media occurs via the aquation mechanism (51). Obviously, this worker also observed the hydroxide independence. Initially, the rate of reaction is given by Equation 28 which, for these experiments, is written as:

$$(dx/dt)_0 = -(d[\text{OH}^-]/dt)_0 = k_1 a . \quad (37)$$

What one measures in the pH-stat experiment is the amount of hydroxide required to offset the decrease in hydroxide concentration caused by the reactions of Equations 34 and 36 as a function of time. Thus, in terms of more convenient experimental variables, the solution of Equation 37 for the specific rate constant is:

$$k_1 = \frac{(dV_{\text{NaOH}}/dt)_0 M_{\text{NaOH}}}{V_{\text{sample}} a} , \quad (38)$$

where:

V_{NaOH} = the volume increment of NaOH added to maintain pH-stat conditions in ml. units;

M_{NaOH} = the concentration of the NaOH in molar units;

V_{sample} = the volume of the complex solution in ml units;

a = the initial total complex concentration in molar units.

In both types of experiment, one requires a value for an initial slope, that is, for the initial rate of change of some measurable with time. One can obtain such an estimate by plotting the observable versus time and graphically evaluating the slope of the linear portion of the curve. This

worker chooses to avoid the estimation of any number from a hand-drawn plot because one invariably introduces human bias. In these cases, however, the experimental scatter was so large that it did not seem to matter if the slopes were obtained by this crude method. That is, although the data from each experiment defined an initial straight line somewhat satisfactorily, the agreement between experiments was quite unsatisfactory. The result of this shows up as a large standard deviation associated with the determined value for the rate constant. Once one has obtained values for $(dA/dt)_0$ or $(dV_{NaOH}/dt)_0$, the calculation of k_1 from Equation 32 or 38, respectively, is straightforward.

Because of the small volume increments involved in the pH-stat experiments, such experiments were not expected to yield results of much more accuracy than the spectrophotometric experiments. Hence, the results from all experiments at a given temperature were averaged together without weighting and a standard deviation was calculated.

C. Anation Kinetics for the Diaquo Species

The $[PtCl_2(en)]$ solutions utilized in these reactions had been allowed to reach equilibrium with respect to the reactions of Equations 1 and 2. Upon initiation of a reaction by mixing such an equilibrium solution with a chloride solution, chloride ions replace aquo ligands in an approach to a new equilibrium condition for these reactions. By observing the absorbance change at 285 nm, an isobestic point for the reaction of Equation 1, one can eliminate any effect due to anation of the mono aquo species. The fact that the chloride ion concentration was always at least 150 times the total complex concentration assured the existence of pseudo first-order conditions. Since the observed pseudo first-order rate constant for the anation

of Equation 2 is two orders of magnitude larger than the first-order rate constant for the aquation reaction of Equation 2, one can neglect the latter term in the rate expression. (It might also be noted that the observed pseudo first-order rate constant for the anation of the diaquo species is at least one order of magnitude greater than the observed pseudo first-order rate constant for the anation of the mono aquo species.) Thus, under the experimental conditions, these reactions are adequately governed by the rate law:

$$\frac{dy}{dt} = -k_{-2}[\text{Cl}^-]y = -k_{\text{obsd.}}y \quad (39)$$

where:

y = the molar concentration of the diaquo species;

k_{-2} = the specific rate constant for anation of the diaquo species in $\text{sec}^{-1} \text{M}^{-1}$ units;

$[\text{Cl}^-]$ = the molar concentration of chloride ion;

$k_{\text{obsd.}}$ = the observed pseudo first-order rate constant for anation of the diaquo species in sec^{-1} units.

The observed rate constants were determined according to the method of Guggenheim (55) from the slopes of plots of $\log(V_{t+\Delta t} - V_t)$ versus t . In its application here, $(V_{t+\Delta t} - V_t)$ is the vertical difference between the successive oscilloscope sweeps, the recorded voltage at any time, V_t or $V_{t+\Delta t}$, being linearly related to the concentration of the diaquo species.

All data was fit by a least squares analysis to the equation:

$$\log(V_{t+\Delta t} - V_t) = -\frac{k_{\text{obsd.}}}{\ln(10.0)} t + \text{constant} \quad (40)$$

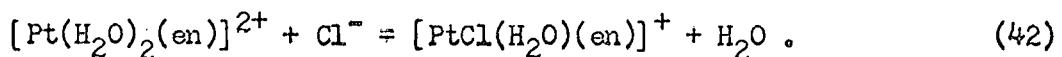
with the subsequent evaluation of $k_{\text{obsd.}}$ from:

$$k_{\text{obsd.}} = -(\text{slope})\ln(10.0) \quad (41)$$

For the purpose of error propagation, an error of ± 0.02 (arbitrary units) in each V was assumed and then propagated unto the quantity $\log(V_{t+\Delta t} - V_t)$. Calculation of weights was based on their assignment, according to the definition, as inversely proportional to the square of the error. Since the time-axis of an oscilloscope is rather precise, the assumption that t was exact seemed justified. Individual values for the observed rate constant, calculated from Equation 41, were assigned weights based on the "goodness of fit" of the Guggenheim plots. Since the accuracy of such experiments was expected to decrease as the halide ion concentration was decreased, a weighted average value for $k_{\text{obsd.}}$ was calculated for each temperature and halide ion concentration. From such weighted averages, the associated errors were calculated from the definition of a standard deviation by replacing the average value in the definition with the experimentally determined weighted average value.

Specific rate constants were calculated from the observed rate constants by means of the relationship contained within Equation 39. In cases where, at a given temperature, two average values for k_2 with their related errors were determined, a grand mean (56) and its associated error were evaluated.

For the corroborating experiment, performed under second-order conditions, a solution of known total complex concentration, a , was forced to completely dihydroxo complex by means of a pH-stat experiment. A small amount of concentrated acid was then added and the approach to an equilibrium condition was observed according to the reaction:



If the successive step, the conversion of the mono aquo species to the dichloro species, is ignored, the rate of the reaction of Equation 42 is given by:

$$\frac{dx}{dt} = k_{-2}(a-x)(2a-x) - k_2 x, \quad (43)$$

where:

k_2 = the specific rate constant for aquation of the mono aquo species in sec^{-1} units;

and the other terms are as previously defined. Since the value for the concentration equilibrium quotient, K_2 , is known, the rate expression of Equation 43 may be used to determine the desired specific rate constant. Thus, upon substitution of the expression:

$$k_2 = K_2 k_{-2}, \quad (44)$$

into the rate expression, one has:

$$\begin{aligned} \frac{dx}{dt} &= k_{-2}(2a^2 - 3ax + x^2 - K_2 x) \\ &= k_{-2}[x^2 - (3a + K_2)x + 2a^2]. \end{aligned} \quad (45)$$

Separation of the variables yields:

$$\frac{dx}{x^2 - (3a + K_2)x + 2a^2} = k_{-2} dt. \quad (46)$$

Integration of Equation 46 from (0,0) to (x,t), followed by rearrangement, yield:

$$\ln \frac{[2x - (3a + K_2) - q][2x_0 - (3a + K_2) + q]}{[2x - (3a + K_2) + q][2x_0 - (3a + K_2) - q]} = qk_{-2}(t - t_0), \quad (47)$$

where:

$$q = (a^2 + 6aK_2 + K_2^2)^{\frac{1}{2}}. \quad (48)$$

The above expression may be simplified by introducing the equilibrium

concentrations. At equilibrium, $dx/dt = 0$, thus, form Equation 45:

$$x_e^2 - (3a + K_2)x_e + 2a^2 = 0, \quad (49)$$

which gives for the equilibrium concentration of the monoquo species:

$$x_e = \frac{3a + K_2 \pm q}{2}, \quad (50)$$

where it can easily be shown that only the minus sign has physical significance. Substitution of the equilibrium value from Equation 50 into the rate expression of Equation 47 gives:

$$\ln \frac{(x - x_e - q)(x_0 - x_e)}{(x - x_e)(x_0 - x_e - q)} = qk_{-2}(t - t_0). \quad (51)$$

Now, for spectrophotometric data, we have that:

$$\begin{aligned} A &= \epsilon_2^1(a - x) + \epsilon_1^1 x \\ &= \epsilon_2^1 a + (\epsilon_1^1 - \epsilon_2^1) x, \end{aligned} \quad (52)$$

thus:

$$x = \frac{A - \epsilon_2^1 a}{1(\epsilon_1^1 - \epsilon_2^1)}, \quad (53)$$

where:

ϵ_2^1 = the molar extinction coefficient of the diaquo species in $M^{-1} \text{ cm}^{-1}$ units;

and the other terms are as previously defined. Substitution of the right-hand side of Equation 53 into Equation 51, followed by the collection of first-order and of second-order terms, gives:

$$\ln \left\{ \frac{(A_0 - A_e) \left(\frac{(A - A_e)}{(A_0 - A_e)} - \frac{q}{(x_0 - x_e)} \right)}{(A - A_e) \left(1 - \frac{q}{(x_0 - x_e)} \right)} \right\} = qk_{-2}(t - t_0) . \quad (54)$$

Thus, by plotting, on semi-log paper, the value of the quantity on the left-hand side of Equation 54 versus $(t - t_0)$, one can obtain a value for the specific rate constant from:

$$k_{-2} = \frac{0.693}{qt_{\frac{1}{2}}} , \quad (55)$$

where $t_{\frac{1}{2}}$ is the half-time.

D. Anation Kinetics for the Monoaquo Species

Since the anation of the diaquo species was essentially completed by the time data was taken for anation of the monoaquo species, it was necessary to consider only the reversible reactions of Equation 1 in the analysis. The rate of the observed reaction may be expressed as:

$$-dx/dt = k_{-1}[Cl^-]x - k_1(a-x) , \quad (56)$$

where:

k_{-1} = the specific rate constant for anation of the monoaquo species in $\text{sec}^{-1} \text{M}^{-1}$ units;

and all other terms are as previously defined. The rate law of Equation 56 may be written as:

$$dx/dt = k_1 a - k_{\text{obsd.}} x , \quad (57)$$

where, for these reactions, the observed rate constant is given by:

$$k_{\text{obsd.}} = k_1 + k_{-1}[Cl^-] . \quad (58)$$

Equation 58 may be written in the form:

$$\frac{d}{dt} \left(x - \frac{k_1 a}{k_{\text{obsd.}}} \right) = -k_{\text{obsd.}} \left(x - \frac{k_1 a}{k_{\text{obsd.}}} \right). \quad (59)$$

The variables may now be separated and the equation integrated as:

$$\int_0^x \frac{d \left(x - \frac{k_1 a}{k_{\text{obsd.}}} \right)}{\left(x - \frac{k_1 a}{k_{\text{obsd.}}} \right)} = \int_0^t -k_{\text{obsd.}} dt, \quad (60)$$

whence:

$$\ln \left(\frac{x - \frac{k_1 a}{k_{\text{obsd.}}}}{x_0 - \frac{k_1 a}{k_{\text{obsd.}}}} \right) = -k_{\text{obsd.}}(t - t_0). \quad (61)$$

Equation 61 is more convenient when written in terms of the equilibrium concentration of the monoquo species. At equilibrium, $dx/dt = 0$, thus, from Equation 57, we have that:

$$k_1 a = k_{\text{obsd.}} x_e. \quad (62)$$

Substitution of Equation 62 into Equation 61 yields:

$$\ln \left(\frac{x - x_e}{x_0 - x_e} \right) = -k_{\text{obsd.}}(t - t_0). \quad (63)$$

In terms of the measured absorbance, A , which is directly proportional to the concentration of the monoquo species, Equation 63 becomes:

$$\ln \left(\frac{A - A_e}{A_0 - A_e} \right) = -k_{\text{obsd.}}(t - t_0), \quad (64)$$

which, in terms of the fraction of the total change, F , is:

$$\ln(1-F) = -k_{\text{obsd.}}(t-t_0) , \quad (65)$$

where F is defined by:

$$F = \left(\frac{A_0 - A}{A_0 - A_e} \right) . \quad (66)$$

As mentioned earlier, the first data point was taken at one minute after mixing. This time delay allowed for essentially complete conversion of diaquo species to monoquo species and provided for re-establishment of thermal equilibrium. The absorbance readings (recorded at 300 nm) and the corresponding values for Δt (Δt measured from one minute after mixing) were the raw data. An error of ± 0.005 in absorbance readings was assumed; the time intervals were taken to be exact since the time-axis drive of the recorder was a rather precise device. Such data were used as input for a computer program which calculated the corresponding $\log(1-F)$ values, propagated the assumed error, calculated weights, and performed a least squares adjustment to fit Equation 65. The output values for the observed rate constant were calculated from:

$$k_{\text{obsd.}} = -(slope)\ln(10.0) , \quad (67)$$

where the slopes of the plots of $\log(1-F)$ versus Δt resulted from the weighted least squares adjustments. The errors associated with the slopes were those based on the "goodness of fit" and such errors were then propagated unto the values for the observed rate constant. These resultant errors for $k_{\text{obsd.}}$ values were used only to determine weights for the calculation of a weighted average value for $k_{\text{obsd.}}$. The standard deviations from such weighted averages were then calculated from the definition of a

standard deviation by replacing the average value in that definition with the weighted average value.

From Equation 58, since k_1 is known from the results of the aquation studies, the value for k_{-1} is calculated as:

$$k_{-1} = \frac{k_{\text{obsd.}} - k_1}{[\text{Cl}^-]} \quad (68)$$

Errors were propagated unto k_{-1} values, and a grand mean was evaluated at each temperature studied. The errors associated with these grand means were those given by the definition (56).

V. RESULTS

A. Aquation Equilibria

Typical titration curves for 25.00 ml samples of equilibrium aqueous solutions of $[\text{PtCl}_2(\text{en})]$ are shown in Figure 6. The equivalent volume was taken as the volume at the inflection point of such curves. The inflection points were located by linear interpolation of the second differential change, that is, by linear interpolation of the quantity: $\Delta(\Delta\text{pH}/\Delta V)$. In the application of this method, the volume increments at which the pH was read were two percent of the total volume of the burette. The same method was employed for standardization of the NaOH; however, since the titration curves for the standardization of NaOH with KHP were steeper near the equivalence points, the pH was read using one percent volume increments. This worker highly recommends the method used for determining the inflection points of titration curves since it is easy to employ and does not require the plotting of any data. In this worker's opinion, any method which employs the plotting of data introduces a natural bias because one subconsciously plots data to give the least amount of experimental scatter as is possibly allowable by the plotting technique. Whenever this worker has been forced to use a graphical method of determining a desired quantity, a least squares fit has been employed.

The results of equilibrium studies are given in Tables 4 through 10 wherein the calculated titre values are the least squares adjusted values. Figure 7 shows a typical least squares plot of Equation 23 with the (a, T) data points superimposed. Table 11 lists the least squares determined values for the concentration equilibrium quotients together with the

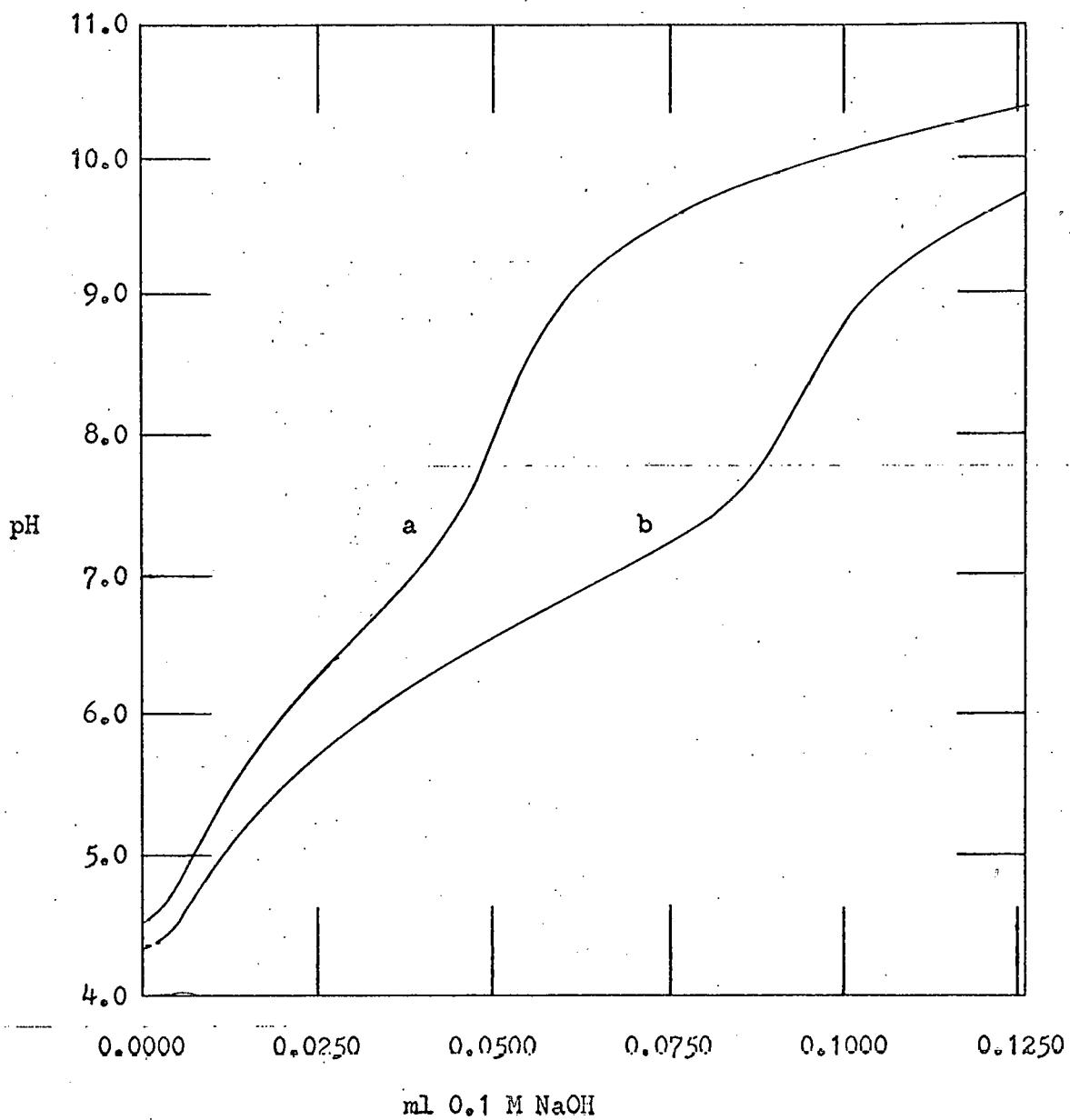


Figure 6. Typical titration curves for 25.00 ml samples of equilibrium aqueous solutions of $\text{PtCl}_2(\text{cn})$

a = curve for one of the titrations used to determine the titre for 0.20021 mM sample at 30.0°C

b = curve for one of the titrations used to determine the titre for 0.40056 mM sample at 25.0°C

Table 4. Results of first equilibrium study at 35.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0019	0.8913	0.8909	0.042
0.80152	0.7536	0.7544	0.101
0.60114	0.6093	0.6066	0.447
0.40076	0.440	0.4435	0.792
0.20038	0.257	0.2562	0.298
0.10019	0.145	0.1456	0.420

Table 5. Results of second equilibrium study at 35.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0261	0.9034	0.9024	0.115
0.82085	0.7622	0.7642	0.260
0.61564	0.6159	0.6146	0.207
0.41043	0.452	0.4495	0.555
0.20521	0.259	0.2598	0.314
0.10261	0.148	0.1478	0.142

Table 6. Results of third equilibrium study at 35.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0079	0.8886	0.8898	0.135
0.80635	0.7498	0.7512	0.182
0.60477	0.5999	0.6018	0.308
0.40318	0.442	0.4379	0.945
0.20159	0.249	0.2515	0.997
0.10079	0.139	0.1427	2.590

Table 7. Results of first equilibrium study at 30.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0060	0.8742	0.8728	0.155
0.80483	0.7426	0.7424	0.026
0.60362	0.5994	0.6003	0.146
0.40242	0.439	0.4419	0.667
0.20121	0.258	0.2576	0.170
0.10060	0.147	0.1470	0.011

Table 8. Results of second equilibrium study at 30.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0010	0.8749	0.8777	0.314
0.80083	0.7507	0.7442	0.868
0.60063	0.6007	0.5995	0.196
0.40042	0.437	0.4393	0.527
0.20021	0.255	0.2545	0.179
0.10010	0.143	0.1449	1.327

Table 9. Results of first equilibrium study at 25.0°C

a	T (experimental)	T (calculated)	Percent difference
1.0008	0.8589	0.8572	0.196
0.80064	0.7287	0.7299	0.159
0.60048	0.5882	0.5909	0.455
0.40032	0.436	0.4357	0.059
0.20016	0.255	0.2545	0.138
0.10008	0.146	0.1455	0.316

Table 10. Results of second equilibrium study at 25.0°C

Δ	T (experimental)	T (calculated)	Percent difference
1.0014	0.8673	0.8667	0.072
0.80113	0.7321	0.7335	0.196
0.60085	0.5917	0.5895	0.376
0.40056	0.429	0.4306	0.374
0.20028	0.251	0.2486	0.973
0.10014	0.138	0.1415	2.448

weighted average values.

In the calculation of a weighted average, the numbers which are averaged are either statistically consistent or statistically inconsistent.

The same formula is valid in both cases, namely:

$$\bar{X} = \frac{\sum_i w_i x_i}{\sum_i w_i}, \quad (69)$$

wherein \bar{X} is the weighted average; w_i is the weight of the i th value, taken to be inversely proportional to the square of the error of the i th value; x_i is the i th value. The errors associated with such weighted averages are, however, not given by a single equation. (The reader is referred to any text that treats the statistical adjustment of data for verification of the above statements.) For weighted averages given in this work, both ways were used to calculate the errors and the larger errors have been listed in all cases.

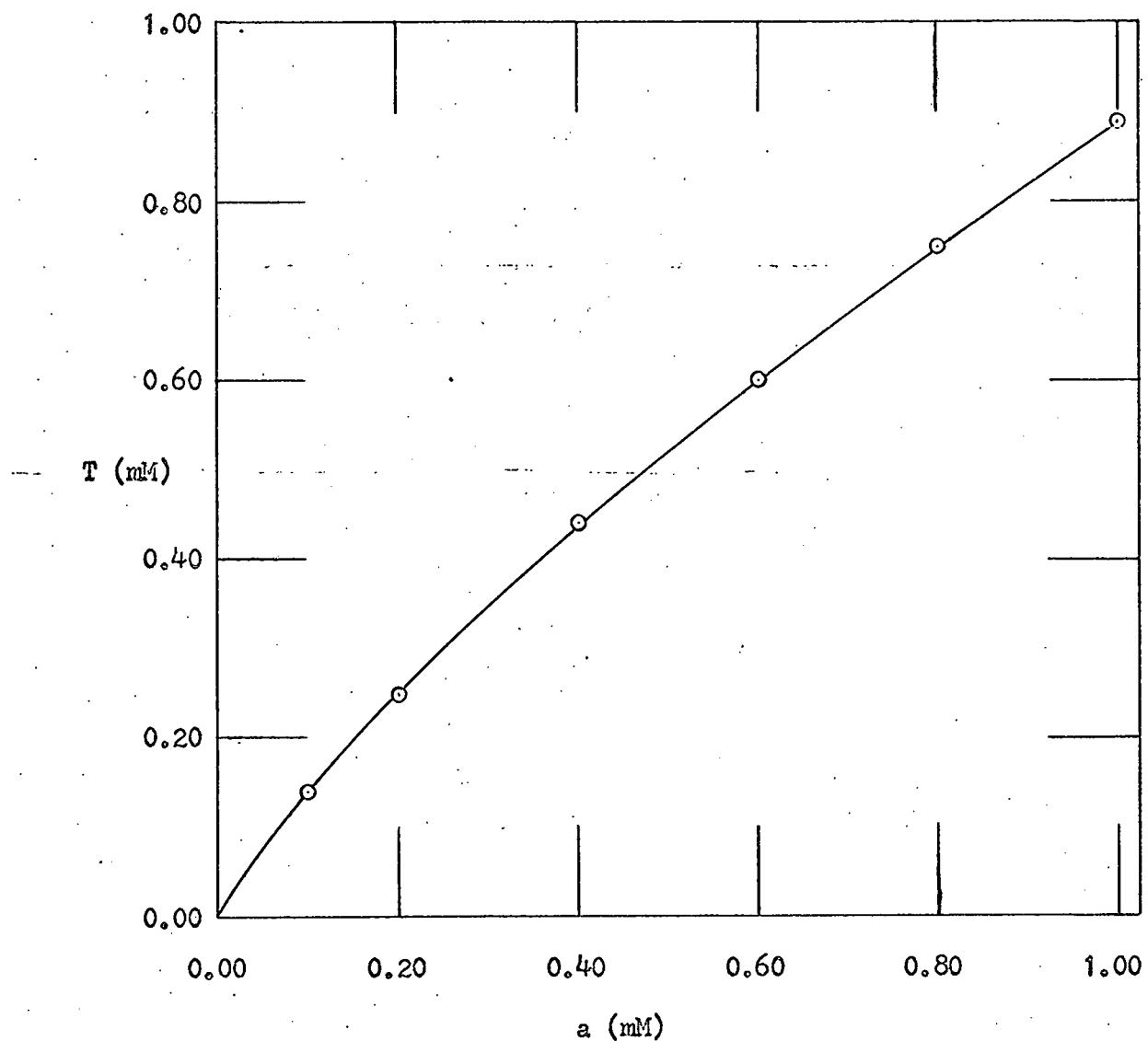


Figure 7. Least squares plot of Equation 23 with the (a, T) data points superimposed for the data of Table 6

Table 11. Summary of results for the concentration equilibrium quotients

T°C	$K_1 \times 10^3$ M	$\sigma_{K_1} \times 10^3$ M	$K_2 \times 10^4$ M	$\sigma_{K_2} \times 10^4$ M
35.00	2.76	0.08	1.41	0.04
	2.73	0.06	1.37	0.04
	2.96	0.18	1.18	0.07
Whtd. ave. =	2.76	0.05	1.38	0.05
30.00	2.30	0.04	1.51	0.03
	2.55	0.10	1.39	0.05
Whtd. ave. =	2.33	0.09	1.48	0.05
25.00	2.16	0.04	1.47	0.03
	2.60	0.15	1.18	0.07
Whtd. ave. =	2.19	0.11	1.43	0.11

B. Aquation Kinetics

Some of the spectra which were recorded during a typical spectrophotometric study of the aquation are shown in Figure 8. A plot depicting the change in absorbance at 300 nm during the early portion of this experiment may be found in Figure 9. All pertinent data from such experiments are listed in Table 12. In this table, are included the values for the specific rate constant calculated according to Equation 32.

The data from pH-stat experiments are listed in Table 13. In Table 13, are included the values for k_1 calculated, in this case, from Equation 38. A plot of the rate of hydroxide consumption during a typical pH-stat experiment appears in Figure 10. From all aquation experiments, an average value for k_1 was calculated at each temperature studied and appear in Table 14.

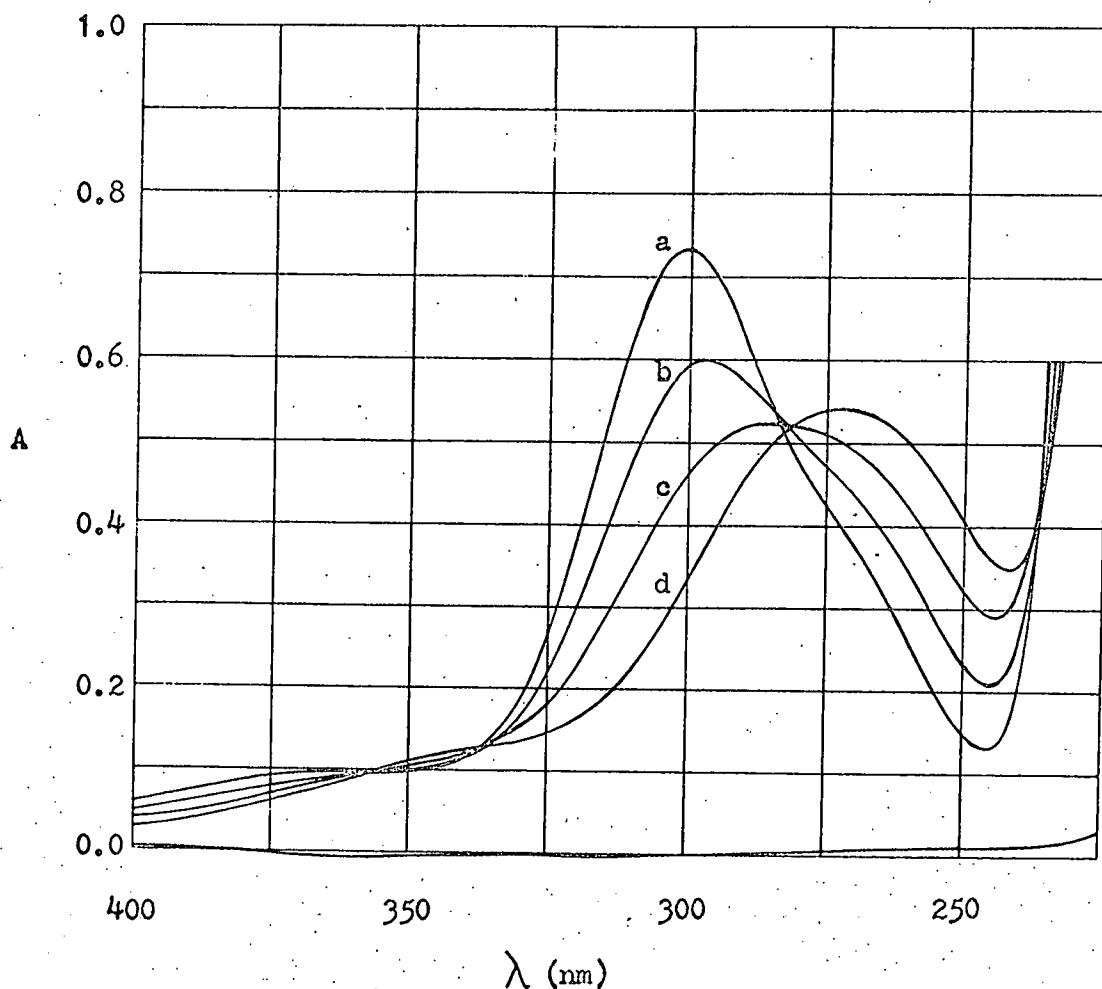


Figure 8. Spectral changes during aquation of 0.323 mM sample of $[\text{PtCl}_2(\text{en})]$ in 0.318 M NaClO_4 . The spectra were recorded at 30.0°C using 10.0 cm cells. The base line was recorded with the 0.318 M NaClO_4 solution in both reference and sample cells.

- a = recorded 6 minutes after dissolution
- b = recorded 2 hours after dissolution
- c = recorded 4 hours after dissolution
- d = recorded 22 hours after dissolution

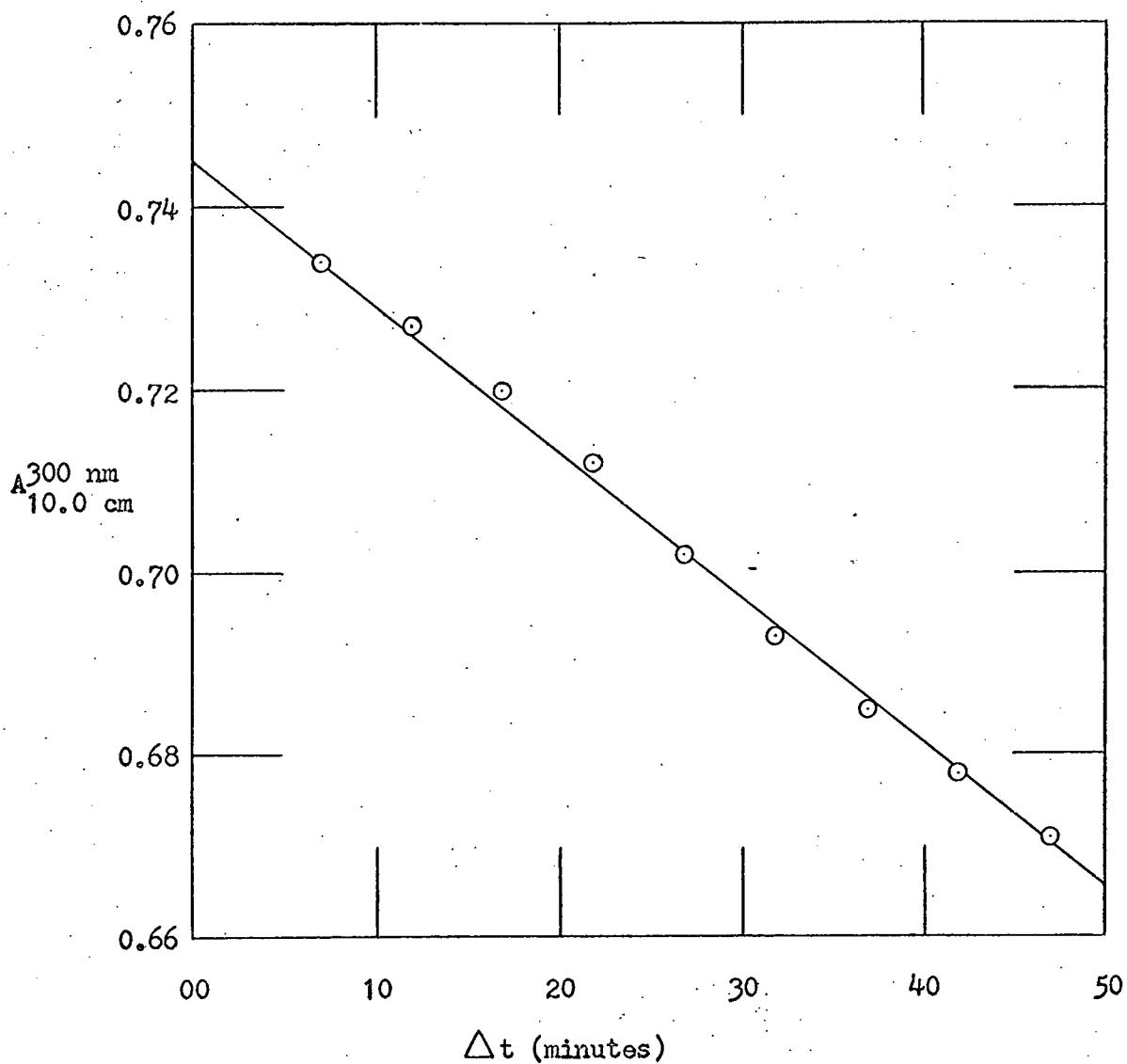


Figure 9. Change in absorbance at 300 nm during the early portion of the experiment from which the spectra of Figure 8 were taken. The values of $(dA/dt)_0$ were determined from plots such as this

Table 12. Summary of results from spectrophotometric studies of aquation kinetics. All absorbance data was taken at 300 nm where:
 $(\epsilon_1 - \epsilon_0) = 138 \text{ M}^{-1} \text{ cm}^{-1}$

T (°C)	$(dA/dt)_0$ (10^5 sec^{-1})	A_0	a (mM)	l (cm)	$k_1 \times 10^5$ (sec^{-1})
35.0	5.50	0.864	0.376	10.0	11.
	66.3	0.986	0.428	10.0	11.
	87.4	1.54	0.670	10.0	9.5
30.0	2.50	0.742	0.323	10.0	5.6
	2.93	0.840	0.365	10.0	5.8
	2.73	0.752	0.327	10.0	6.1
	3.07	0.930	0.405	10.0	5.5
25.0	3.02	0.919	0.400	10.0	5.5
	1.07	0.588	0.512	5.00	3.0
	2.50	1.25	1.09	5.00	3.3

Table 13. Summary of results from pH-stat studies of aquation kinetics. The sample volume was 25.00 ml in all experiments

T (°C)	$(dV_{\text{NaOH}}/dt)_0$ (10^6 ml sec^{-1})	pH	a (mM)	M_{NaOH}	$k_1 \times 10^5$ (sec^{-1})
35.0	6.33	8.5	0.313	0.1370	11.
	9.83	9.0	0.480	0.1370	11.
	7.00	9.0	0.373	0.1370	10.
30.0	5.80	8.0	0.238	0.1370	13.
	4.80	8.0	0.323	0.1365	8.1
	5.83	8.0	0.365	0.1345	8.6
	5.33	8.0	0.327	0.1321	8.6
25.00	3.08	8.0	0.405	0.1262	3.8
	3.49	8.0	0.400	0.1262	4.4
	10.9	10.0	1.09	0.1082	4.3
	3.28	11.0	0.802	0.2034	3.3
	3.33	10.5	0.802	0.2034	3.4
	3.18	10.0	0.802	0.2034	3.2
	3.16	9.5	0.802	0.2034	3.2
	4.38	11.0	1.00	0.2034	3.5

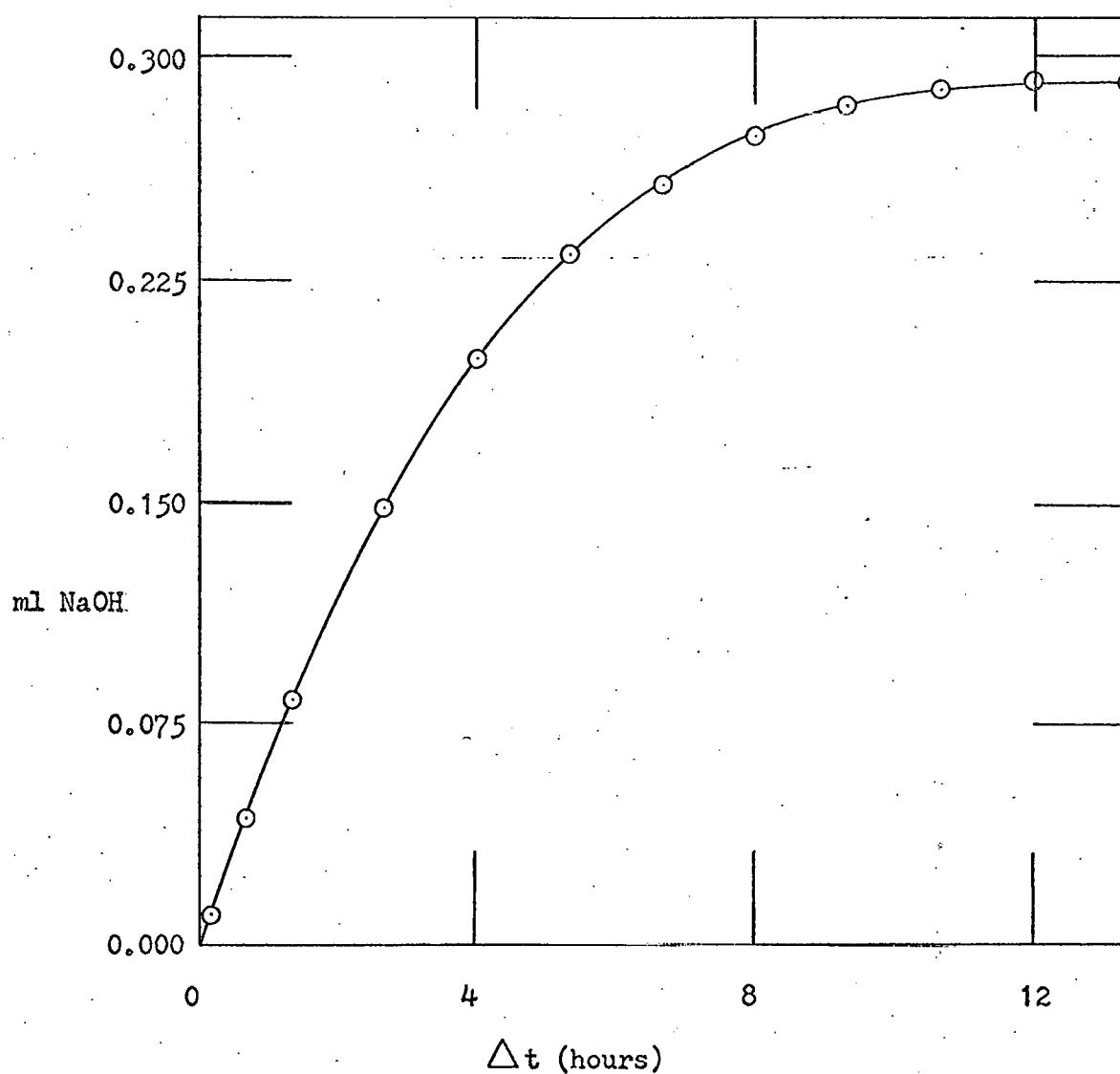


Figure 10. Hydroxide consumption during hydrolysis of $[\text{PtCl}_2(\text{en})]$. The values of $(dV_{\text{NaOH}}/dt)_0$ were determined from original recorder plots or from data taken from the digital read-out of the automatic burette as a function of time

Table 14. Summary of the experimentally determined weighted average values for the specific rate constant for aquation of the dichloro species

Constant	Value	T°C
$k_1 \times 10^5 \text{ sec}^{-1}$	11. \pm 1. 6.2 \pm 1.7 3.4 \pm 0.4	35.0 30.0 25.0

C. Anation Kinetics for the Diaquo Species

Typical results from a stopped-flow kinetics experiment are illustrated by the photograph of an oscilloscope trace shown in Figure 11 and by the associated data of Table 15. The corresponding Guggenheim plot is to be found in Figure 12 wherein the solid line is the least squares line and the experimental data points are superimposed. In Tables 16, 17 and 18, the results of all such experiments are tabulated; the resultant weighted average values for $k_{\text{obsd.}}$ are included. The values for k_{-2} , together with their weighted averages and errors, are listed in Table 19.

The spectra at various times during the second-order experiment are shown in Figure 13, wherein the first recorded spectrum should very closely approximate that of pure diaquo species. These spectra were recorded at 30.0°C and the data used for the calculations were taken at 255 nm. From this experiment, the value for the specific rate constant for anation of the diaquo species was calculated to be: $3.95 \times 10^{-1} \text{ sec}^{-1} \text{ M}^{-1}$. The agreement with the weighted average value of $4.18 \times 10^{-1} \text{ sec}^{-1} \text{ M}^{-1}$ obtained from 18 stopped-flow experiments is somewhat fortuitous, especially in consider-

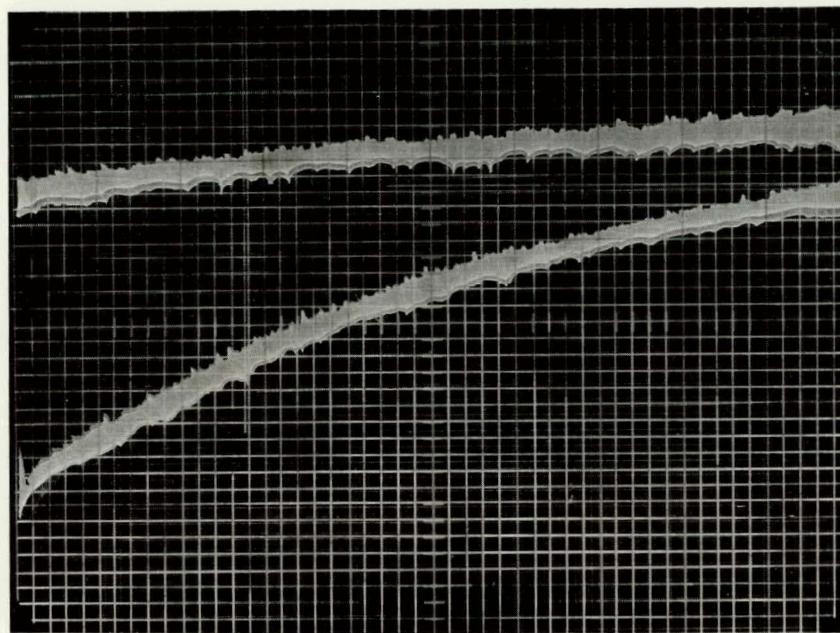


Figure 11. Photograph of oscilloscope trace for the first experiment of Table 16 (sweep rate = 2 seconds/cm)

Table 15. Raw data as read from the photograph of Figure 11 for the first experiment of Table 16. The V in this table is an abbreviation for $(V_{t+\Delta t} - V_t)$

Δt (sec)	V	$\log(V)$	$\sigma_{\log(V)}$	Weight
0.00	2.96	0.47129	0.00440	1.0000
2.00	2.54	0.40483	0.00513	0.7364
4.00	2.10	0.32222	0.00620	0.5033
6.00	1.82	0.26007	0.00716	0.3781
8.00	1.54	0.18752	0.00846	0.2707
10.00	1.36	0.13354	0.00958	0.2111
12.00	1.14	0.05690	0.01143	0.1483
14.00	1.00	0.00000	0.01303	0.1141
16.00	0.88	-0.05552	0.01481	0.0884
18.00	0.78	-0.10791	0.01670	0.0694

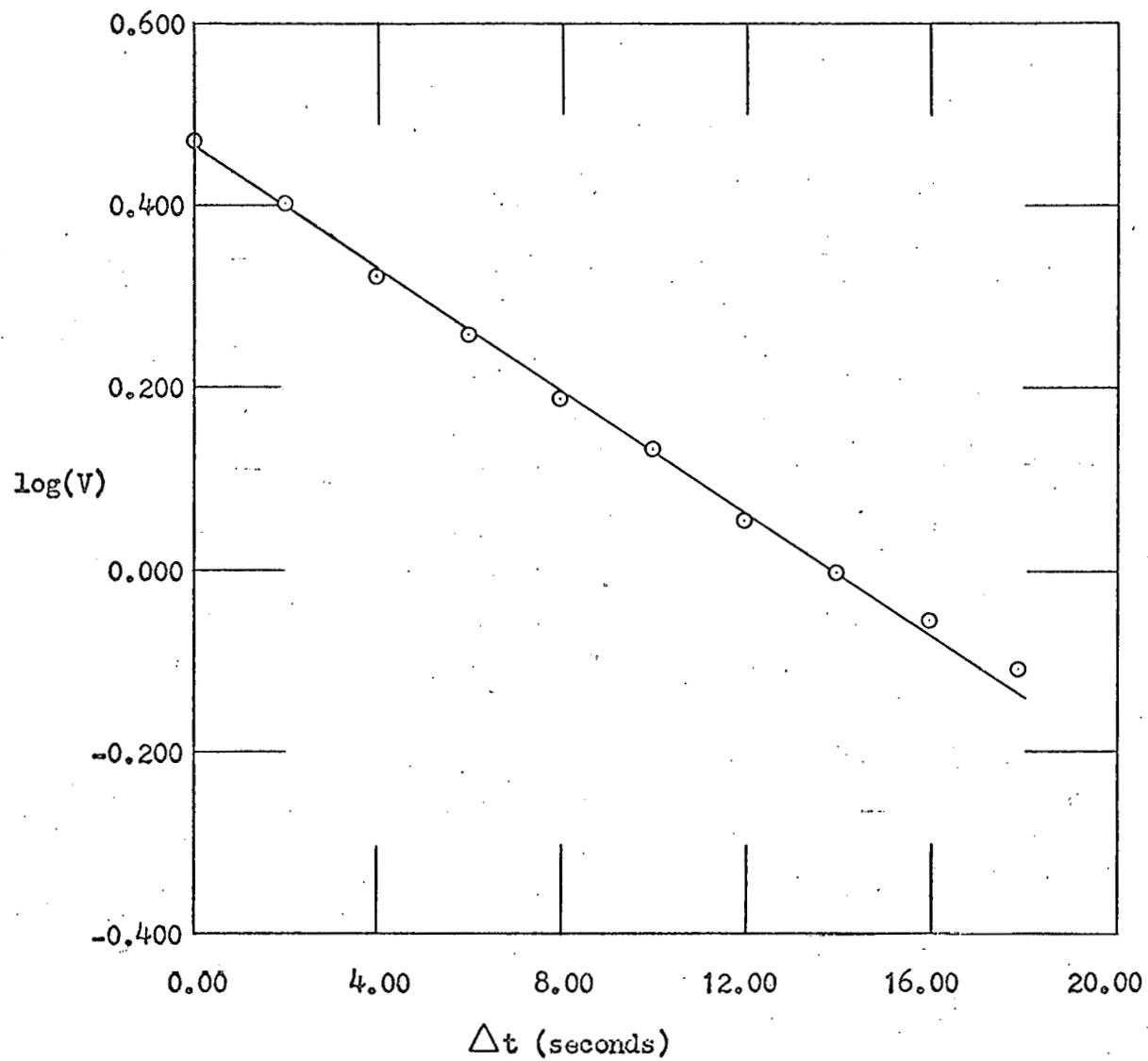


Figure 12. Guggenheim plot for the data of Table 15 corresponding to the first experiment of Table 16. The solid line is the least squares line and the points are experimental data. The V of this figure is an abbreviation for $(V_{t+\Delta t} - V_t)$

Table 16. Summary of results for anation of the diaquo species at 35.0°C. In this and the following two tables, the errors listed for the observed rate constants are those based on the "goodness of fit" of the Guggenheim plots. Such errors were used only for weighting in the calculation of the listed weighted averages. The errors associated with the weighted average values are standard deviations which were calculated from the definition

Complex	Chloride	$k_{\text{obsd.}} \times 10^2$ (sec ⁻¹)	$\sigma_{k_{\text{obsd.}}} \times 10^2$ (sec ⁻¹)
0.50032	0.159	7.73 6.89 6.70 7.46 7.87 6.61 6.80 7.19 7.16 8.12 8.44 7.48 8.46 7.09	0.14 0.22 0.17 0.11 0.17 0.11 0.16 0.15 0.19 0.29 0.14 0.24 0.18 0.09
0.40024		7.87 9.07 8.33 10.52 8.62	0.16 0.12 0.23 0.24 0.10
0.30018		7.73	0.97
Weighted average =	0.0795	4.99 5.47 4.67 4.73 4.99 3.12 5.78 5.73 5.39	0.16 0.17 0.81 0.10 0.12 0.15 0.10 0.20 0.19
0.50032		5.02	0.79
0.40024			
0.30018			
Weighted average =			

Table 17. Summary of results for anation of the diaquo species at 30.0°C

Complex (mM)	Chloride (M)	$k_{\text{obsd.}} \times 10^2$ (sec ⁻¹)	$\sigma_{k_{\text{obsd.}}} \times 10^2$ (sec ⁻¹)
0.50032	0.159	6.94	0.08
		5.90	0.10
		6.20	0.10
		6.53	0.07
		6.25	0.10
		6.63	0.09
0.40024		6.81	0.14
		7.65	0.12
		6.26	0.15
		6.35	0.18
		6.03	0.18
		7.58	0.08
0.30016		7.16	0.25
		6.62	0.06
		6.67	0.53
0.50032	0.0795	3.23	0.16
		3.77	0.12
		3.40	0.12
		2.37	0.16
		3.30	0.61

ation of the assumptions involved in treating the second-order data. Nevertheless, the experiment does offer valuable support to the fact that one had actually observed anation of the diaquo species in both cases.

D. Anation Kinetics for the Monoaquo Species

The raw data from a typical experiment, together with the associated calculated values and their errors, are listed in Table 20. The corresponding $\log(1-F)$ plot appears in Figure 14. All pertinent data and resul-

Table 18. Summary of results for anation of the diaquo species at 25.0°C

Complex (mM)	Chloride (M)	$k_{\text{obsd.}} \times 10^2$ (sec ⁻¹)	$\sigma_{k_{\text{obsd.}}} \times 10^2$ (sec ⁻¹)
0.50032	0.159	5.92	0.17
		5.32	0.14
		5.85	0.10
		5.35	0.10
		4.40	0.07
		4.46	0.14
		5.25	0.18
		4.65	0.11
		4.59	0.18
		4.31	0.13
0.20012		5.10	0.12
		5.37	0.05
		4.10	0.08
		4.87	0.08
		4.83	0.10
		Weighted average =	4.95
			0.55

Table 19. Summary of the experimentally determined values for the specific rate constant for anation of the diaquo species and the weighted average values. The first entry at a given temperature is the value obtained from experiments with a chloride ion concentration of 0.159 M. The second entry at a given temperature is the value obtained from experiments with a chloride ion concentration of 0.0795 M

T (°C)	$k_{-2} \times 10^1$ (sec ⁻¹ M ⁻¹)	$\sigma_{k_{-2}} \times 10^1$ (sec ⁻¹ M ⁻¹)	$\bar{k}_{-2} \times 10^1$ (sec ⁻¹ M ⁻¹)	$\sigma_{\bar{k}_{-2}} \times 10^1$ (sec ⁻¹ M ⁻¹)
35.0	4.86	0.61	5.24	0.65
	6.32	0.99		
30.0	4.19	0.33	4.18	0.30
	4.15	0.72		
25.0	3.11	0.35	3.11	0.35

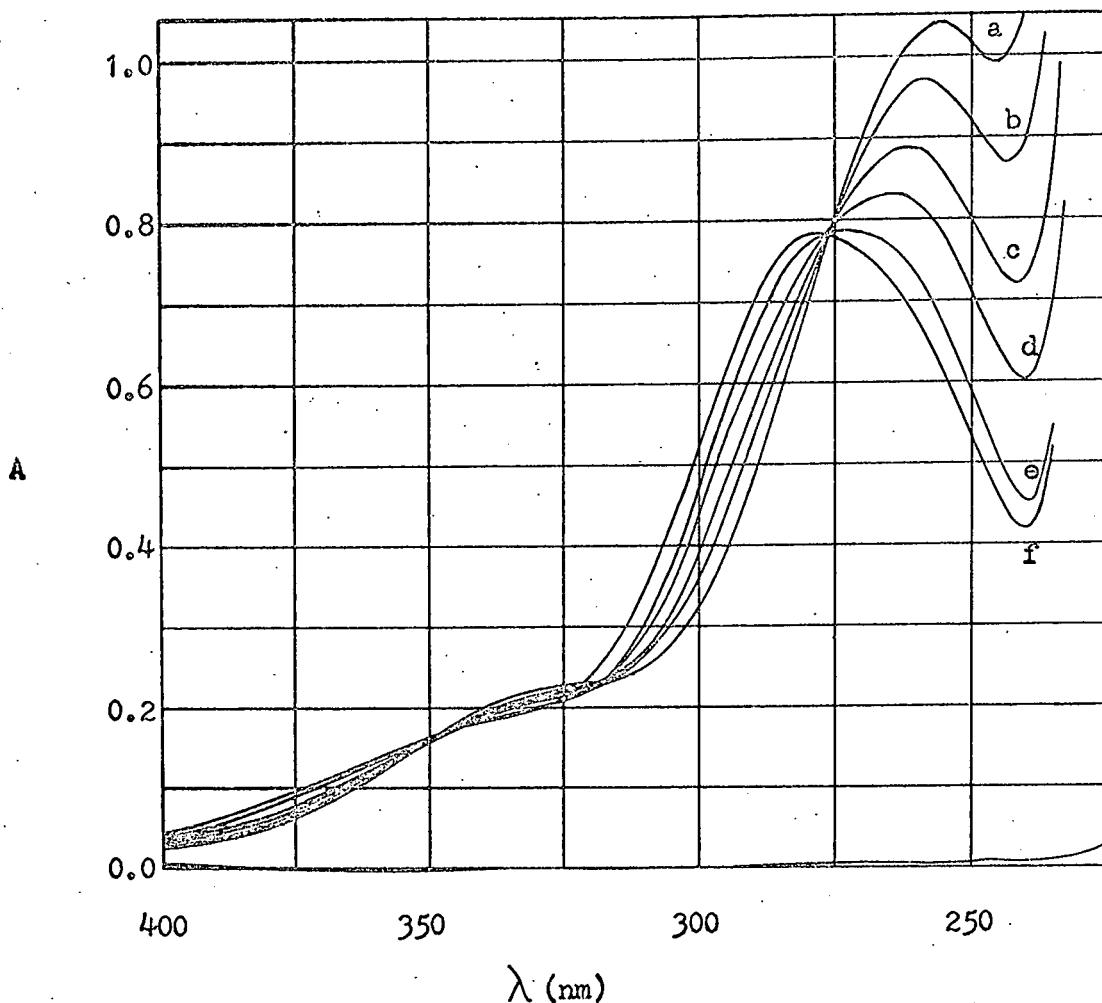


Figure 13. Spectral changes during anation of 0.512 mM sample of the diaquo species, $[\text{Pt}(\text{H}_2\text{O})_2(\text{en})]^{2+}$. The spectra were recorded at 30.0°C using 10.0 cm cells.

- a = recorded 0.67 minutes after addition of HClO_4
- b = recorded 8.33 minutes after addition of HClO_4
- c = recorded 20.3 minutes after addition of HClO_4
- d = recorded 35.3 minutes after addition of HClO_4
- e = recorded 85.3 minutes after addition of HClO_4
- f = recorded 233. minutes after addition of HClO_4

Table 20. Raw data for the first experiment of Table 21

Δt (min)	$A^{300 \text{ nm}}$	$A_e - A$	$(1-F)$	$\log(1-F)$	$\sigma_{\log(1-F)}$	Weight
0.00	0.749	0.342	1.000	0.00000	0.00898	1.0000
0.25	0.778	0.313	0.915	-0.03848	0.00942	0.9081
0.50	0.807	0.284	0.830	-0.08071	0.01002	0.8026
0.75	0.833	0.258	0.754	-0.12241	0.01074	0.6985
1.00	0.858	0.233	0.681	-0.16667	0.01166	0.5929
1.25	0.878	0.213	0.623	-0.20565	0.01261	0.5070
1.50	0.899	0.192	0.561	-0.25073	0.01389	0.4181
1.75	0.917	0.174	0.509	-0.29348	0.01529	0.3451
2.00	0.932	0.159	0.465	-0.33263	0.01674	0.2877
2.25	0.948	0.143	0.418	-0.37869	0.01868	0.2310
2.50	0.961	0.130	0.380	-0.42008	0.02065	0.1890
2.75	0.971	0.120	0.351	-0.45485	0.02249	0.1594
3.00	0.982	0.109	0.319	-0.49660	0.02493	0.1298
3.25	0.991	0.100	0.292	-0.53403	0.02735	0.1078
3.50	0.999	0.092	0.269	-0.57024	0.02992	0.0901
3.75	1.007	0.084	0.246	-0.60975	0.03300	0.0741
4.00	1.018	0.073	0.213	-0.67070	0.03837	0.0548
4.25	1.024	0.067	0.196	-0.70795	0.04207	0.0456
4.50	1.030	0.061	0.178	-0.74870	0.04651	0.0373
20.67	1.091					

tant $k_{\text{obsd.}}$ values, their weighted averages and errors are given in Tables 21, 22 and 23. Table 24 lists the calculated k_{-1} values, their weighted averages and errors.

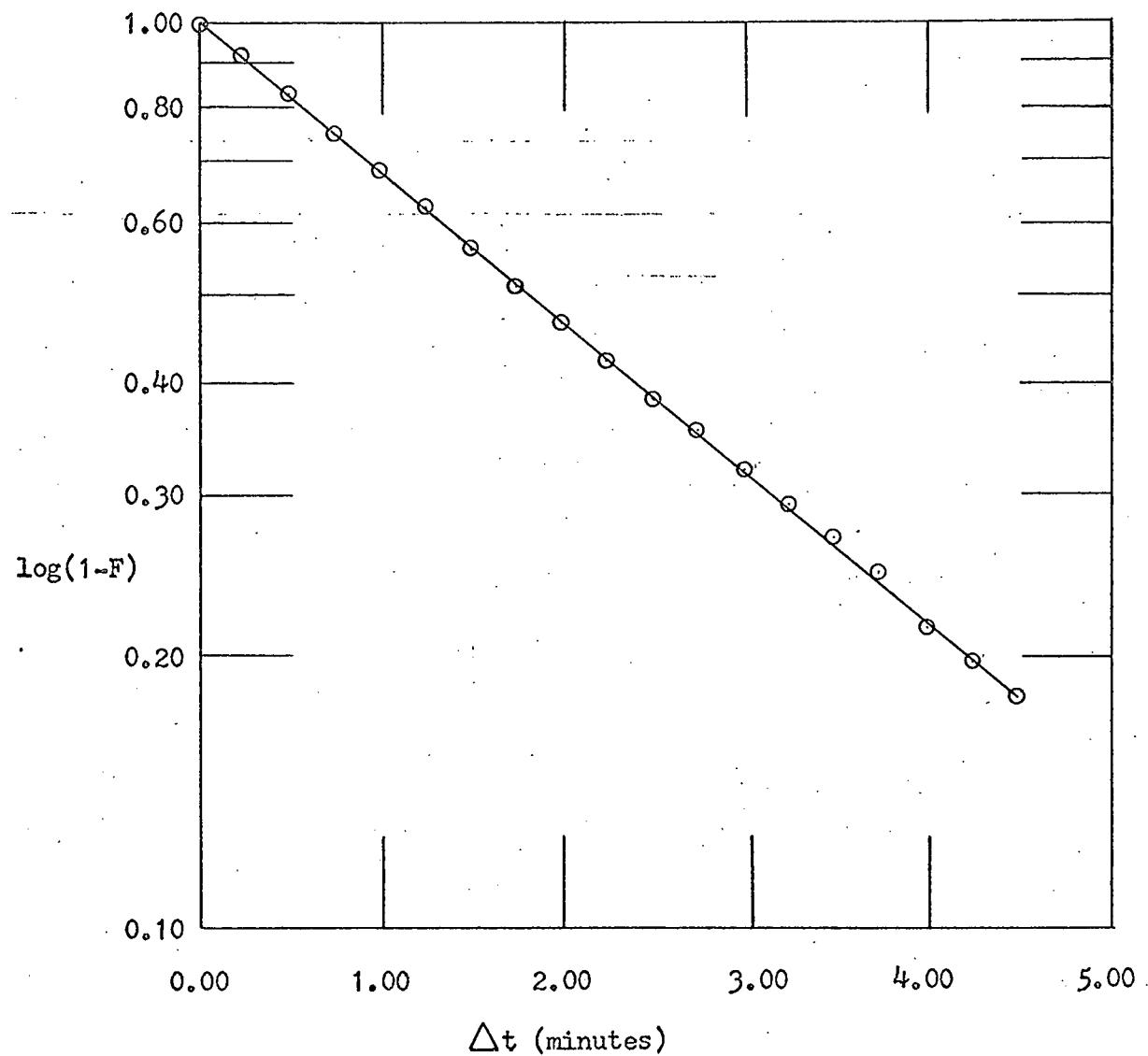


Figure 14. $\log(1-F)$ plot for the data of Table 20 corresponding to the first experiment of Table 21. The solid line is the least squares line and the points are experimental data points

Table 21. Summary of results for anation of the monoquo species at 35.0°C. In this and the following two tables, the errors listed for the observed rate constants are those based on the "goodness of fit" of the $\log(1-F)$ plots. Such errors were used only for weighting in the calculation of the listed weighted averages. The errors associated with the weighted average values are standard deviations which were calculated from the definition

Complex (mM)	Chloride (M)	$t_{\frac{1}{2}}$ (min)	$k_{\text{obsd.}} \times 10^3$ (sec $^{-1}$)	$\sigma_{k_{\text{obsd.}}} \times 10^3$ (sec $^{-1}$)
0.50395	0.159	1.82	6.36	0.02
		1.81	6.39	0.02
		1.78	6.50	0.01
		1.79	6.44	0.02
		1.85	6.23	0.02
		1.83	6.32	0.02
0.40316		1.87	6.18	0.02
0.30237		1.84	6.27	0.03
0.20158		1.89	6.13	0.03
Weighted average =			6.36	0.13
0.50395	0.0795	3.37	3.42	0.01
		3.46	3.34	0.01
		3.41	3.39	0.01
		3.38	3.42	0.02
		3.54	3.26	0.02
Weighted average =			3.38	0.07

Table 22. Summary of results for anation of the mono aquo species at 30.0°C

Complex (mM)	Chloride (M)	$t_{\frac{1}{2}}$ (min)	$k_{\text{obsd.}} \times 10^3$ (sec $^{-1}$)	$\sigma_{k_{\text{obsd.}}} \times 10^3$ (sec $^{-1}$)
0.50052	0.159	2.89	4.00	0.02
		2.89	4.00	0.02
		2.91	3.98	0.02
		2.88	4.01	0.02
		2.90	3.99	0.03
		2.88	4.01	0.02
		2.86	4.05	0.01
0.40041		2.95	3.91	0.02
		2.95	3.92	0.03
		3.01	3.84	0.03
0.30031		3.01	3.84	0.03
		3.07	3.76	0.02
Weighted average =			3.98	0.10
0.50052	0.0795	5.47	2.11	0.01
		5.61	2.06	0.01
0.40041		5.41	2.13	0.01
0.30031		5.46	2.11	0.01
0.20021		5.70	2.03	0.02
Weighted average =			2.10	0.04

Table 23. Summary of results for anation of the mono aquo species at 25.0°C. The last four experiments listed in this table were conducted in HClO_4 solution (rather than NaClO_4) to verify the pH independence of the reaction. The results from these four experiments were not used in calculating the specific rate constant

Complex	Chloride	$t_{\frac{1}{2}}$	$k_{\text{obsd.}} \times 10^3$	$\sigma_{k_{\text{obsd.}}} \times 10^3$
(mM)	(M)	(min)	(sec ⁻¹)	(sec ⁻¹)
0.50070	0.159	4.74	2.44	0.011
		4.51	2.56	0.008
		4.64	2.49	0.009
		4.61	2.51	0.010
		4.66	2.48	0.005
		4.57	2.53	0.008
		4.60	2.51	0.007
0.40056		4.77	2.42	0.005
0.30042		4.68	2.47	0.006
		4.62	2.50	0.083
0.20028		4.75	2.43	0.105
		4.88	2.37	0.085
Weighted average =			2.48	0.05
0.50020	0.0795	8.96	1.29	0.003
0.40016		8.88	1.30	0.006
0.30012		9.13	1.27	0.005
0.20008		10.15	1.14	0.010
Weighted average =			1.28	0.08
0.50032	0.159	4.40	2.63	0.006
0.40024		4.59	2.52	0.005
0.30018		4.52	2.56	0.007
0.20012		4.60	2.51	0.011
Weighted average =			2.56	0.05

Table 24. Summary of the experimentally determined values for the specific rate constant for anation of the mono aquo species and their weighted average values. The first entry at a given temperature is the value obtained from experiments with a chloride ion concentration of 0.159 M. The second entry at a given temperature is the value obtained from experiments with a chloride ion concentration of 0.0795 M

T (°C)	$k_{-1} \times 10^2$ (sec ⁻¹ M ⁻¹)	$\sigma_{k_{-1}} \times 10^2$ (sec ⁻¹ M ⁻¹)	$\bar{k}_{-1} \times 10^2$ (sec ⁻¹ M ⁻¹)	$\sigma_{\bar{k}_{-1}} \times 10^2$ (sec ⁻¹ M ⁻¹)
35.0	3.93	0.08	4.01	0.09
	4.11	0.09		
30.0	2.47	0.06	2.53	0.05
	2.57	0.05		
25.0	1.54	0.03	1.54	0.03
	1.57	0.10		

VI. DISCUSSION

A. Spectra

A Gaussian analysis was performed for the spectrum of a solution of the complex in high chloride. It is interesting to note the remarkable similarity between the locations of the absorption bands in the visible and ultraviolet regions for $[\text{PtCl}_2(\text{en})]$ and $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$. Such a comparison is given in Table 25. Equally interesting is the fact that the bands

Table 25. Frequency of maxima ($\nu \times 10^4 \text{ cm}^{-1}$), extinction coefficients at the maxima ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$) and half-widths of the bands ($\nu_{\frac{1}{2}} \times 10^4 \text{ cm}^{-1}$) in the Gaussian analysed spectra of aqueous solutions of $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$ and $[\text{PtCl}_2(\text{en})]$. The values for the ammine complex are those of Chatt, *et al.* (20)

$\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$			$[\text{PtCl}_2(\text{en})]$		
ν	ϵ	$\nu_{\frac{1}{2}}$	ν	ϵ	$\nu_{\frac{1}{2}}$
2.40	3.2	0.16	2.49	12	0.30
2.73	23	0.23	2.73	31	0.36
3.31	128	0.22	3.32	226	0.40
3.72	68.5	0.21	3.69	94	0.36
4.76	4500		3.9	10	
			4.3	2000	

for the ethylenediamine complex are all a factor of two to five more intense than the corresponding bands for the diammine complex (considering both extinction coefficients and half-widths). This is believed to be a result of the lower symmetry of the former compared with that of the latter. The Gaussian analysed spectrum is shown in Figure 15.

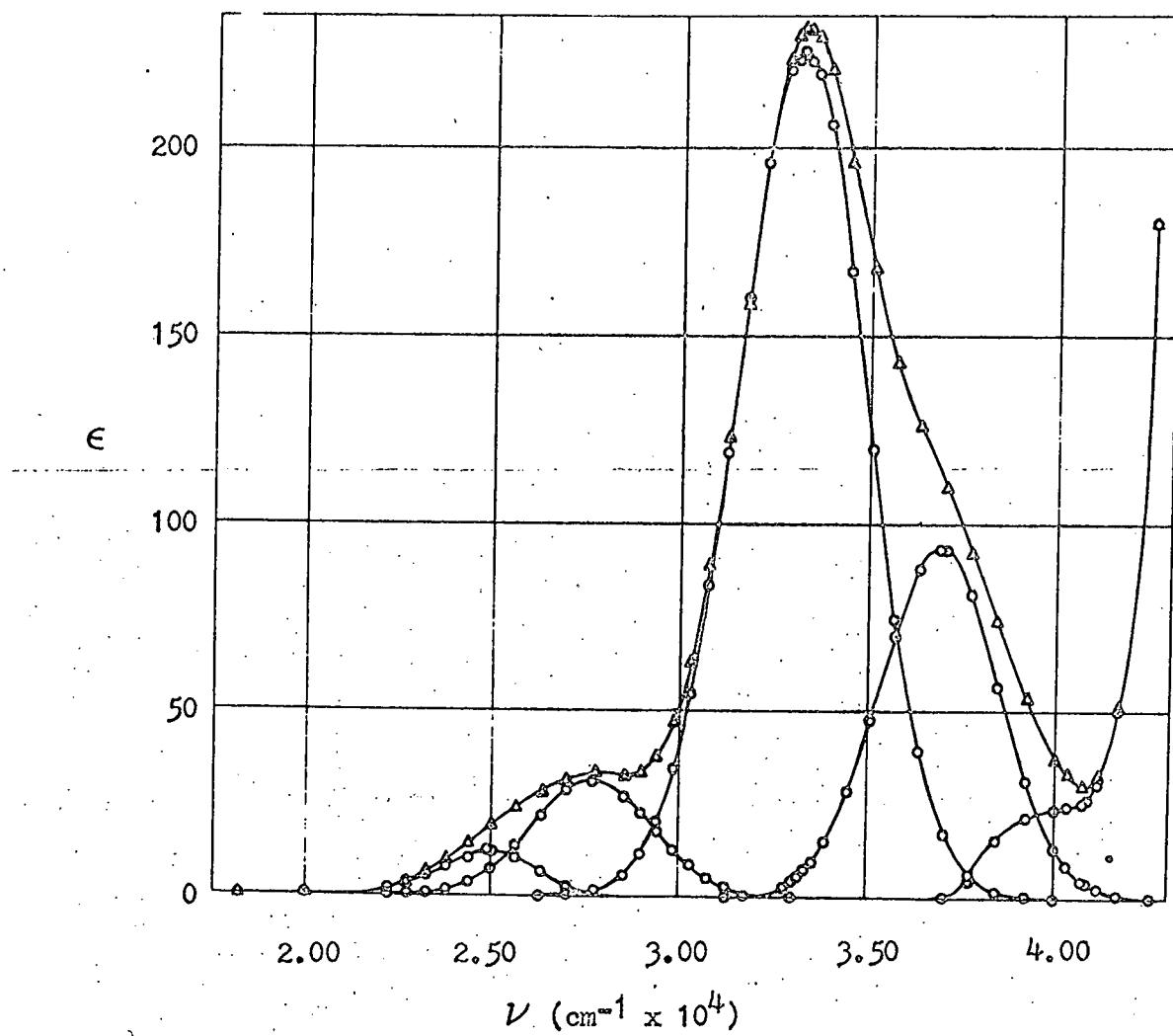


Figure 15. Gaussian analysed spectrum of $[\text{PtCl}_2(\text{en})]$ in 0.318 M chloride solution. The sum of the Gaussian peaks was essentially identical to the observed spectrum

\circ = Gaussian peaks

Δ = sum of the Gaussian peaks

This worker has observed a strong dependence of the absorption of plane-polarized light upon the orientation of single crystals of $[\text{PtCl}_2(\text{en})]$. The extremes are recorded with light polarized parallel to and perpendicular to the needle axis of the crystal. For the orientation which yields minimum absorption, one records a spectrum similar to both the solution spectrum and crystal spectra using unpolarized light in the region between $18,000 \text{ cm}^{-1}$ and $36,000 \text{ cm}^{-1}$. At higher energies, the crystal shows increasing absorption whereas the absorption in solution decreases until a minimum is reached at $40,800 \text{ cm}^{-1}$. Beyond this region, one observes the intense charge transfer in solution. The crystal exhibits a strong dichroism so that with the crystal orientation of maximum absorption at room temperature, the absorption is at least a factor of three higher in the region between $18,000 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$. Beyond $30,000 \text{ cm}^{-1}$, the crystals in this orientation exhibited absorbances beyond the limits of the spectrophotometer. Recently, Hunter¹ has recorded spectra of several thin crystals of $[\text{PtCl}_2(\text{en})]$ at low temperatures using polarized light. He has successfully obtained polarized spectra through transition energies as high as $35,000 \text{ cm}^{-1}$. One interesting feature of Hunter's results is the appearance of a pronounced shoulder on the long wavelength side of the band at $34,200 \text{ cm}^{-1}$ in the polarization of maximum absorption. It seems likely that the complexity of the absorption phenomena in the region between $20,000 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$ will necessitate a description in terms of transitions to several ligand field states related to triplet states. Unfortunately, Hunter's data are unable to provide corroboration for this

¹Hunter, L. D., Ames, Iowa. Spectral data. Private communication. 1969.

worker's proposal of the existence of a low intensity band in solutions at $\sim 39,000 \text{ cm}^{-1}$.

A similar analogy, between the spectrum of $\text{trans-}[\text{PtCl}_2(\text{NH}_3)_2]$ and that of $\text{trans-}[\text{PtCl}_2\langle(\text{n-C}_5\text{H}_{11})_2\text{NH}\rangle_2]$, has been noted by Chatt, et al. (20). In this comparison, however, one finds similarities in both band locations and intensities. If one compares the spectrum of $[\text{PtCl}(\text{dien})]^+$ (dien = diethylenetriamine) with that of $[\text{PtCl}(\text{NH}_3)_3]^+$ the analogy again appears. Such comparisons are interesting but provide little meaningful information concerning the assignment of absorption bands in terms of specific transitions. This worker is anxiously awaiting the completion of Hunter's work.

Finally, it is worth noting that this worker has obtained spectra of solutions wherein the primary absorbing species was $[\text{Pt}(\text{H}_2\text{O})_2(\text{en})]^{2+}$. Such solutions were obtained by the addition of HClO_4 to samples containing principally the dihydroxo(ethylenediamine)platinum(II) complex. The latter resulted from pH-stat studies of the hydrolysis of the dichloro complex in basic solutions. Since the spectrum of essentially pure $[\text{PtCl}_2(\text{en})]$ was also available from the solutions of the compound in high chloride, it was possible to calculate, by difference, the spectrum of the monoquo species. According to the presentation in section IV, A, the concentration of the diaquo species in solutions which are at equilibrium with respect to the reactions of Equations 1 and 2 is given by Equation 19. Substitution of this value into Equation 14, followed by rearrangement, gives for the equilibrium concentration of the monoquo species:

$$x_e = \frac{T^2}{T + 2K_2} \quad (70)$$

For the purpose of the following discussion, the symbol ϵ_{total} is defined

for equilibrium solutions by the expression:

$$A_{\text{total}} = \epsilon_{\text{total}} l_a. \quad (71)$$

The right-hand side of this expression must obey the relationship:

$$\epsilon_{\text{total}} l_a = \epsilon_0 l (a - x_e - y_e) + \epsilon_1 l x_e + \epsilon_2 l y_e, \quad (72)$$

thus:

$$\epsilon_1 = \frac{a}{x_e} \epsilon_{\text{total}} - \frac{(a - x_e - y_e)}{x_e} \epsilon_0 - \frac{y_e}{x_e} \epsilon_2. \quad (73)$$

The values for ϵ_{total} were evaluated from the spectrum of the solution corresponding to the first entry of Table 10. (For this recording, $l = 5.004 \text{ cm.}$) For the evaluation of ϵ_2 , data were taken from the first spectrum of Figure 13. In the calculation of the equilibrium concentrations of the three species, the least squares adjusted values for T (0.857 mM from Table 9) and K_2 ($1.43 \times 10^{-4} \text{ M}$ from Table 11) were used. The resultant values for the extinction coefficients of the three species are listed in Table 26 and the associated spectra are shown in Figure 16. Elleman, Reishus and Martin (38) have reported the spectrum of a solution which contained $[\text{PtCl}_2(\text{H}_2\text{O})(\text{NH}_3)]^+$ as the dominant species. Their solution was obtained by passing an aged solution of $[\text{PtCl}_3(\text{NH}_3)]^-$ through an anion exchanger, thus a small amount of $[\text{PtCl}(\text{H}_2\text{O})_2(\text{NH}_3)]^+$ probably also contributed to the recorded spectrum. Other than this case, spectra of Pt(II) complexes containing aquo ligands are generally unavailable in the literature.

B. Kinetics and Equilibria

The values for all the constants associated with the reactions of Equation 1 are listed in Table 27. Apparently, the previously reported value of $5.3 \times 10^{-5} \text{ sec}^{-1}$ for k_1 at 25°C (51) is somewhat high.

Table 26. Molar extinction coefficients ($M^{-1} \text{ cm}^{-1}$) as a function of wavelength for the three complex species discussed in this work

λ (nm)	ϵ_0	ϵ_1	ϵ_2
400	19	8	4
395			4
390	24	11	6
385			8
380	28	19	10
375			12
370	31	26	16
365			20
360	32	32	24
355			27
350	32	37	32
345	34	37	36
340	36	39	40
335	44	39	42
330	59	37	43
325	84	39	45
320	119	37	45
315	160	42	46
310	205	48	49
305	224	71	55
300	232	96	64
295	220	125	76
290	196	152	95
285	168	169	114
280	143	178	135
275	126	175	156
270	110	170	174
265	92	159	190
260	73	144	199
255	53	126	203
250	37	103	199
245	30	83	193
240	51	72	207
235	180	74	270

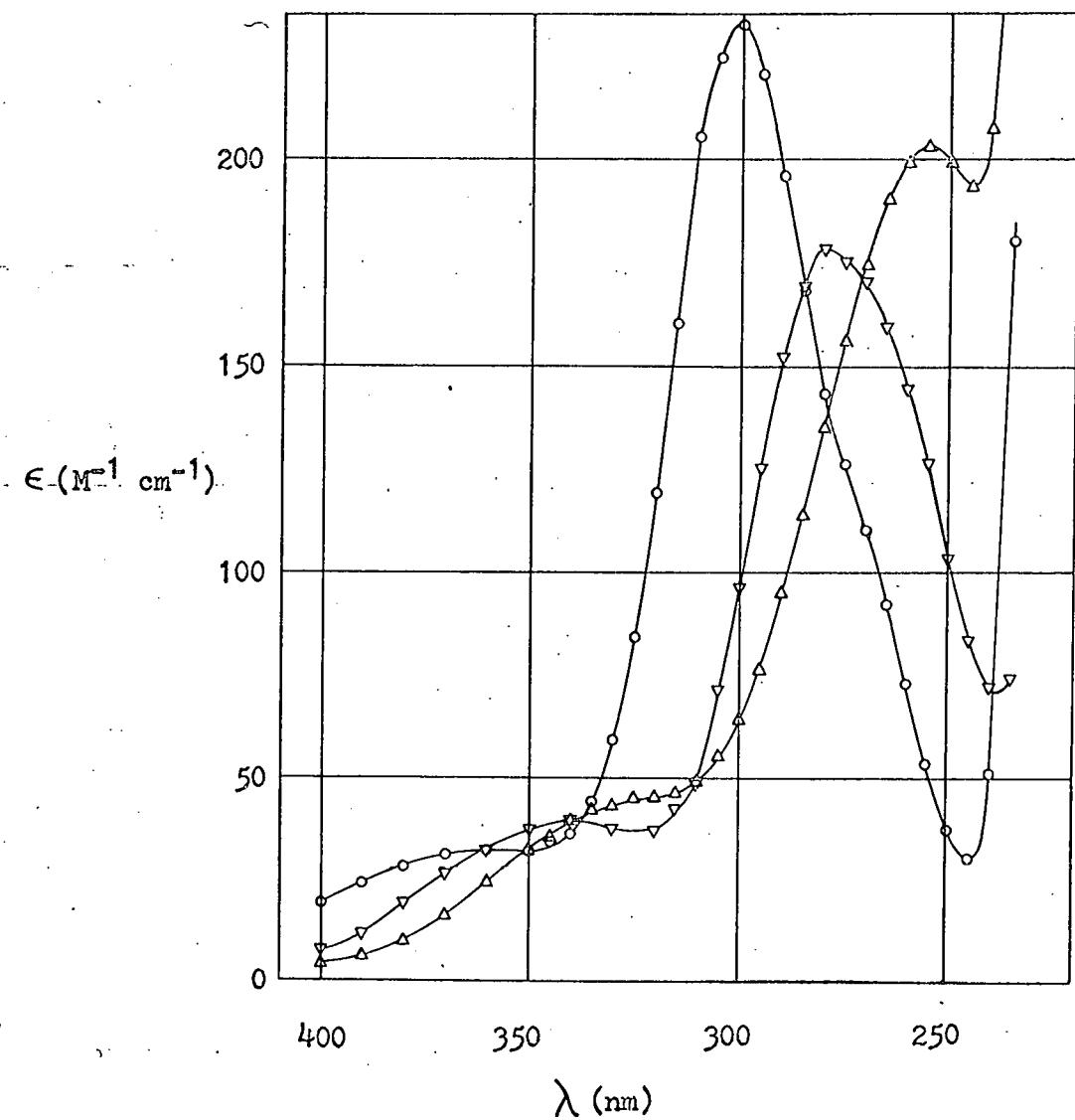


Figure 16. Spectra of the three complex species discussed in this work.

\circ = spectrum of $[\text{PtCl}_2(\text{en})]$

∇ = spectrum of $[\text{PtCl}(\text{H}_2\text{O})(\text{en})]^+$

Δ = spectrum of $[\text{Pt}(\text{H}_2\text{O})_2(\text{en})]^{2+}$

Table 27. Summary of experimentally determined values for the constants associated with the reactions of Equation 1

Constant	Value	T°C
$K_1 \times 10^3 \text{ M}$	2.76 ± 0.05	35.0
$k_1 \times 10^5 \text{ sec}^{-1}$	$11. \pm 1.$	
$k_{-1} \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$	4.01 ± 0.09	
$K_1 \times 10^3 \text{ M}$	2.33 ± 0.09	30.0
$k_1 \times 10^5 \text{ sec}^{-1}$	6.2 ± 1.7	
$k_{-1} \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$	2.53 ± 0.05	
$K_1 \times 10^3 \text{ M}$	2.19 ± 0.11	25.0
$k_1 \times 10^5 \text{ sec}^{-1}$	3.4 ± 0.4	
$k_{-1} \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$	1.54 ± 0.03	

It was not possible, by the methods employed by this worker, to experimentally determine the rate of the second aquation reaction. The main reason for this is the similarity of the rates of the two successive aquation reactions. However, having determined K_2 and k_{-2} , one can evaluate k_2 according to the expression:

$$k_2 = K_2 k_{-2} \quad (74)$$

The values for the constants associated with the reactions of Equation 2 are listed in Table 28. (The formulas which were used to calculate weighted averages and their associated errors, and the formulas for propagating

Table 28. Summary of experimentally determined values, and, in the case of k_2 , the values calculated from experimentally determined values for the constants associated with the reactions of Equation 2

Constant	Value	T°C
$K_2 \times 10^4 \text{ M}$	1.38 ± 0.05	35.0
$k_2 \times 10^5 \text{ sec}^{-1}$	7.23 ± 0.94	
$k_{-2} \times 10^1 \text{ sec}^{-1} \text{ M}^{-1}$	5.24 ± 0.65	
$K_2 \times 10^4 \text{ M}$	1.48 ± 0.05	30.0
$k_2 \times 10^5 \text{ sec}^{-1}$	6.18 ± 0.49	
$k_{-2} \times 10^1 \text{ sec}^{-1} \text{ M}^{-1}$	4.18 ± 0.30	
$K_2 \times 10^4 \text{ M}$	1.43 ± 0.11	25.0
$k_2 \times 10^5 \text{ sec}^{-1}$	4.45 ± 0.61	
$k_{-2} \times 10^1 \text{ sec}^{-1} \text{ M}^{-1}$	3.11 ± 0.35	

errors and other formulas which were used in the statistical adjustment of data, other than those formulas listed in this work, may be found in the text by Worthing and Geffner (56).)

From the values for the concentration equilibrium quotients at various temperatures, the enthalpies of the aquation reactions can be estimated. The temperature dependence of the thermodynamic equilibrium constant is given by the familiar expression:

$$d(\ln K^\circ)/dT = \Delta H^\circ/RT^2, \quad (75)$$

where, as previously defined, we have that:

$$K^\circ = K \Gamma, \quad (76)$$

thus:

$$d(\ln K^\circ)/dT = K d\Gamma/dT + \Gamma d(\ln K)/dT. \quad (77)$$

If one adopts the rather common assumption that activity coefficients are functions only of the ionic strength and of the magnitude of the charge on the ion, the following relationships are acceptable approximations:

$$\gamma_1 = \gamma_+ = \gamma_{\infty}; \quad (78)$$

$$\gamma_2 = \gamma_{2+}; \quad (79)$$

$$d\Gamma/dT = 0. \quad (80)$$

Furthermore, it will be assumed, as is usually done, that:

$$\gamma_0 = 1. \quad (81)$$

In cognizance of Equation 80, Equation 75 is adequately approximated by:

$$d(\ln K)/dT = \Delta H^\circ/RT^2, \quad (82)$$

which, upon integration, yields:

$$\log K = \frac{\Delta H^\circ}{RT \ln(10.0)} \frac{1}{T} + \text{constant}. \quad (83)$$

Thus, the enthalpy of reaction may be obtained from the slope of a plot of $\log K$ versus $1/T$ according to:

$$\Delta H^\circ = -(\text{slope})R \ln(10.0). \quad (84)$$

The enthalpies of the aquation reactions were estimated from Equation 84 utilizing the results of least squares adjustments to Equation 83. (Admittedly, a least squares fit to three points is somewhat superfluous; however, from the available least squares program and error estimates, one obtains

proper weighting of the points very conveniently.)

The standard free energy change associated with a reaction is given by the fundamental thermodynamic relationship:

$$\Delta F^\circ = -RT\ln K^\circ = -RT\ln K + RT\ln \Gamma, \quad (85)$$

wherein, it might be a rather poor approximation to assume that the $RT\ln \Gamma$ term is essentially zero. The value for γ_1 was taken equal to γ_2 for hydrochloric acid in potassium chloride solutions of the same ionic strength (57). Values of the quantity $\gamma_{C_2O_4^{2-}}/\gamma_{HC_2O_4^-}\gamma_{Cl^-}$ which were indicated in the potentiometric determination of K_2 for oxalic acid (58) were plotted as a function of ionic strength. A value for γ_{2+} was computed from this graph by multiplying values taken from this curve by γ_1^2 . At an ionic strength of 0.318 M, γ_1 attains the value of 0.725 and γ_2/γ_1^2 has a value of 0.493 (assuming negligible differences between molarities and molalities). Thus, for the aquation reactions herein described, the following approximations were used:

$$\Gamma_1 = \frac{\gamma_+ \gamma_-}{\gamma_0} = \gamma_1^2 = 0.526, \quad (86)$$

and:

$$\Gamma_2 = \frac{\gamma_{2+} \gamma_-}{\gamma_+} = \frac{\gamma_2}{\gamma_1^2} \gamma_1^2 = (0.493)(0.526) = 0.259. \quad (87)$$

The standard free energy changes associated with the aquation reactions were then calculated from Equation 85. The related entropy changes were calculated from the free energy changes and the enthalpy changes according to another fundamental thermodynamic relationship:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}. \quad (88)$$

The enthalpy and entropy of activation associated with the various reactions were estimated from transition state theory (59) according to the equation:

$$k = \frac{k_B T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (89)$$

where:

h = Planck's constant;

k_B = the Boltzmann constant;

R = the gas constant.

For the purpose of evaluating the enthalpy of activation, the relationship:

$$\Delta H^* = E_A - RT \quad (90)$$

was invoked, following the estimation of the Arrhenius energy, E_A , from the slope of a plot of the logarithm of the specific rate constant versus $1/T$.

All of the reaction and activation parameters which were evaluated appear in Table 29. Since the specific rate constants which were used with Equation 89 were those for rate expressions written in terms of concentrations, the discrepancies between the differences in entropies of activation and the entropies of reaction were not unexpected.

It is interesting to compare the values of the concentration equilibrium quotients and of the rate constants obtained as a result of this work with the values obtained by other workers for related complexes of Pt(II). Such a comparison is presented in Table 30. Tucker, Colvin and Martin (60) have noted the systematics for the concentration equilibrium quotients of the chloroammine series of Pt(II) complexes. Apparently, the charge on the species has no primary effect on the rate constants. Thus, the observed rate constants for the first aquation, in which a chloride ion is lost from

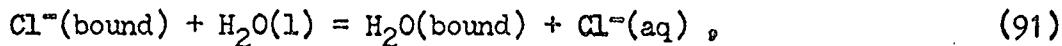
Table 29. Activation and reaction parameters, evaluated at 25.0°C, for the reactions of Equations 1 and 2

Constant	ΔH kcal mole ⁻¹	ΔS eu
$k_1 = 3.4 \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$	21	-16
$k_{-1} = 1.54 \pm 0.03 \times 10^{-2} \text{ sec}^{-1} \text{ M}^{-1}$	17	-10
Difference =	4	-6
$K_1 = 2.19 \pm 0.11 \times 10^{-3} \text{ M}$	4	0
$k_2 = 4.45 \pm 0.61 \times 10^{-5} \text{ sec}^{-1}$	8	-51
$k_{-2} = 3.11 \pm 0.35 \times 10^{-1} \text{ sec}^{-1} \text{ M}^{-1}$	9	-31
Difference =	-1	-20
$K_2 = 1.43 \pm 0.11 \times 10^{-4} \text{ M}$	-1	-22

species ranging in charge from -2 to +1, differ by less than a factor of 16.

A comparison of the activation parameters is given in Table 31. Such aquation reactions of Pt(II) complexes generally involve substantially negative entropies of activation. Typically, the activation enthalpy is about 20 kcal mole⁻¹.

The large difference between the entropies of the successive aquation reactions of $[\text{PtCl}_2(\text{en})]$ can be predicted. Both reactions can be represented by:



for which $\Delta S^\circ = -2$ eu. This entropy change was calculated using the values (in eu) of 8.1 for chloride bound to a dipositive metal ion, 16.7 for

Table 30. Concentration equilibrium quotients and rate constants for the acid hydrolysis of the chloroammine series and related complexes of platinum(II). The values for the chloroammine series are those of Tucker *et al.* (60) where the numbers in parentheses are estimated from a value for $k_{-ct}/(k_{-ct} + k_{-tc})$ of 0.06 at 20°C. The values for the dien complex are those of Gray (61)

Complex		Equil. quotient		Rate constant	
		M x 10 ⁵		sec ⁻¹ x 10 ⁵	
		First	Second	First	Second
$[\text{PtCl}_4]^{2-}$		1500	50	3.9	3.3
$[\text{PtCl}_3(\text{NH}_3)]^-$	<u>trans</u>	1300		0.62	(12.5)
		130	4	5.6	(8)
<u>cis</u> - $[\text{PtCl}_2(\text{NH}_3)_2]$		330	40	2.5	3.3
$[\text{PtCl}_2(\text{en})]$		219	14.3	3.4	4.45
<u>trans</u> - $[\text{PtCl}_2(\text{NH}_3)_2]$		32	2	9.8	5
$[\text{PtCl}(\text{NH}_3)_3]^+$		27		2.6	
$[\text{PtCl}(\text{dien})]^+$		37		10.	

$\text{H}_2\text{O(l)}$, 9.4 for bound H_2O and 13.2 for $\text{Cl}^-(\text{aq})$. These values were taken from Latimer (63) and must be considered as approximations in their application here; however, they should provide the magnitude of the change involved. To complete the prediction, one must also consider the effect of the change in charge on the complex. For this estimation, the values given by Latimer and Jolly (64) for aluminum-fluoride complexes were used. For the reactions of Equations 92 and 93 on the following page, they list

Table 31. Activation parameters for the acid hydrolysis reactions of some platinum(II) complexes. Values other than those resulting from this work, taken from Bellucco *et al.* (62) and references cited therein, and from Martin (29)

Complex		ΔH^\ddagger kcal mole ⁻¹	ΔS^\ddagger eu
$[\text{PtCl}_4]^{2-}$		21	- 8
$[\text{PtCl}_3(\text{NH}_3)]^-$	<u>trans</u>	15	-30
		20	- 9
<u>cis</u> - $[\text{PtCl}_2(\text{NH}_3)_2]$		20	-14
$[\text{PtCl}_2(\text{en})]$		21	-16
<u>trans</u> - $[\text{PtCl}_2(\text{NH}_3)_2]$		19	-11
$[\text{PtCl}(\text{NH}_3)_3]^+$		18	-18
$[\text{PtCl}(\text{dien})]^+$		20	-10
$[\text{PtCl}_3(\text{H}_2\text{O})]^-$		25	+ 2
<u>cis</u> - $[\text{PtCl}(\text{NH}_3)_2(\text{H}_2\text{O})]^+$		20	-11
$[\text{PtCl}(\text{H}_2\text{O})(\text{en})]^+$		8	-51



charge effects of 3 and 12 eu, respectively. The changes in charge for the reverse of the above reactions correspond to the changes involved in the aquation reactions of $[\text{PtCl}_2(\text{en})]$. Thus, on the basis of such approximations, one estimates the values as -5 and -14 eu, respectively, for the

aquations reactions of this work. A significant difference in the entropies of these reactions is, therefore, to be expected.

VII. LITERATURE CITED

1. Magnus, G., Pogg. Ann., 14, 242 (1828).
2. Werner, A., Z. anorg. Chem., 3, 267 (1893).
3. Bethe, H., Ann. Physik, 3, 133 (1929).
4. Ilse, F. E. and Hartmann, H., Z. physik. Chem., 192, 239 (1951).
5. Hückel, E., Z. Phys., 70, 204 (1931).
6. Wolfsberg, M. and Helmholz, L., J. Chem. Phys., 20, 837 (1952).
7. Ballhausen, C. J. and Gray, H. B., Inorg. Chem., 1, 111 (1962).
8. Gray, H. B. and Ballhausen, C. J., J. Amer. Chem. Soc., 85, 260 (1963).
9. Viste, A. and Gray, H. B., Inorg. Chem., 3, 1113 (1964).
10. Basch, H. and Gray, H. B., Inorg. Chem., 6, 365 (1967).
11. Cotton, F. A. and Haas, T. E., Inorg. Chem., 3, 1004 (1964).
12. Cotton, F. A. and Harris, C. B., Inorg. Chem., 6, 369 (1967).
13. Cotton, F. A. and Harris, C. B., Inorg. Chem., 6, 376 (1967).
14. Fenske, R. F. and Sweeney, C. C., Inorg. Chem., 3, 1105 (1964).
15. Fenske, R. F., Inorg. Chem., 4, 33 (1965).
16. Fenske, R. F., Caulton, K. G., Radtke, D. D. and Sweeney, C. C., Inorg. Chem., 5, 951 (1966).
17. Cotton, F. A. Chemical Applications of Group Theory. New York, New York, Interscience Publishers. 1963.
18. Martin, D. S., Jr. and Lenhardt, C. A., Inorg. Chem., 3, 1368 (1964).
19. Fenske, R. F., Martin, D. S., Jr. and Ruedenberg, K., Inorg. Chem., 1, 441 (1962).
20. Chatt, J., Gamen, G. A. and Orgel, L. E., J. Chem. Soc. (London), 1958, 486 (1958).
21. Martin, D. S., Jr., Tucker, M. A. and Kassman, A. J., Inorg. Chem., 4, 1682 (1965).

22. Martin, D. S., Jr., Foss, J. G., McCarville, M. E., Tucker, M. A. and Kassman, A. J., *Inorg. Chem.*, 5, 491 (1966).
23. McCaffery, A. J., Schatz, P. N. and Stephens, P. J., *J. Amer. Chem. Soc.*, 90, 5730 (1968).
24. Mason, W. R., III and Gray, H. B., *J. Amer. Chem. Soc.*, 90, 5721 (1968).
25. Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Reactions*. 2nd ed. New York, New York, John Wiley and Sons, Inc. 1967.
26. Basolo, F. and Pearson, R. G. *The Trans Effect in Metal Complexes*. In Cotton, F. A., ed. *Progress in Inorganic Chemistry*. Vol. 4. New York, New York, Interscience Publishers. 1962.
27. Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Chemistry*. In Gould, R. F., ed. *Advances in Chemistry Series*. No. 49. Washington, D. C., American Chemical Society. 1965.
28. Langford, C. H. and Gray, H. B. *Ligand Substitution Processes*. New York, New York, W. A. Benjamin, Inc. 1965.
29. Martin, D. S., Jr., *Inorg. Chim. Acta Reviews*, 1, 87 (1967).
30. Belluco, U., Cattalini, L., Basolo, F., Pearson, R. G. and Turco, A., *J. Amer. Chem. Soc.*, 87, 241 (1965).
31. Pearson, R. G., *J. Amer. Chem. Soc.*, 85, 3533 (1963).
32. Lokken, S. J. and Martin, D. S., Jr., *Inorg. Chem.*, 2, 562 (1963).
33. Teggins, J. E., Gano, D. R., Tucker, M. A. and Martin, D. S., Jr., *Inorg. Chem.*, 6, 69 (1967).
34. Teggins, J. E. and Martin, D. S., Jr., *Inorg. Chem.*, 6, 1003 (1967).
35. Grinberg, A. A. and Shagisultanova, G. A., *Zhur. Neorg. Khim.*, 5, 280 (1960).
36. Nikolaeva, N. M. and Pastukhova, E. D., *Zhur. Neorg. Khim.*, 12, 1514 (1967).
37. Grantham, L. F., Elleman, T. S. and Martin, D. S., Jr., *J. Amer. Chem. Soc.*, 77, 2965 (1955).
38. Elleman, T. S., Reishus, J. W. and Martin, D. S., Jr., *J. Amer. Chem. Soc.*, 80, 536 (1958).
39. Sanders, C. I. and Martin, D. S., Jr., *J. Amer. Chem. Soc.*, 83, 807 (1961).

40. Reishus, J. W. and Martin, D. S., Jr., *J. Amer. Chem. Soc.*, 83, 2457 (1961).
41. Martin, D. S., Jr. and Adams, R. J. *Trans-dichlorodiammineplatinum(II)*. Acid Hydrolysis and Isotopic Exchange of the Chloride Ligands. In Kirschner, S., ed. *Advances in the Chemistry of the Coordination Compounds*. pp. 579-589. New York, New York, The Macmillan Co. 1961.
42. Aprile, F. and Martin, D. S., Jr., *Inorg. Chem.*, 1, 551 (1962).
43. Gano, D. R., Vandegrift, G. F. and Martin, D. S., Jr., *Inorg. Chim. Acta*, 2, 219 (1968).
44. Martin, D. S., Jr. and Bahn, E. L., *Inorg. Chem.*, 6, 1653 (1967).
45. Elding, L. I. and Leden, I., *Acta Chem. Scand.*, 20, 706 (1966).
46. Bjerrum, J., *Kgl. Dansk Videnskab Selskab., Mat.-Fys. Medd.*, 21, Nr. 4 (1944).
47. Newman, L. and Hume, D. N., *J. Amer. Chem. Soc.*, 79, 4571 (1957).
48. Basolo, F., Bailer, J. C., Jr. and Tarr, B. R., *J. Amer. Chem. Soc.*, 72, 2433 (1950).
49. Keller, R. N. *Platinum(II)chloride*. In Fernelius, W. C., ed. *Inorganic Synthesis*. Vol. 2. New York, New York, McGraw-Hill Book Co., Inc. 1939.
50. Diehl, H. and Smith, G. F. *Quantitative Analysis*. New York, New York, John Wiley and Sons, Inc. 1957.
51. Banerjea, D., Basolo, F. and Pearson, R. G., *J. Amer. Chem. Soc.*, 79, 4055 (1957).
52. Wentworth, W. E., *J. Chem. Ed.*, 42, 96 (1965).
53. Deming, W. E. *Statistical Adjustment of Data*. New York, New York, John Wiley and Sons, Inc. 1943.
54. Hodgman, C. D., ed. *Handbook of Chemistry and Physics*. 41st ed. Cleveland, Ohio, Chemical Rubber Publishing Co. 1959.
55. Guggenheim, E. A., *Phil. Mag.*, 2, 538 (1926).
56. Worthing, A. G. and Geffner, J. *Treatment of Experimental Data*. New York, New York, John Wiley and Sons, Inc. 1948.
57. Harned, H. S. and Ehlers, R. W., *J. Amer. Chem. Soc.*, 55, 2179 (1933).

58. Pinching, G. D. and Bates, R. G., J. Research Nat. Bur. Standards, 40, 405 (1948).
59. Benson, S. W. The Foundations of Chemical Kinetics. New York, New York, McGraw-Hill Book Co., Inc. 1960.
60. Tucker, M. A., Colvin, C. B. and Martin, D. S., Jr., Inorg. Chem., 3, 1373 (1964).
61. Gray, H. B., J. Amer. Chem. Soc., 84, 1548 (1962).
62. Bellucco, U., Ettorre, R., Basolo, F., Pearson, R. G. and Turco, A., Inorg. Chem., 5, 591 (1966).
63. Latimer, W. M. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. 2nd ed. Englewood Cliffs, New Jersey, Prentice-Hall, Inc. 1961.
64. Latimer, W. M. and Jolly, W. L., J. Amer. Chem. Soc., 75, 1548 (1953).

VIII. ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. Don S. Martin, Jr. for the guidance he has provided, the patience he has shown and the many hours he has spent with this author during the course of this research.

The author also wishes to thank Dr. James Espenson for help with, and use of, the stopped-flow instrument.

A number of group members and summer research people deserve thanks for their assistance and stimulating discussions.

Finally, the author's wife, Carol; son, Terry; and daughter, Sherry have certainly earned merit by enduring cohabitation with this author during the period when this dissertation was prepared. An expression of gratitude to them is totally inadequate.

IX. APPENDIX

The development presented herein follows closely that of Wentworth (52).

Experimentally, n pairs of measurements of the variables are made which will be designated as (a_i, T_i) ; $i = 1, \dots, n$. A single function, F , relates these variables and the two parameters, α and β , for which one wishes estimates. The function is:

$$F(a, T, \alpha, \beta) = T^3 + \alpha T^2 + (\beta - a\alpha)T - 2a\beta = 0. \quad (94)$$

Estimates of the parameters may be found, which will be designated by $\bar{\alpha}$ and $\bar{\beta}$, based on the principle of least squares. The least squares adjusted values of the variable T will be designated by \bar{T}_i . The a variable will be assumed to be exact. The residual of the i th measurement is given by:

$$v_i = (T_i - \bar{T}_i). \quad (95)$$

Assuming that satisfactory first approximations for the parameters, α^0 and β^0 , are obtainable, the differences between these first approximations and the least squares values are given by:

$$\Delta \alpha = (\alpha^0 - \bar{\alpha}) \quad (96)$$

and

$$\Delta \beta = (\beta^0 - \bar{\beta}). \quad (97)$$

The mathematical statement of the least squares problem is that one desires to obtain a minimization of the sum of the weighted squares of the residuals, that is, one seeks a minimization of:

$$S = \sum_i w_i v_i^2, \quad (98)$$

subject to the restricting equations:

$$F_i(a_i, \bar{T}_i, \bar{\alpha}, \bar{\beta}) = 0 ; \quad i = 1, \dots, n. \quad (99)$$

The weights are defined by:

$$w_i = \frac{\sigma_o^2}{\sigma_i^2}, \quad (100)$$

where σ_i is the standard deviation of the i th measurement of T ; and σ_o is, by definition, the standard deviation of a measured value of unit weight. In practice, however, σ_o^2 is an arbitrary constant which is chosen to make the magnitude of the weights convenient, and which will not effect the value of any quantity determined by the method.

The solution of the problem is simplified considerably if the restricting Equations 99 are linear with respect to both variables and parameters. (Of course, Equation 94 is linear in the parameters and could be treated as a function of the form: $y = \beta x + \alpha$. Such a treatment would, however, involve variables of little physical significance. Furthermore, both variables would be functions of T which would force one to consider both x and y subject to error - a problem of considerable complexity.) To simplify the restricting equations, one expands in a Taylor series about the point $(a_i, T_i, \alpha^0, \beta^0)$ and truncates the series after the first order terms. The Taylor series expansion of the restricting Equations 99 is of the form:

$$F_i(a_i, \bar{T}_i, \bar{\alpha}, \bar{\beta}) = F_i^0(a_i, T_i, \alpha^0, \beta^0) + F_{iT}(T_i - T_i) + F_{i\alpha}(\bar{\alpha} - \alpha^0) + F_{i\beta}(\bar{\beta} - \beta^0) \quad (101)$$

where:

$$F_{iT} = (\delta F_i / \delta T) \Big|_{(a_i, T_i, \alpha^0, \beta^0)} ; \quad (102)$$

$$F_{i\alpha} = (\delta F_i / \delta \alpha) \Big|_{(a_i, T_i, \alpha^0, \beta^0)} ; \quad (103)$$

$$F_{i\beta} = (\delta F_i / \delta \beta) \Big|_{(a_i, T_i, \alpha^0, \beta^0)} . \quad (104)$$

In terms of the residuals of Equation 95, and of the differences of Equations 96 and 97, Equation 101 becomes:

$$F_i(a_i, \bar{T}_i, \bar{\alpha}, \bar{\beta}) = F_i^0(a_i, T_i, \alpha^0, \beta^0) - F_{iT} V_i - F_{i\alpha} \Delta \alpha - F_{i\beta} \Delta \beta \quad (105)$$

which yields the reduced restricting equations:

$$F_i^0(a_i, T_i, \alpha^0, \beta^0) = F_{iT} V_i + F_{i\alpha} \Delta \alpha + F_{i\beta} \Delta \beta ; \quad i = 1, \dots, n. \quad (106)$$

Now, in order for S of Equation 98 to be a minimum, it is necessary that:

$$\delta S / \delta V_i = 2 \sum_i w_i V_i = 0 , \quad (107)$$

or, it must be that:

$$dS = (\delta S / \delta V_i) dV_i = 0 . \quad (108)$$

Combination of Equations 107 and 108 yields:

$$\frac{1}{2} dS = \sum_i w_i V_i dV_i = 0 . \quad (109)$$

The variations in the residuals, dV_i , must satisfy the differential of the restricting Equations 106, thus:

$$F_{iT} dV_i + F_{i\alpha} d\Delta \alpha + F_{i\beta} d\Delta \beta = 0 ; \quad i = 1, \dots, n. \quad (110)$$

The solution of the problem is now one of satisfying Equation 109 subject to the restricting Equations 110.

Introduction of n arbitrary multipliers, $-\lambda_1, \dots, -\lambda_n$, and multiplication of each times Equations 110 yields:

$$-\lambda_i F_{iT} dV_i - \lambda_i F_{iA} d\Delta\alpha - \lambda_i F_{i\beta} d\Delta\beta = 0 ; \quad i = 1, \dots, n. \quad (111)$$

Addition of Equations 111 and Equations 109, followed by collection of coefficients of the differentials, gives:

$$\sum_i (w_i V_i - \lambda_i F_{iT}) dV_i - \sum_i \lambda_i F_{iA} d\Delta\alpha - \sum_i \lambda_i F_{i\beta} d\Delta\beta = 0. \quad (112)$$

In order to have a meaningful solution of Equation 112, the coefficient of each differential must equal zero, that is:

$$w_i V_i - \lambda_i F_{iT} = 0 ; \quad i = 1, \dots, n; \quad (113)$$

$$\sum_i \lambda_i F_{iA} = 0; \quad (114)$$

$$\sum_i \lambda_i F_{i\beta} = 0. \quad (115)$$

Equations 113 can be solved for the residuals, yielding:

$$V_i = \frac{\lambda_i F_{iT}}{w_i} ; \quad i = 1, \dots, n. \quad (116)$$

Substitution of these values into the restricting Equations 106 gives:

$$F_i^o(a_i, T_i, \alpha^o, \beta^o) = \frac{\lambda_i (F_{iT})^2}{w_i} + F_{iA} \Delta\alpha + F_{i\beta} \Delta\beta. \quad (117)$$

Introduction of the definition:

$$L_i = \frac{(F_{iT})^2}{w_i}, \quad (118)$$

followed by its substitution into Equation 117, yields, after rearrangement:

$$\lambda_i = \frac{1}{L_i} (F_i^0 - F_i \alpha \Delta \alpha - F_i \beta \Delta \beta) . \quad (119)$$

The λ_i can be eliminated by substitution of Equation 119 into Equations 114 and 115 to yield:

$$\sum_i \frac{F_i \alpha}{L_i} \Delta \alpha + \sum_i \frac{F_i \beta}{L_i} \Delta \beta = \sum_i \frac{-F_i \alpha}{L_i} \frac{F_i^0}{F_i} , \quad (120)$$

and

$$\sum_i \frac{F_i \beta}{L_i} \Delta \alpha + \sum_i \frac{F_i \beta}{L_i} \Delta \beta = \sum_i \frac{F_i \beta}{L_i} \frac{F_i^0}{F_i} . \quad (121)$$

These are the normal equations and are simply a pair of linear equations which can be solved for $\Delta \alpha$ and $\Delta \beta$.

For the purpose of continuing, Equations 120 and 121 are now written as:

$$b_{11} \Delta \alpha + b_{12} \Delta \beta = c_1 \quad (122)$$

and

$$b_{21} \Delta \alpha + b_{22} \Delta \beta = c_2 . \quad (123)$$

The corresponding elements of the matrix inverse to the coefficient matrix for Equations 122 and 123 are given the symbols: d_{kl} . From the inverse matrix, it can easily be shown that:

$$\Delta \alpha = d_{11} c_1 + d_{12} c_2 \quad (124)$$

and

$$\Delta \beta = d_{21} c_1 + d_{22} c_2 . \quad (125)$$

The desired parameter estimates are then calculated from Equations 96 and 97. The utility of the inverse matrix solution rests in the fact that the

variances of the parameters are simply given by:

$$\sigma_{\alpha}^2 = d_{11} \sigma_o^2 \quad (126)$$

and

$$\sigma_{\beta}^2 = d_{22} \sigma_o^2. \quad (127)$$