DEDICATION

This thesis is respectfully dedicated to my wife, to my parents and close friends. Their counsel and encouragement has brought me over many obstacles

UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

THE PREPARATION AND KINETICS OF CHLORO-1,4,7-TRIETHYLDIETHYLENETRIAMINE GOLD(III)

This thesis is submitted to the Committee of Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

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LIST OF ABBREVIATIONS

The following abbreviations will be used throughout the text.

Abbreviation	Name & Formula
amine	any dien or substituted dien
amine$_{-H}$	the conjugate base of amine
dien	diethylenetriamine $NH_2CH_2CH_2NHCH_2CH_2NH_2$
dien$_{-H}$	the conjugate base of dien $NH_2CH_2CH_2NCH_2CH_2NH_2^-$
Et$_4$dien	1,1,7,7-tetraethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$
Et$_4$dien$_{-H}$	the conjugate base of Et$_4$dien $(C_2H_5)_2NCH_2CH_2NCH_2CH_2N(C_2H_5)_2^-$
Me$_4$dien	1,1,7,7-tetramethlydiethylenetriamine $(CH_3)_2NCH_2CH_2NHCH_2CH_2N(CH_3)_2$
Me$_4$dien$_{-H}$	the conjugate base of Me$_4$dien $(CH_3)_2NCH_2CH_2NCH_2CH_2N(CH_3)_2^-$
Me$_2$dien	1,1-dimethlydiethylenetriamine $(CH_3)_2NCH_2CH_2NHCH_2CH_2NH_2$
Me$_2$dien$_{-H}$	the conjugate base of Me$_2$dien $(CH_3)_2NCH_2CH_2NCH_2CH_2NH_2^-$

Abbreviation	Name & Formula
Et_2dien	1,1-diethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$
Et_2dien_{-H}	the conjugate base of Et_2dien $(C_2H_5)_2NCH_2CH_2NCH_2CH_2NH_2^-$
$MeEt_4dien$	4-methyl-1,1,7,7-tetraethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2N(CH_3)CH_2CH_2N(C_2H_5)_2$
Me_5dien	1,1,4,7,7-pentamethlydiethylenetriamine $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$
Me_3dien	1,4,7-trimethyldiethylenetriamine $(CH_3)NHCH_2CH_2N(CH_3)CH_2CH_2NH(CH_3)$
Me_3dien_{-H}	the conjugate base of Me_3dien $(CH_3)NHCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)^-$
Et_3dien	1,4,7-triethyldiethylenetriamine $(C_2H_5)NHCH_2CH_2N(C_2H_5)CH_2CH_2NH(C_2H_5)$
Et_3dien_{-H}	the conjugate base of Et_3dien $(C_2H_5)NHCH_2CH_2N(C_2H_5)CH_2CH_2N(C_2H_5)^-$

ABSTRACT

The square-planar complex $[Au(1,4,7\text{-}Et_3dien)Cl](PF_6)_2$ has been synthesized and its aqueous solution chemistry investigated. The rate of bromide substitution for chloride has been studied along with the rate of the chelate unwrapping reaction for the bromo-complex. These results are compared with work on previously studied gold complexes.

INDRODUCTION

The rates of substitution reactions of square-planar metal complexes have been found to depend on the nature and concentration of the reactant. Complexes of Pd(II) and Pt(II) have been extensively studied and in recent years several Au(III) complexes have also been investigated. The general rate law for ligand substitution in square-planar metal complexes is :

$$\text{Rate} = [k_1 + k_2\,(\text{Y})\,]\,[\text{complex}]^{1}$$

where k_1 and k_2 are first and second order rate constants respectively, and Y is the entering group.

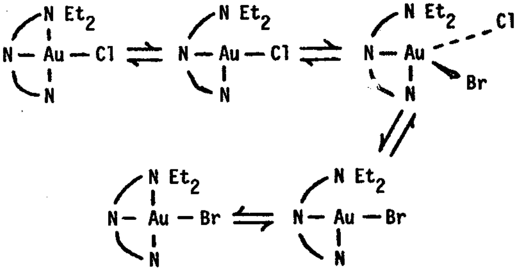
Studies of square-planar complexes of Pd(II) and Pt(II) have shouw that the reaction rates of certain N-alkyl substituted diethylenetriamine compounds are nearly independent of reagent concentration [2]. This inhibition of the attack of the substituting nucleophile has been attributed to steric hinderance by the alkyl groups lying above and below the plane of the metal ion.

The aqueous solution chemistry of complexes of the type $[\text{Au(amine)X}]^{+2}$ and $[\text{Au(amine}_{-H})\text{X}]^{+}$ has been reported [3] as involving the acid-base equilibra shown in R-1

$$[\text{Au(amine)X}]^{+2} \underset{H^{+}}{\overset{OH^{-}}{\rightleftharpoons}} [\text{Au(amine}_{-H})\text{X}]^{+} \underset{X^{-}}{\overset{OH^{-}}{\rightleftharpoons}} [\text{Au(amine}_{-H})\text{OH}]^{+} \qquad \text{(R-1)}$$

where amine = dien; 1,1-Me_2dien; 1,1-Et_2dien; 1,1,7,7-Me_4dien, and X = Cl^-, Br^-. These complexes show the following characteristics. (1) Au(III)$amine_{-H}$ complexes hydrolyze in neutral solutions, (2) excess halide ion slows hydroysis in certain pH ranges, (3) the conjugate acids of these complexes are stable in perchloric acid, (4) the conjugate acids of these complexes undergo decomposition to tetrahalo anions in hydrohalic acids (HBr, HCl etc.)[2,3,4].

It has been suggested that the bromide substitution of $[Au(Et_2dien)Cl]^{+2}$ occurs via the ring opening mechanism shown in R-2[5]:



(R-2)

This mechanism was also used to explain the faster rate of bromide substitution of $[Au(MeEt_4dien)Cl]^{+2}$ over $[Au(Me_5dien)Cl]^{+2}$[6].

The Au(III) complexes discussed above fall into two groups; those that contain no dissociable hydrogen atoms and thus cannot form a conjugate base,(e.g. $[Au(Me_5dien)Cl]^{+2}$ and $[Au(MeEt_4dien)Cl]^{+2}$) and those that form such bases by loss of a hydrogen, most probably the one bonded to the central nitrogen of the diethylenetriamine chelate ligand. This hydrogen is believed to be the most acidic.

This paper reports the results of an investigation of the aqueous solution chemistry and the Br^- substitution rate of a complex which can only form a conjugate base by the loss of a hydrogen from a terminal nitrogen of the chelate ring. The rate of the chelate unwrapping reaction for the bromo-complex is also reported.

EXPERIMENTAL

Materials: Fine gold powder (purity 99.9%) and ammonium hexaflurophosphate (purity 96%) were obtained from Ventron Corp. Alpha Inorganics. The 1,4,7-triethyldiethyenetriamine was obtained from Ames Laboratories and used without further purification. All other chemicals used were reagent grade or better.

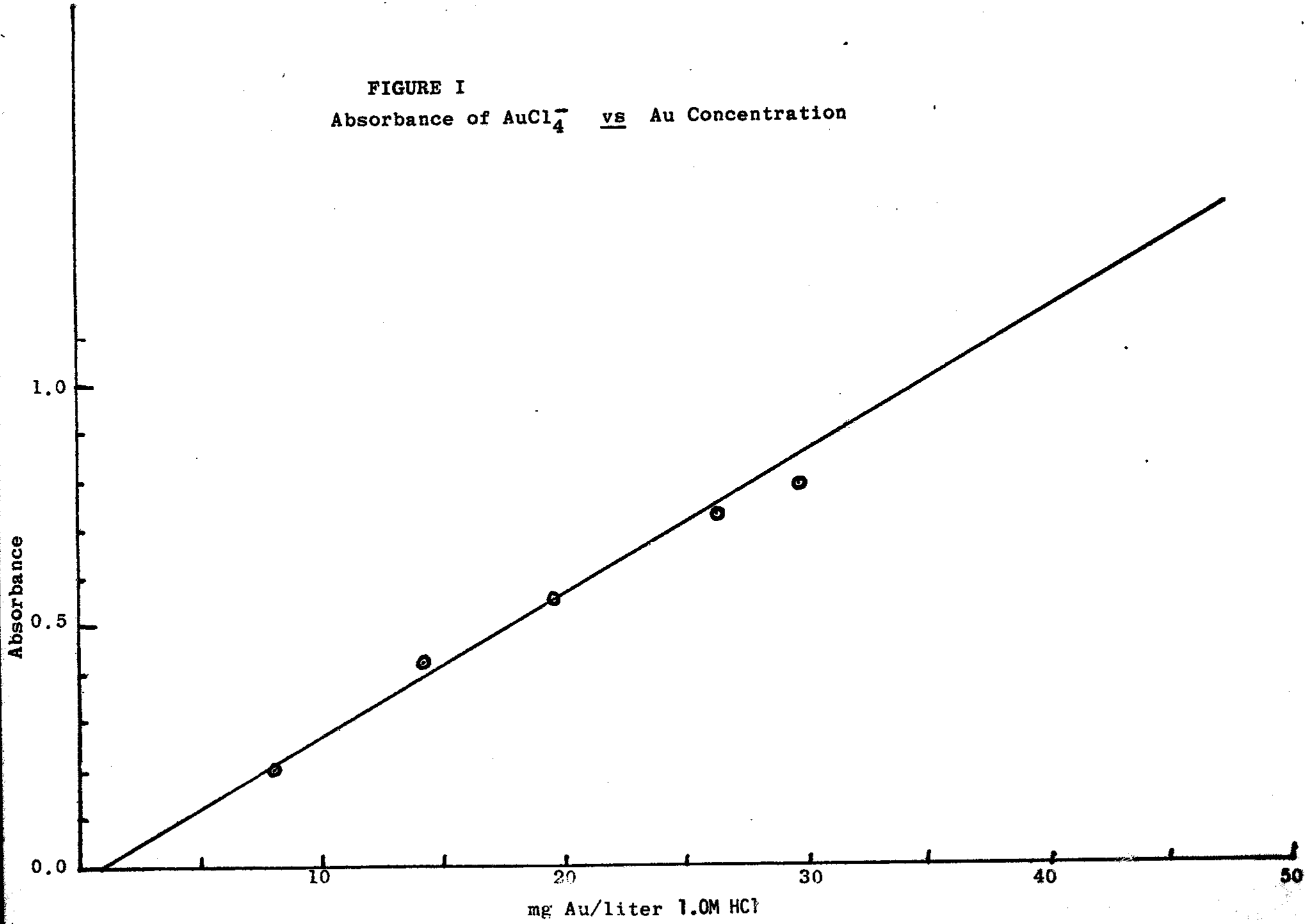
Analyses: All gold analyses were performed in triplicate. A small, accurately weighed amount of product was placed in a ten ml beaker and processed as described under Synthesis of $HAuCl_4$. Before the solution was allowed to cool it was diluted in a flask to a volume of 100 ml with 1M HCl. The tetrachloroauric acid solution had a final concentration in the 10^{-4}M range. From the absorbances of these solutions at 315nm the concentrations of gold were read from a previously prepared curve of Absorbance vs concentration of $HAuCl_4$. This calibration curve is shown in Figure I.

Another method to determine the gold content of the product was done via the combustion method. A small accurately weighed amount of product was added to a crucible and cover that had been previously fired to constant weight. The crucible, cover and product was accurately weighed. They were then fired to a constant weight driving off all combustible parts of the product and leaving the gold behind. The gold contained in the product was then obtained by weight difference.

Synthesis of $HAuCl_4$: One gram of gold powder was treated with

FIGURE I

Absorbance of $AuCl_4^-$ *vs* Au Concentration



one ml of concentrated HNO_3 and three ml of concentrated HCl in a small (10 ml) beaker. This was covered with a watch glass and heated gently. The solution was boiled to a small volume and three ml of concentrated HCl added three consecutive times. Yellowish crystals of the desired product formed on cooling.

Synthesis of $[Au(Et_3dien)Cl](PF_6)_2$: Five mmoles of $HAuCl_4$ (1 gram Au) were dissolved in 100 ml of distilled water. Five grams of LiCl were added and the solution cooled to 0°C. Five mmoles of 1,4,7-triethyldiethylenetriamine were added dropwise keeping the pH below 4.0. A yellowish precipitate formed on the addition of the dien. At the completion of this process five mls of a one mmole per ml solution of LiOH were added. Some precipitate dissolved and the solution turned a greenish tint. The mixture was then filtered. To the filtrate was added five grams of NH_4PF_6 in a ten ml solution. The solution was then frozen in a liquid nitrogen bath and evaporated to a small volume under vacuum at which point crystals were formed. The mixture was filtered and the crystals recovered. The crystals were dissolved in a minimal amount of 10^{-3}M HCl (20-30 mls). The solution was again evaporated under vacuum until crystals were formed. The mixture was filtered and the crystals recovered. They were washed with three ten ml aliquots of ether, placed into a desiccator and allowed to dry at 5°C in a refrigerator.

Analysis: Calculated for $[Au(Et_3dien)Cl](PF_6)_2$ Au,27.75% Found; by conversion to $HAuCl_4$ 28.85% ; by combustion method 26.29%

Synthesis of $[Au(Et_3dien)Br]^{+2}$ ion in solution: A ten ml solution containing 71.4 mgs (0.100 mmole) of $[Au(Et_3dien)Cl](PF_6)_2$ was adjusted to pH 10.0 with NaOH. this solution was passed through a column containing a strong base anion exchange resin in the OH^- form. The column was rinsed with distilled water to give a final volme of 45 ml. To this five mls of 1M $HClO_4$ was added to give a solution containing 0.10 mmoles $[Au(Et_3dien)H_2O]^{+3}$ in 0.1M $HClO_4$. To this solution was added 10.3 mgs (0.10 mmoles) NaBr and the solution diluted to 250 mls in a volumetric flask using 0.1M $HClO_4$. A rapid replacement of Br^- for H_2O occured and a 4.0×10^{-4}M solution of $[Au(Et_3dien)Br]^{+2}$ resulted.

Hydrolysis Studies: In the first experiment 56 mgs (0.05 mmoles) of $[Au(Et_3dien)Cl](PF_6)_2$ were dissolved in 100 mls of 0.1M HCl to produce a solution with a complex concentration of 8×10^{-4}M. This solution was placed in a water jacketed beaker kept at 25°C ± .1°C. The pH, which was initially 2.0, was adjusted with NaOH. After each pH change a spectrum was obtained using either a Perkin-Elmer 202 Spectraphotometer or a Cary 118 Spectrophotometer in the wavelength range of 270-390 nm. After each absorption measurement the sample was returned to the jacketed beaker.

In a second experiment 56 mgs of $[Au(Et_3dien)Cl](PF_6)_2$ was dissolved in less than 100 ml H_2O, brought to pH 11.0 with NaOH and allowed to pass through a strong base anion exchange resin in OH^- form to remove Cl^-. The effluent and washings from this column were collected and diluted to 100 ml in a volumetric flask. The initial pH of 10.7 was decreased with $HClO_4$ and spectral changes studied under the same conditions as previously described.

In a third experiment the same amount of $[Au(Et_3dien)Cl](PF_6)_2$ was dissolved in water. Chloride ion was again removed by ion exchange and sufficent $HClO_4$ added to yield on dilution to 100 ml a 0.01M concentration of acid. Small amounts of a dilute NaBr solution were added until a total of 0.10 mmole Br^- was present. Spestral changes were recorded during each addition of Br^-.

Kinetic Studies: The replacement of Cl^- for Br^- in $[Au(Et_3dien)Cl]^{+2}$ was studied as follows. A solution of 4×10^{-4}M $[Au(Et_3dien)Cl]^{+2}$ was prepared in 0.1M $HClO_4$. Kinetic studies were run by allowing the solution to react with an equal volume of a 0.1M $HClO_4$ solution containing various bromide concentrations. Each solution had enough $NaClO_4$ in it to maintain after mixing, a total ionic strengh of 0.2.

Rates were determined using an Aminco-Morrow Stopped Flow Apparatus in conjuction with a monochromator from a Beckman D.U.. The photomultiplier tube was connected through an Amnico Morrow High Performance Kinetic Photometer to the vertical input of a Tektronix 3A1 Storage Oscilloscope. The resulting traces of change in percent transmittance vs time were recorded using a Polaroid Oscilloscope Camera. Typical traces are shown in Figure II. All reactions were carried out at a temperature of 25± .1°C. The wavelength used was 315 nm. Bromide concentrations, after mixing, were varied from 0.01M to 0.05M. Percent transmittance values obtained from the oscilloscope traces were converted to absorbance values and psuedo first order rate constants calculated from plots of :

$$\ln\left[\frac{A_t - A_\infty}{A_0 - A_\infty}\right] \text{ vs time}$$

where A_0, A_t, and A_∞ represent absorbance at time t=0, t=t, $t=\infty$. A typical plot is shown in Figure III.

To study the kinetics of chelate ligand removal a solution of the complex ion $[Au(Et_3dien)Br]^{+2}$ was prepared as described in the Experimental section. The kinetics of reaction R-5 (see page 23) were studied using a Perkin-Elmer 202 Ultraviolet-Visible Spectrophotometer in conjuction with a Hewlett-Packard Model 17501A Strip Chart Recorder.

Equal volumes of the complex solution and a solution containing Br^- ion were simultaneously pipetted into the cell of the spectrophotometer and a trace of absorance vs time was obtained. As in the previous kinetic study the bromide solution contained enough $NaClO_4$ to produce, after mixing, a final ionic strength of 0.2 and the bromide concentrations in the range of 0.01M to 0.05M. All

FIGURE II

FIG. II-A

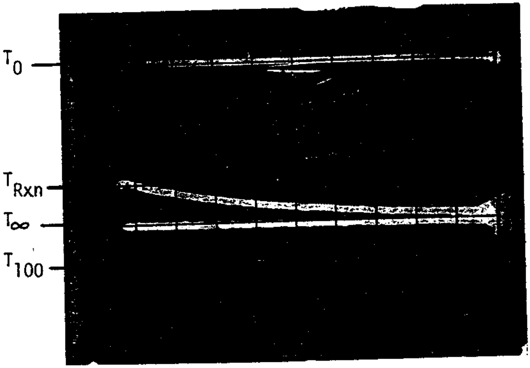
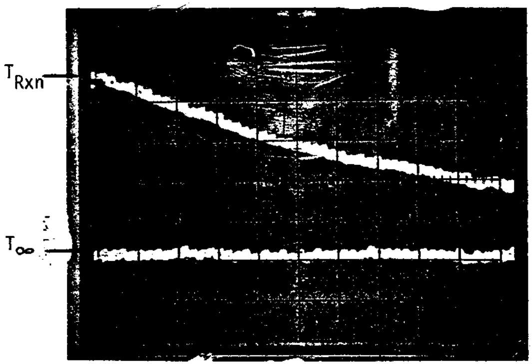
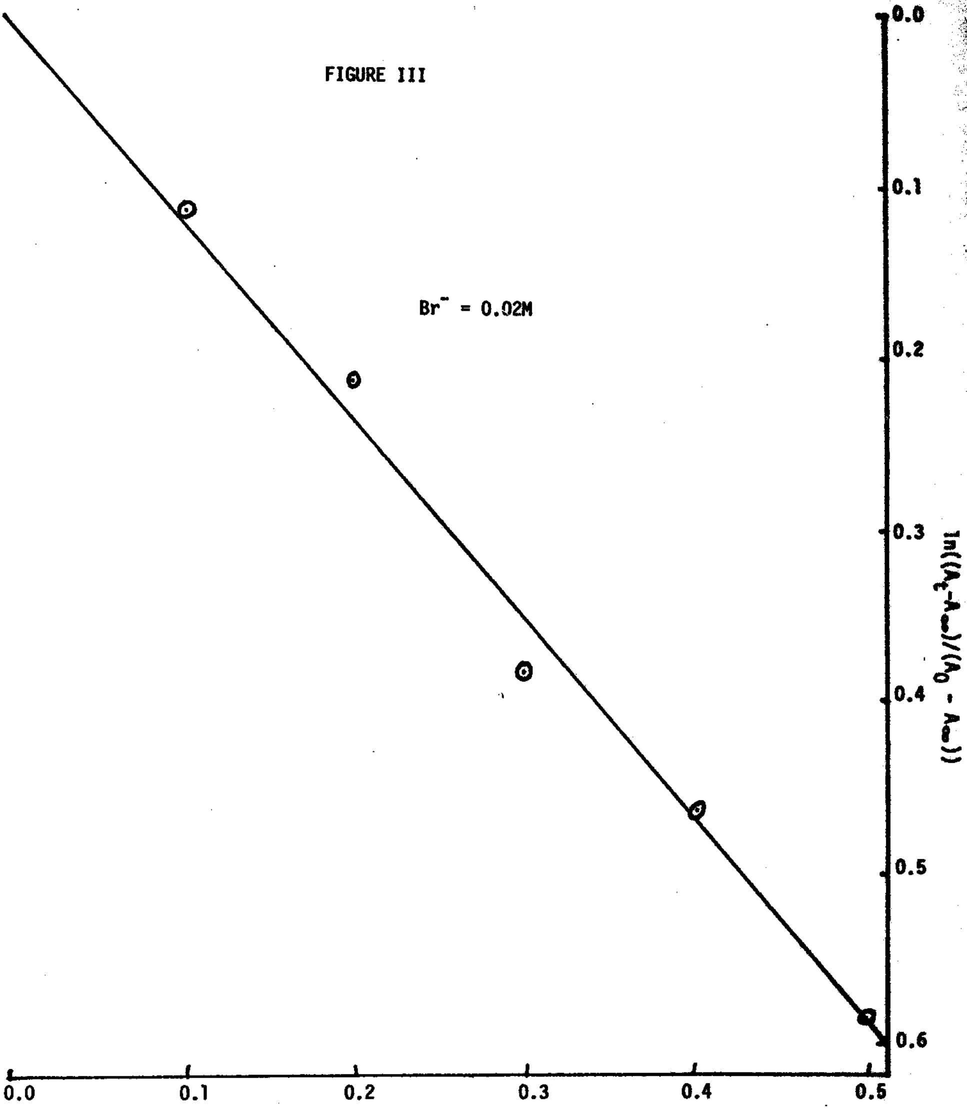


FIG. II-B



Typical Oscilloscope Trace For Reactio of $[Au(Et_3dien)Cl]^{+2}$ with Br^-: Fig.II-A is a full view, Fig. II-B is an expanded view of the reaction. T_{100} = 100% Transmittance; T_{Rxn} = Transmittance of reaction; T_∞ = Reaction transmittance at infinite time; T_0 = 0% Transmittance

FIGURE III



Typical Plot of $\ln((A_t - A_\infty)/(A_0 - A_\infty))$ vs time for the reaction of $[Au(Et_3dien)Cl]^{+2}$ with Br^- @ 25°C.

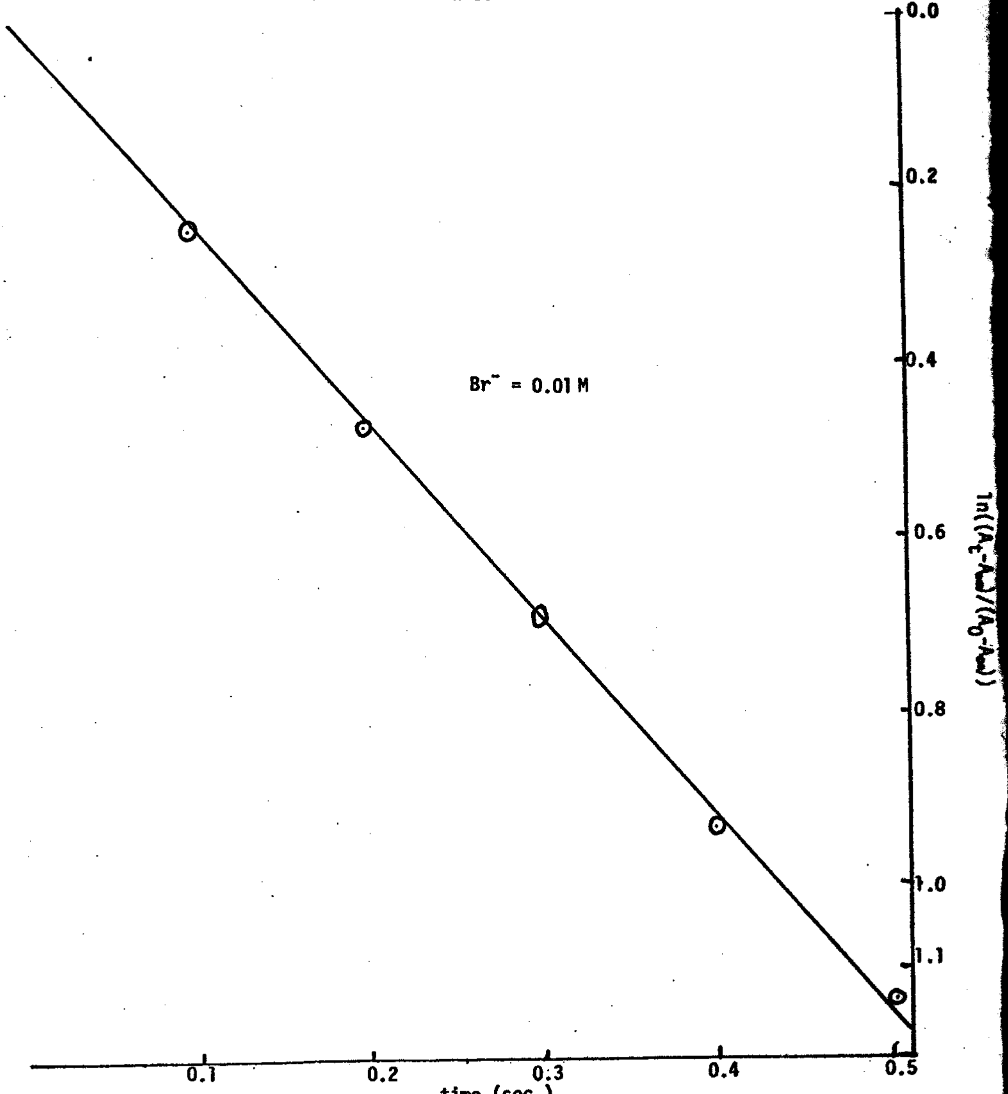
reactions were run at $25^{0} \pm .1^{0}C$ at a wavelength of 385 nm.

Psuedo first order rate constants were again obtained from plots of:

$$\ln\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) \ \underline{vs} \ \text{time.}$$

A typical plot is shown in Figure IV.

FIGURE IV



Typical Plot of $\ln((A_t-A_\infty)/(A_0-A_\infty))$ vs time for the reaction of $Au(Et_3\text{-dien})Br^{+2}$ with Br^- @ 25°C

RESULTS AND DISCUSSION

The Hydrolytic Behavior of $[Au(Et_3dien)Cl]^{+2}$: $[Au(amine)Cl]^{+2}$ complexes where amine is diethylenetriamine with a hydrogen on the central nitrogen have been studied[3] and hydrolyze according to the reaction sequence R-1 (see page 1).

It has been shown that each step in the reaction is accompanied by smooth spectral transitions and well defined isosbestic points[5]. Table A summarizes the spectral properties of these ions as determined by previous workers[2,3,5].

When amine is a dien ligand with no hydrogen attached to nitrogen, the first step in reaction sequence R-1 cannot occur. These complexes decompose either before or shortly after substitution of hydroxide for chloride.

The hydrolytic behavior of the complex $[Au(Me_3dien)Cl]^{+2}$ has been recently studied[4]. Since the complex $[Au(Et_3dien)Cl]^{+2}$ is similar to the Me_3dien complex and both differ from previously studied complexes in that only hydrogens attached to terminal nitrogens can be lost, it was of interest to study the Et_3dien complex and compare it with the Me_3dien complex.

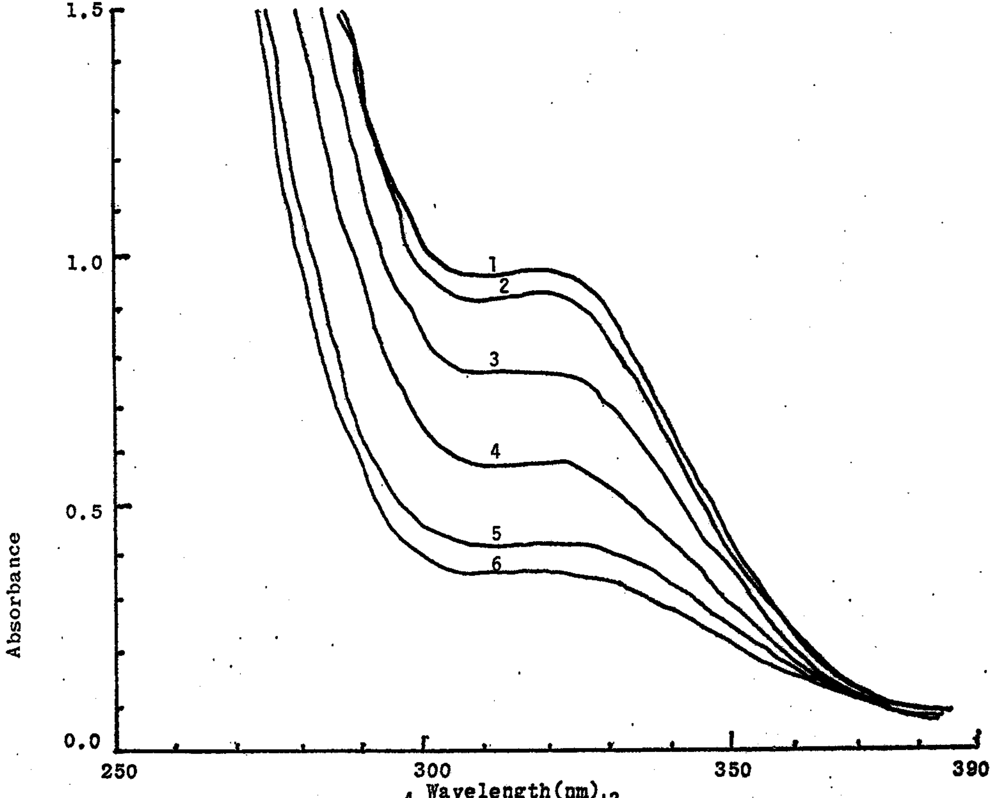
The changes in the absorption spectrum of $[Au(Et_3dien)Cl]^{+2}$ as the pH is varied from 2 to 11 are shown in Figures V, VI, and VII. As expected the spectral changes observed are different from those accompanying reaction sequence R-1. The initial decreases in absorbance at all wavelengths as the pH is increased from 2 to 6 cannot be due to the conversion of $[Au(Et_3dien)Cl]^{+2}$ to $[Au(Et_3dien_{-H})Cl]^{+2}$ since the latter

TABLE A

Spectral properties of ions in R-1

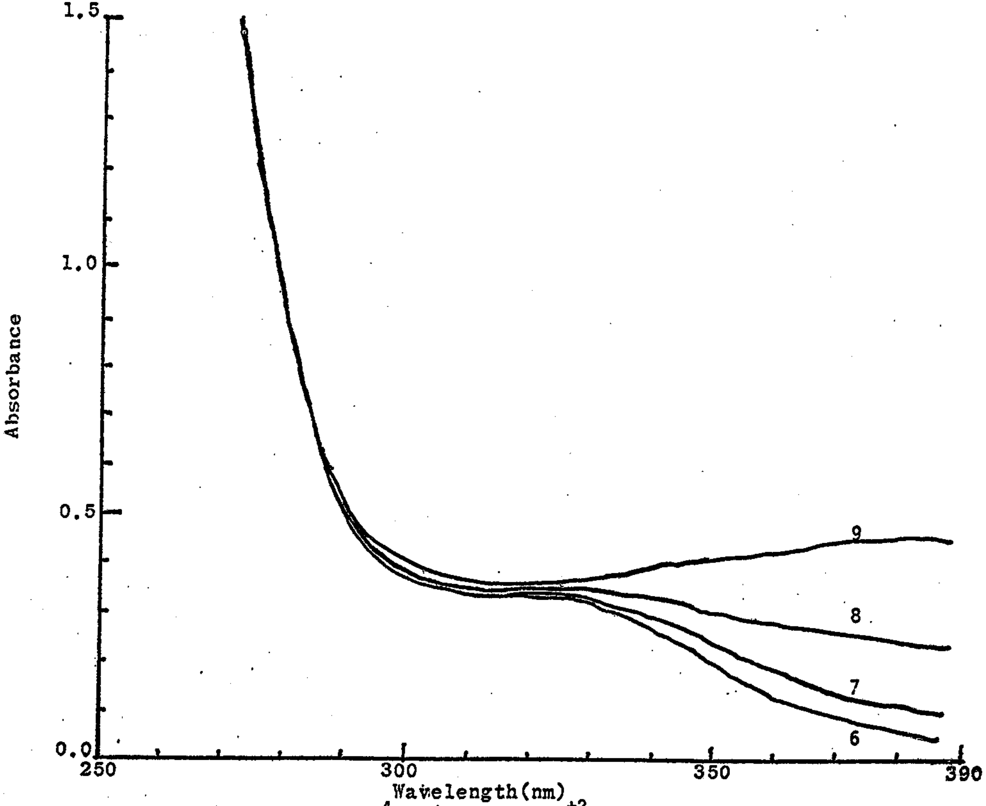
Ion	max(nm)
$[Au(amine)Cl]^{+2}$	300-315
$[Au(amine_{-H})Cl]^{+2}$	370-400
$[Au(amine_{-H})OH]^{+2}$	350-370

FIGURE V



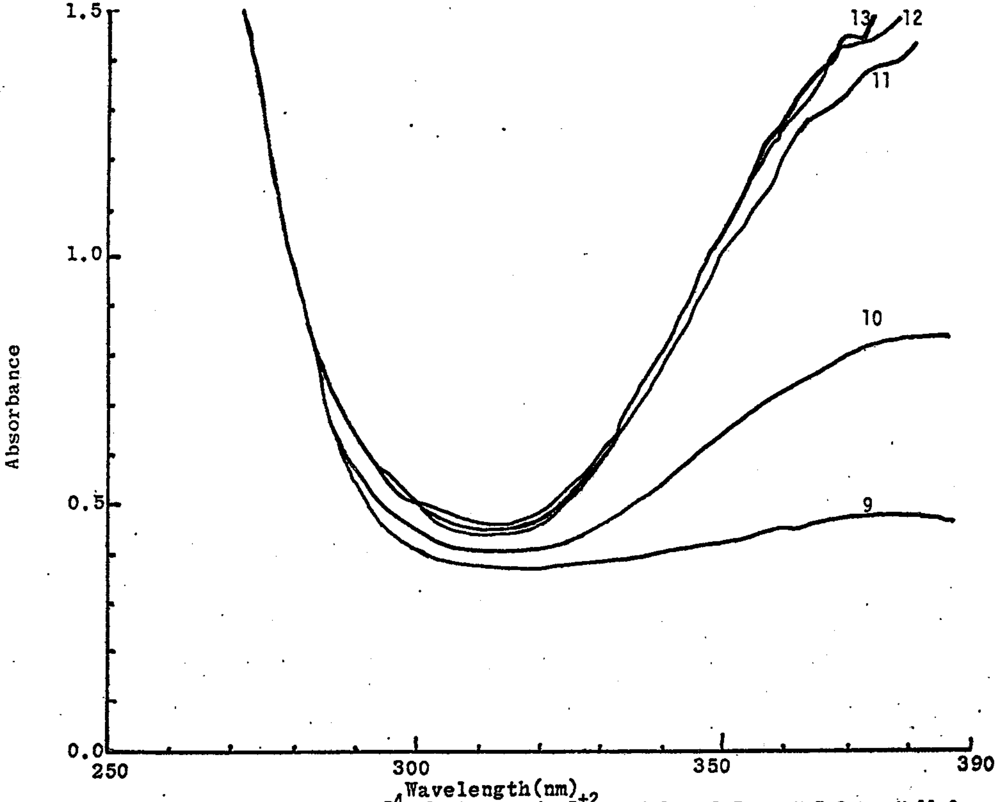
Absorption spectra of 8×10^{-4} M $[Au(Et_3dien)Cl]^{+2}$ in 0.1M HCl from pH=2.0 to pH=6.0
1 pH=2.0; 2 pH=3.0; 3 pH=3.6; 4 pH=4.2; 5 pH=5.3; 6 pH=6.0

FIGURE VI



Absorption spectra of 8 x 10^{-4}M $[Au(Et_3dien)Cl]^{+2}$ in 0.1M HCl From pH=6.0 to pH=7.6
6 pH=6.0; 7 pH=6.5; 8 pH=6.9; 9 pH=7.6

FIGURE VII



Absorption spectra of 8 x 10^{-4}M $[Au(Et_3dien)Cl]^{+2}$ in 0.1M HCl From pH=7.6 to pH=11.0

9 pH=7.6; 10 pH=8.4; 11 pH=9.2; 12 pH=10.1; 13 pH=11.0

should exhibit an absorbance maximum in the 370-400nm range. At more basic pH's (above 6.0) the absorbance does increase producing a broad band at 380nm which could reflect the presence in solution of either $[Au(Et_3dien_{-H})Cl]^+$ or $[Au(Et_3dien_{-H})OH]^+$.

These results should be compared with those shown in Figures VIII, IX, and X. The latter curves were obtained by generating $[Au(Et_3dien_{-H})OH]^+$ in solution, removing the Cl^- by ion exchange and then recording spectral changes as the pH was varied from 10.7 to 3.5 with $HClO_4$. Comparison of spectrum 1, Figure VIII and spectrum 13, Figure VII reveals that the final product in the first study is $[Au(Et_3dien_{-H})OH]^+$.

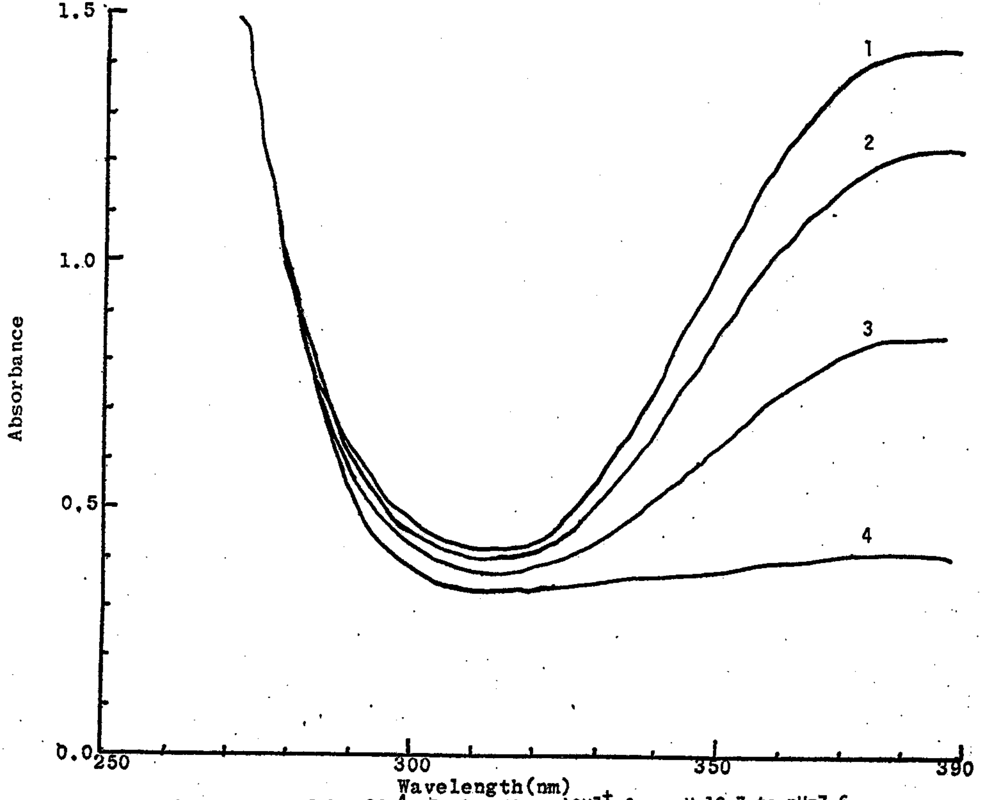
Acidification of this ion in the absence of Cl^- could result in the initial formation of either $[Au(Et_3dien)OH]^{+2}$ or $[Au(Et_3dien_{-H})H_2O]^{+2}$. In strongly acidic solution $[Au(Et_3dien)H_2O]^{+3}$ would be formed. Thus spectrum 8, Figure X must be that of $[Au(Et_3dien)H_2O]^{+3}$. Comparison of the spectrum with spectrum 6, Figure V suggests that $[Au(Et_3dien)Cl]^{+2}$, unlike previously studied ions in this series, hydrolyzes according to the reaction sequence shown in R-3

$$[Au(Et_3dien)Cl]^{+2} \underset{}{\overset{\substack{-Cl^- \\ +OH^-}}{\rightleftharpoons}} [Au(Et_3dien)OH]^{+2} \overset{+OH^-}{\rightleftharpoons} [Au(Et_3dien_{-H})OH]^+$$

R-3

This is the same sequence observed for $[Au(Me_3dien)Cl]^{+2}$ (4).

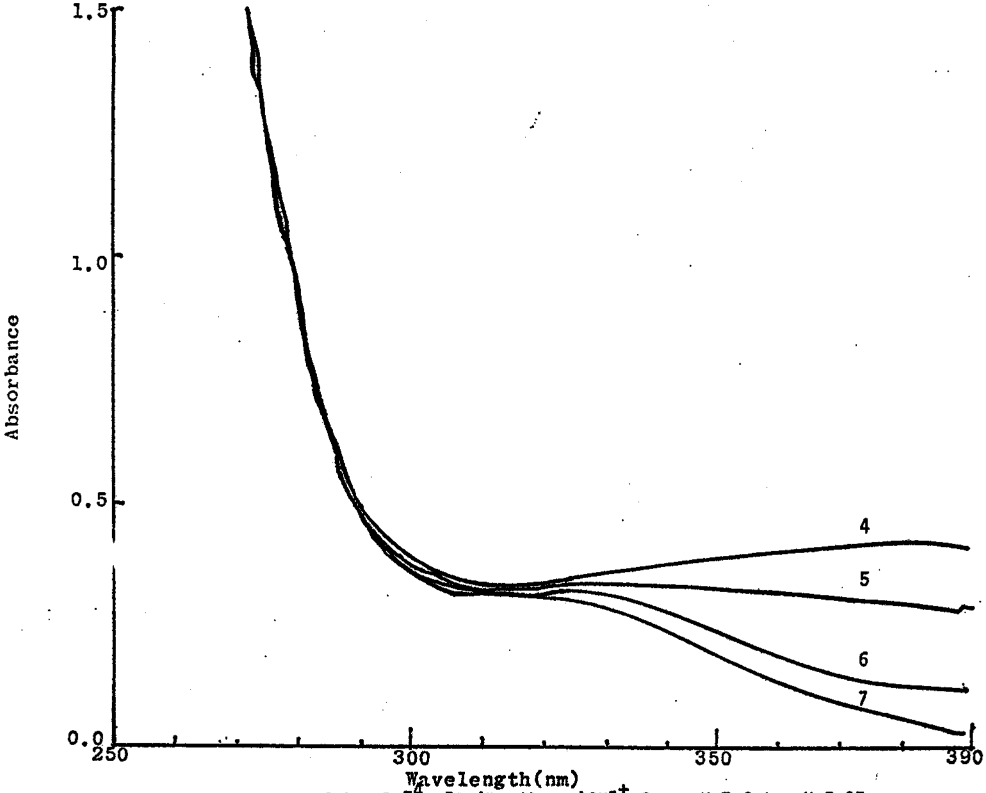
FIGURE VIII



Absorption spectra of 8 x 10^{-4}M [Au(Et_3dien$_{-H}$)OH]$^+$ from pH=10.7 to pH=7.6

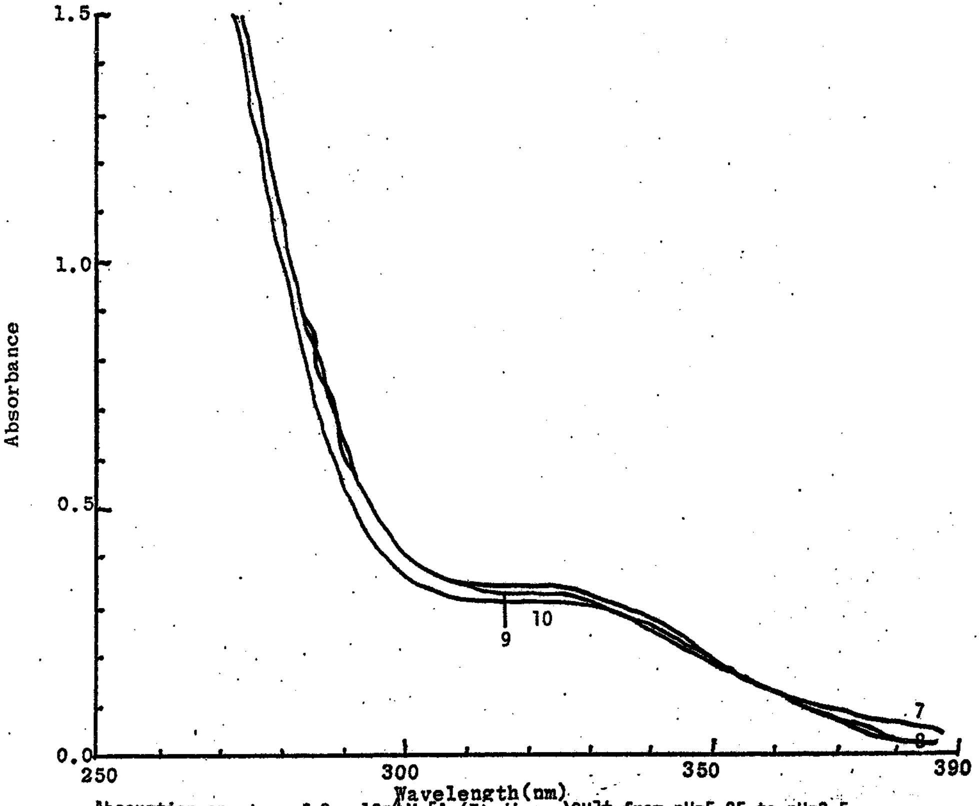
1 pH=10.7; 2 pH=8.9; 3 pH=8.5; 4 pH=7.6

FIGURE IX



Absorption spectra of 8 x 10^{-4}M $[Au(Et_3dien_{-H})OH]^+$ from pH=7.6 to pH=5.95
4 pH=7.6; 5 pH=7.0; 6 pH=6.6; 7 pH=5.95

FIGERE X



Absorption spectra of 8 x 10^{-4}M $[Au(Et_3dien_{-H})OH]^+$ from pH=5.95 to pH=3.5

7 pH=5.95; 8 pH=5.1; 9 pH=4.0; 10 pH=3.5

The Kinetic Behavior of $[Au(Et_3dien)Cl]^{+2}$ in the presence of Br^-

The hydrolytic behavior studies of $[Au(Et_3dien)Cl]^{+2}$ show that the replacement kinetics of Cl^- for Br^- should occur at a low pH. The relative stablities of $[Au(Et_3dien)Br]^{+2}$ and $[AuBr_4]^-$ were determined. Figure XI shows the result of adding Br^- to a solution of $[Au(Et_3dien)H_2O]^{+3}$. The spectral changes indicate that rapid replacement of Br^- for H_2O occurs. Thus curve G is the spectrum of the stable complex $[Au(Et_3dien)Br]^{+2}$ which forms when the mole ratio of added bromide to complex is 1:1. However $[Au(Et_3dien)H_2O]^{+3}$ in a large excess of Br^- does not result in curve G. Instead the curve shown in Figure XII, which is characteristic of $[AuBr_4]^-$, results. The same result is obtained if excess bromide is added directly to a solution of $[Au(Et_3dien)Cl]^{+2}$.

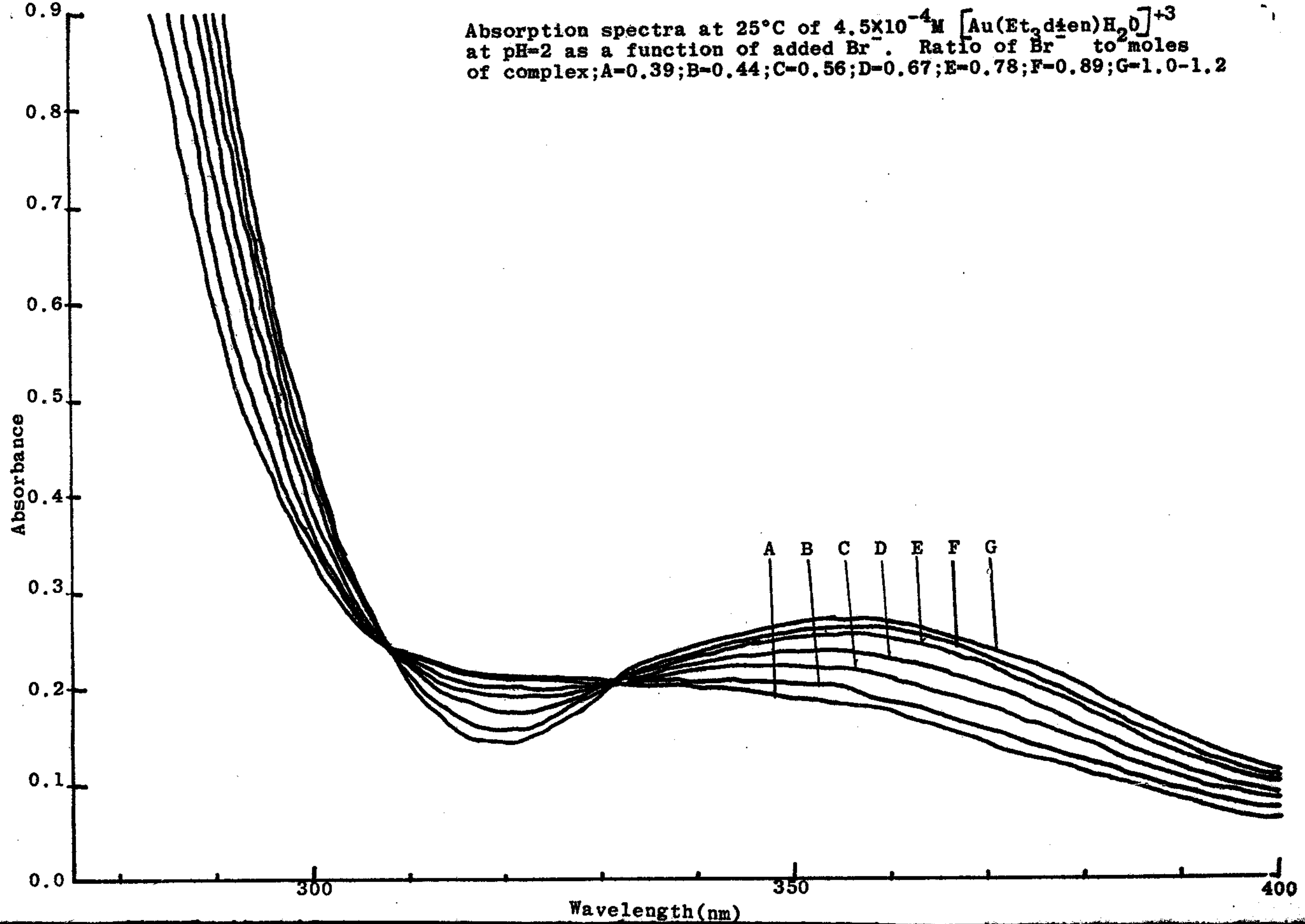
These results indicate that at pH ~ 2.0 the reactions R-4 and R-5 occur in sequence.

$$[Au(Et_3dien)Cl]^{+2} + Br^- \rightarrow [Au(Et_3dien)Br]^{+2} + Cl^- \qquad \text{R-4}$$

$$[Au(Et_3dien)Br]^{+2} + 3\,Br^- \rightarrow [AuBr_4]^- + Et_3dien \qquad \text{R-5}$$

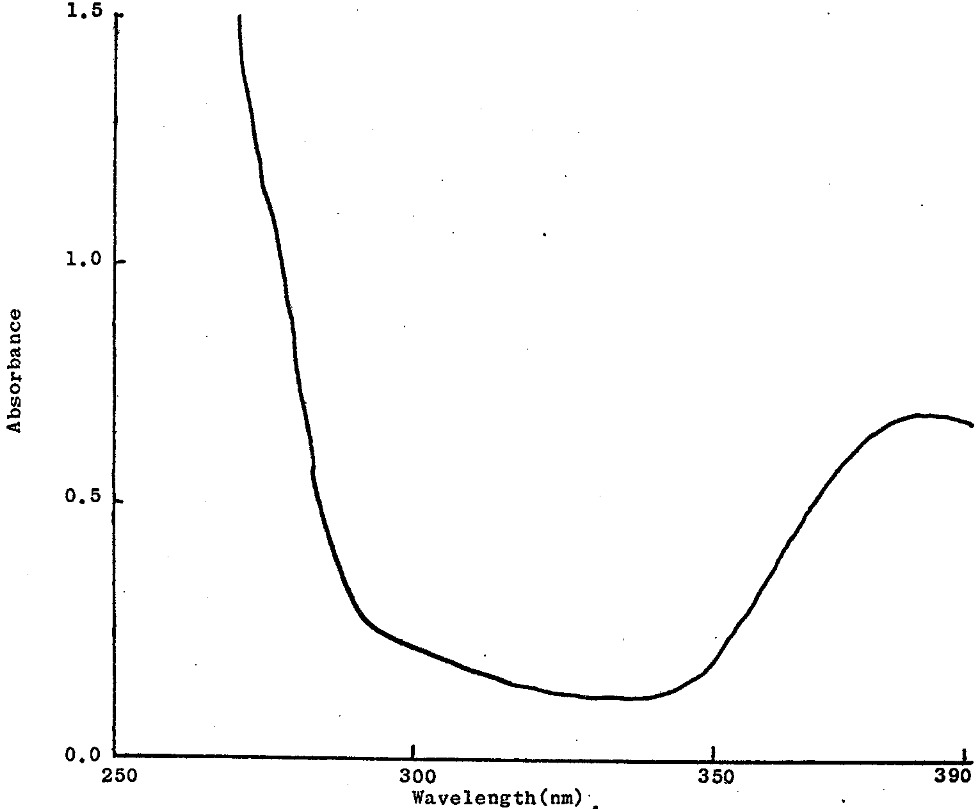
Furthermore, the rate of spectral changes observed in the previous studies suggests that reaction R-4 occurs much faster than reaction R-5 so that essentially all of the monochloro salt is converted to the monobromo salt before any significant quantity of $[AuBr_4]^-$ is formed. To more fully understand these reactions the kinetics of reactions R-4 and R-5 were studied.

FIGURE XI



Absorption spectra at 25°C of 4.5×10^{-4}M $[Au(Et_3dien)H_2O]^{+3}$ at pH=2 as a function of added Br^-. Ratio of Br^- to moles of complex;A=0.39;B=0.44;C=0.56;D=0.67;E=0.78;F=0.89;G=1.0-1.2

FIGURE XII



Absorption spectra of $AuBr_4^-$ @ 4×10^{-4}M

Table B is a list of psuedo-first order rate constants for reaction R-4 at each bromide concentration studied. Each value is the average of four or more determinations and are reproducible within 10%. Figure XIII is a plot of these observed rate constants versus bromide concentration. The y intercept equals k_1, the solvent path rate constant, and the slope k_2, the bromide path rate constant. From the plot it is determined that $k_1 = 0.33\ sec^{-1}$ and k_2 (or k_{Br^-}) = $36.1\ M^{-1}\ sec^{-1}$.

A comparision of these results with the results of kinetic studies of other $[Au(dien)X]^{+2}$ complexes is shown in Table C.

The lower reaction rate for $[Au(Et_3dien)Cl]^{+2}$ relative to $[Au(Me_3dien)Cl]^{+2}$ and $[Au(Me_5dien)Cl]^{+2}$ can be attributed to the greater steric hinderance exhibited by the ethyl groups.

Table D presents the pseudo-first order rate constants for chelate ligand replacement at the various bromide concentrations used.

These results are plotted in Figures XIV, XV, and XVI versus $[Br^-]$, $[Br^-]^2$, and $[Br^-]^3$ respectively. These plots indicate that this reaction is third order with respect to bromide ion. The rate constant calculated from Figure XVI is $1.6 \times 10^3\ l^4\ mole^{-4}\ sec^{-1}$.

The fact that the ligand unwrapping reaction is third order in bromide was unexpected. A previous study with a similar complex[4], $[Au(Me_3dien)Cl]^{+2}$ showed a second order

TABLE B

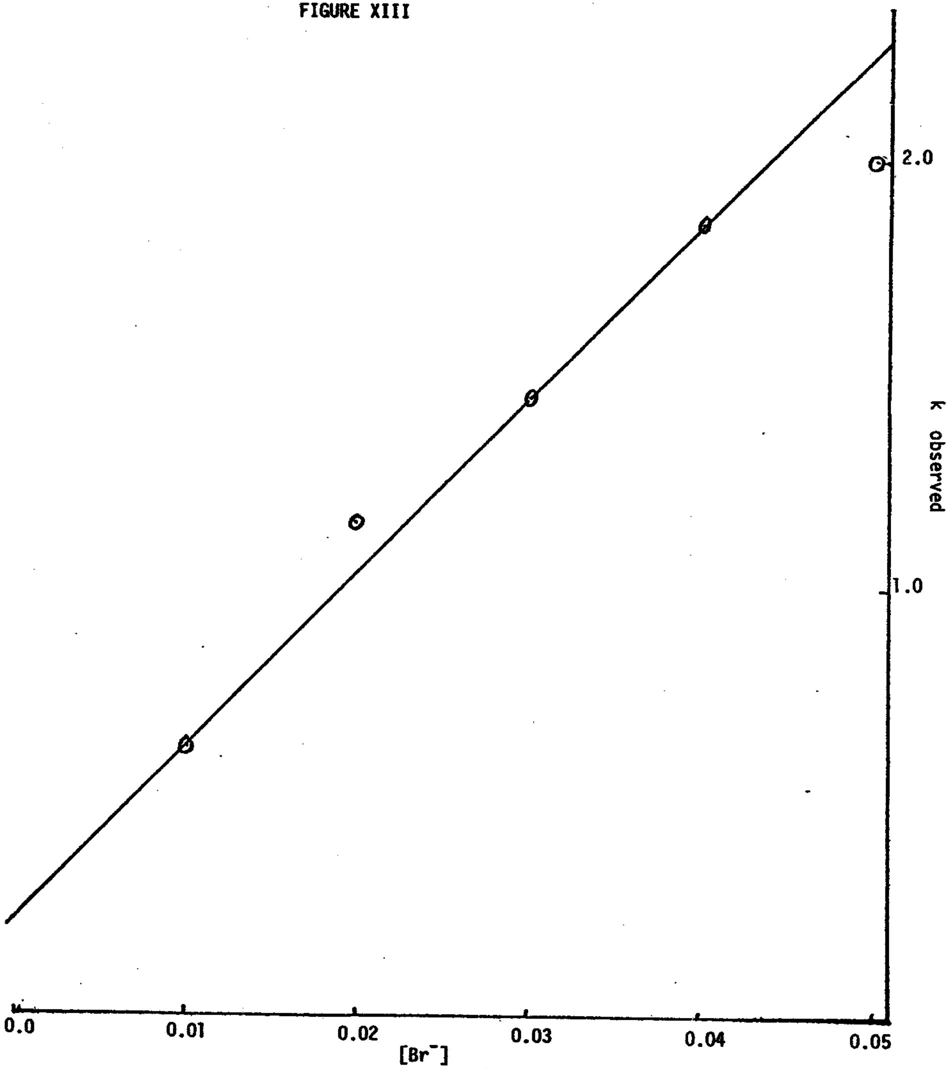
Psuedo First Order Rate Constants For:

$[Au(Et_3dien)Cl]^{+2} + Br^- \rightarrow [Au(Et_3dien)Br]^{+2} + Cl^-$

$\mu = 0.2$ with $NaClO_4$ Temperature = 25°C

$[Br^-]$ M	k_{obs} (sec^{-1})
0.01	0.6
0.02	1.1
0.03	1.4
0.04	1.7
0.05	2.0

FIGURE XIII



Observed Rate Constants for $[Au(Et_3dien)Cl]^{+2}$ vs Bromide Concentration @ 25° C

TABLE C

Rate Constants for the Reaction:

$[Au(amine)Cl]^{+2} + Br^- \longrightarrow [Au(amine)Br]^{+2} + Cl^-$

in 0.1M $HClO_4$ at 25°C

Complex	$k_1(sec^{-1})$	$k_2(M^{-1}sec^{-1})$	Ref.
$[Au(dien)Cl]^{+2}$	0.00	380	9
$[Au(Me_3dien)Cl]^{+2}$	0.20	170	4
$[Au(Et_3dien)Cl]^{+2}$	0.33	36	This Work
$[Au(Me_5dien)Cl]^{+2}$	—	123*	10

* at pH = 5.8

TABLE D

Pseudo-first Order Rate Constants for:

$[Au(Et_3dien)Br]^{+2} + 3\ Br^- \rightarrow AuBr_4^- + Et_3dien$

in 0.1M $HClO_4$ $\mu = 0.2$ with $NaClO_4$ at 25°C

$[Br^-]$M	k_{obs} (sec^{-1})
0.01	0.004
0.02	0.025
0.03	0.052
0.04	0.110
0.05	0.213

FIGURE XIV

Observed Rate Constants for the Reaction $\left[Au(Et_3\text{-dien})Br\right]^{+2} + 3Br^- \rightarrow AuBr_4^-$ versus Bromide Concentration

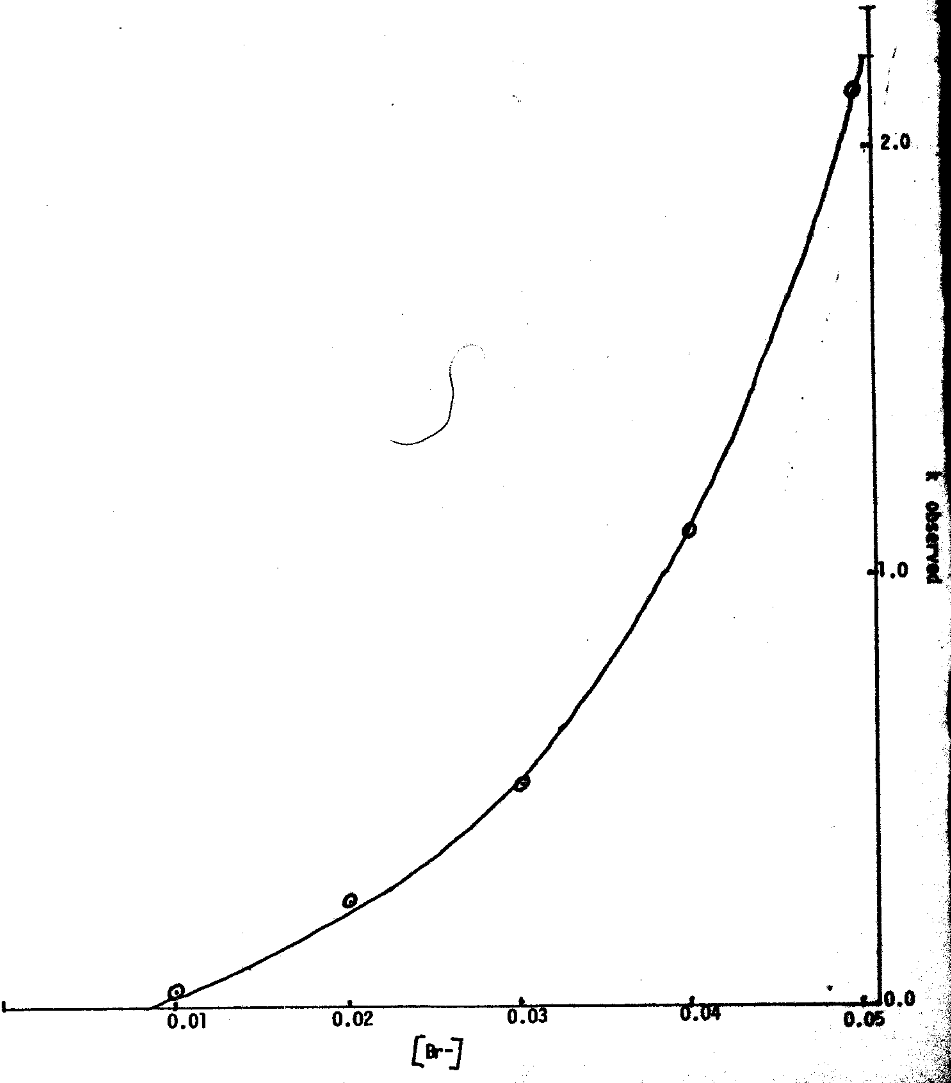
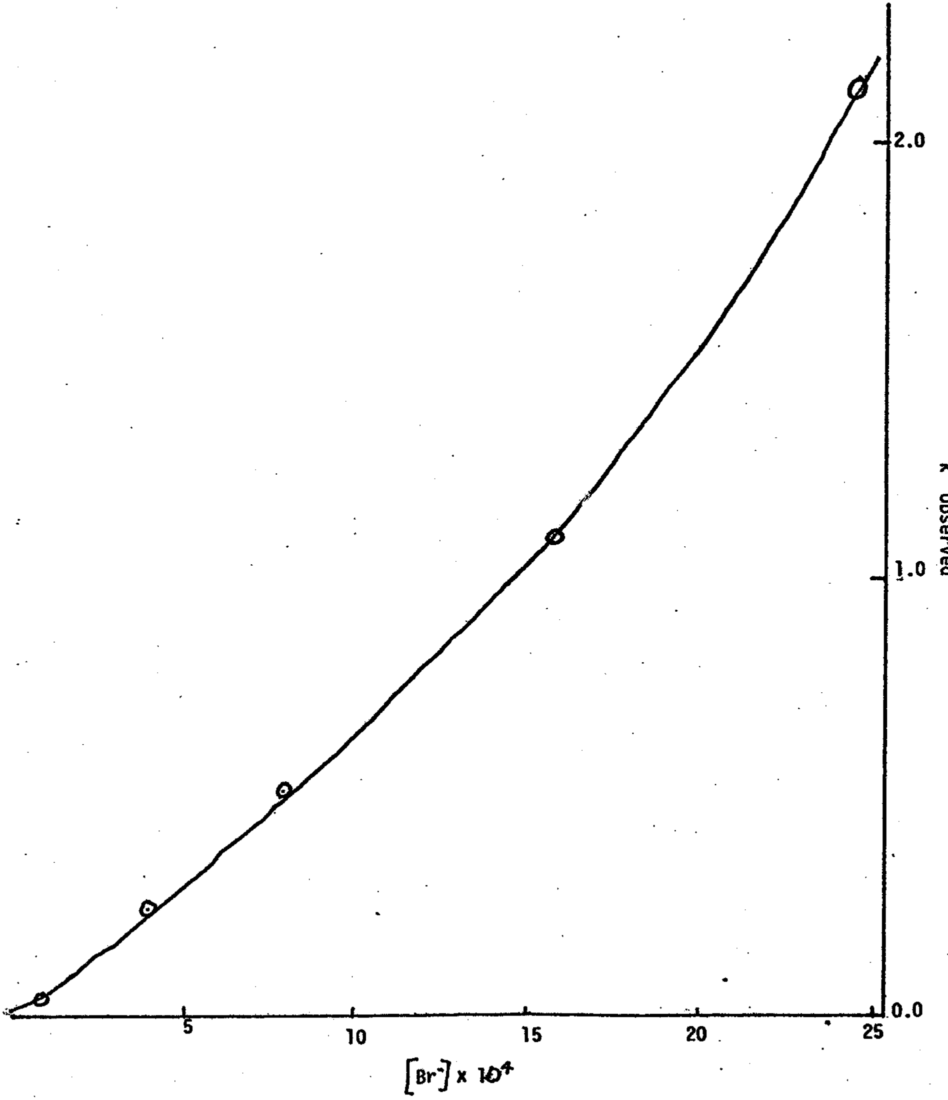


FIGURE XV

Observed Rate Constants for the Reaction $[Au(Et_3\text{-dien})Br]^{+2} + 3Br^- \rightarrow AuBr_4^-$ versus $[Br^-]^2$



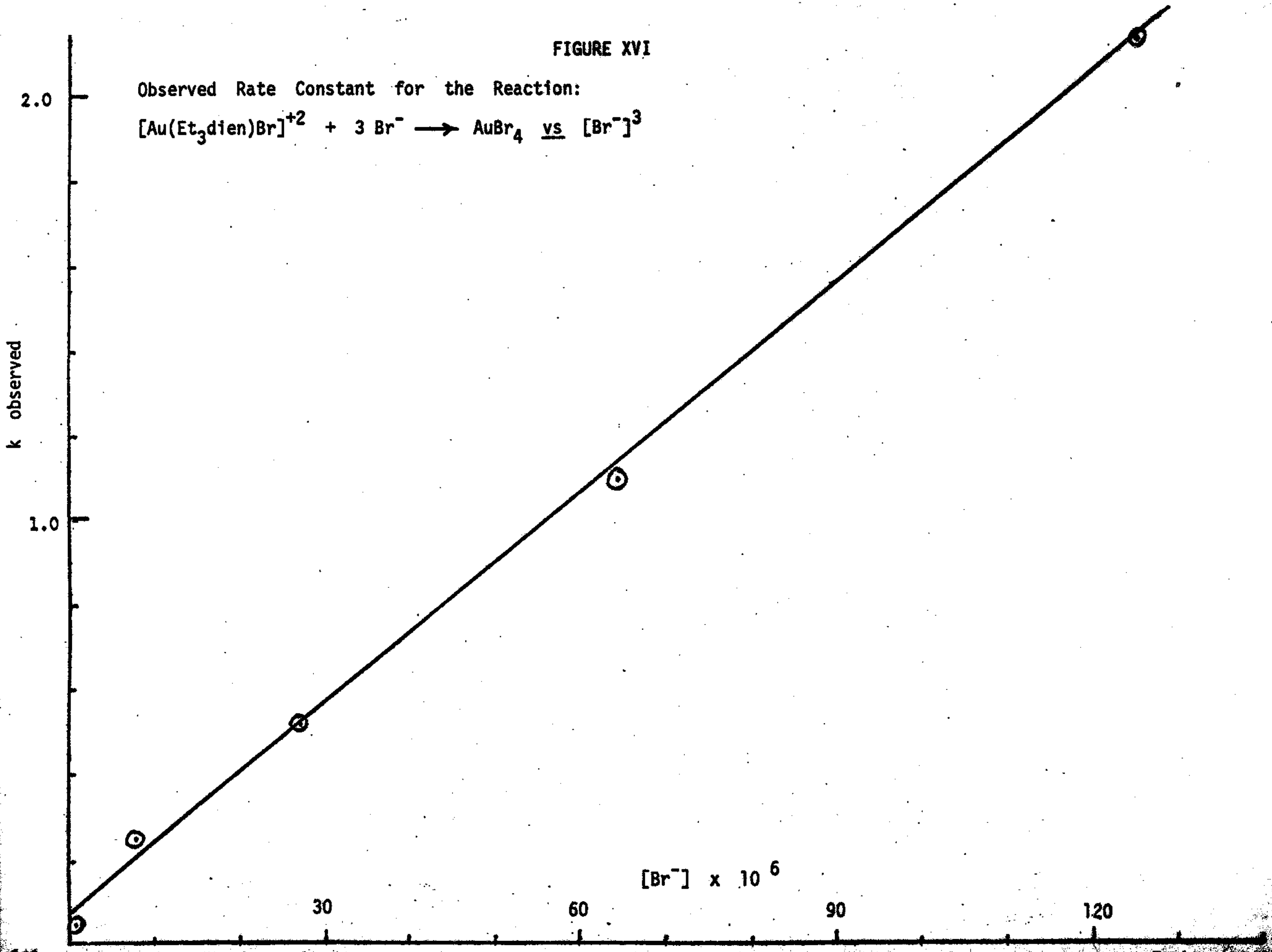


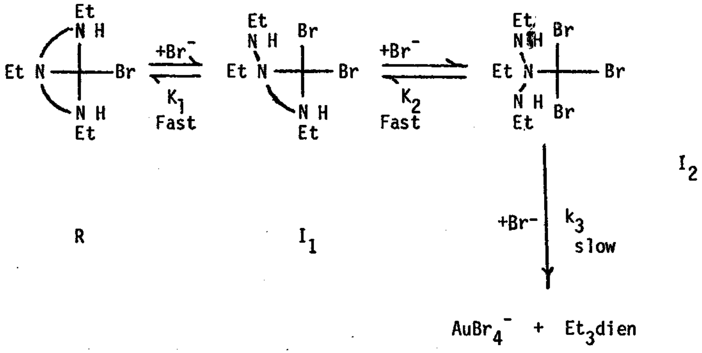
FIGURE XVI

Observed Rate Constant for the Reaction:

$[Au(Et_3dien)Br]^{+2} + 3\ Br^- \longrightarrow AuBr_4$ *vs* $[Br^-]^3$

dependence on bromide.

The third order kinetics of reaction R-5 suggets that the breaking of the third Au-N bond is rate determining. This third order rate dependence on Br^- can be rationalized as arising from the reaction sequence R-6



R-6

The rate of formation of $[AuBr_4^-]$ is

$$\frac{d\,[AuBr_4^-]}{dt} = k_3[I_2][Br^-]$$

Since $K_1 = \frac{[I_1]}{[Br^-]\,R}$

so that $I_1 = K_1[Br^-][R]$

and since $K_2 = \frac{[I_2]}{[I_1][Br^-]}$

so that $I_2 = K_2[I_1][Br^-] = K_1K_2 [Br^-]^2 R$

therefore

$$\frac{d[AuBr_4^-]}{dt} = K_1K_2k_3[R][Br^-]^3$$

From the above result it can be seen that $k_{obs} = K_1K_2k_3[Br^-]^3$

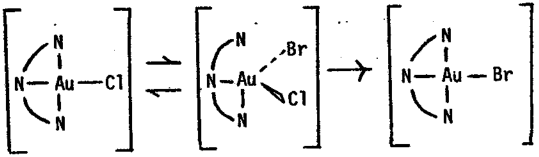
The third order dependence on Br^- for this complex implies that the thermodynamic stability of two of the Au-N bonds is less than the stability of the third Au-N bond. It is reasonable to assume that the two less stable bonds are those involving the terminal nitrogen atoms of Et_3dien since these nitrogens have similiar environments. Apparently these bonds are also less stable than the corresponding bonds in $[Au(Me_3dien)Br]^{+2}$ which showed a second order dependence on Br^-.

Previous studies of $[Au(amine)X]^{+2}$ complexes, where X is Br^- or Cl^-, have suggested that in acidic solutions the presence of ethyl groups on the terminal nitrogen of the chelate exerts a specific effect leading to ring opening[5]. It has also been found that ethyl substitution on the terminal nitrogen of diethylenetriamine decreases the formation constant of diethylenetriamine complexes of copper to a greater extent than methyl substitution on these nitrogens[8].

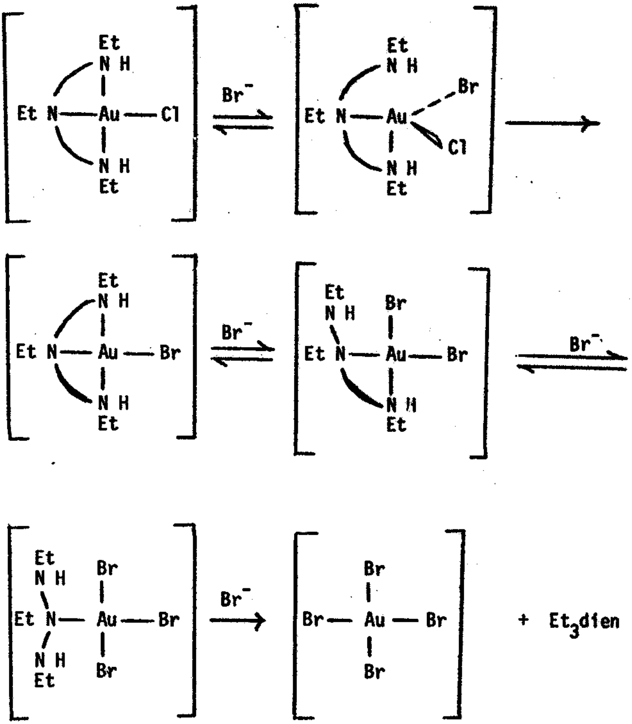
Thus the apparently greater stability of EtNH-Au vs MeNH-Au observed here is not without precedent.

The fact that the breaking of the final Au-N bond is rate determining can be ascribed to steric hinderance exerted from the "dangling" ethyl groups above and below the plane of the gold and bromide atoms, which makes it more difficult for the final bromide ion to attack.

It has been previously shown that the substitution of Br^- for Cl^- in $[Au(amine)Cl]^{+2}$ complexes occurs through a ring opening substitution process[3,4,5,9] such as:



This is also believed to occur with this complex. Thus the general mechanism for $[Au(Et_3dien)Cl]^{+2}$ in excess $[Br^-]$ can be represented as shown in reaction sequence R-7.



R-7

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