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The preparation and kinetics of a sterically hindered gold (III) complex

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Schenectady, New York

THE PREPARATION AND KINETICS
OF A STERICALLY HINDERED
GOLD(III) COMPLEX

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 Master of Science in Chemistry.

by Michael R. Golden *MS 1978*

By _____Michael R. Golden_____

Approved _____Charles F. Weick_____
                     Thesis Advisor

Approved _____Caron Ferarol_____
                Committee on Graduate Studies

Date _____5/9/78_____

DEDICATION

This thesis is lovingly dedicated to my wife, Gail,
whose constant help and understanding made this work
possible.

ACKNOWLEDGEMENT

I deeply wish to thank Professor Charles F. Weick, my
Research Advisor, for his many evening and summer hours
which were given in guidance and encouragement. Thanks to
his dedication to teaching, this project was completed.

I also wish to thank my wife, Gail, for her many hours
of help and companionship in the laboratory.

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LIST OF ABBREVIATIONS

The following abbreviations will be used throughout the text of this paper:

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' - tetraethyldiethylene-triamine
	$(C_2H_5)_2NCH_2CH_2NHCH_2CH_2N(C_2H_5)_2$
Et$_4$dien$_{-H}$	the conjugate base of Et$_4$dien
	$(C_2H_5)_2NCH_2CH_2NCH_2CH_2N(C_2H_5)_2^-$
Et$_2$dien	1,1' - diethyldiethylenetriamine
	$(C_2H_5)_2NCH_2CH_2NHCH_2CH_2NH_2$
Et$_2$dien$_{-H}$	the conjugate base of Et$_2$dien
	$(C_2H_5)_2NCH_2CH_2NCH_2CH_2NH_2^-$
Me$_4$dien	1,1',7,7' - tetramethyldiethylene-triamine
	$(CH_3)_2NCH_2CH_2NHCH_2CH_2N(CH_3)_2$
Me$_4$dien$_{-H}$	the conjugate base of Me$_4$dien
	$(CH_3)_2NCH_2CH_2NCH_2CH_2N(CH_3)_2^-$

Abbreviation	Name & Formula
Me_2dien	1,1 - dimethyldiethylenetri-amine $(CH_3)_2NCH_2CH_2NHCH_2CH_2NH_2$
Me_2dien_{-H}	the conjugate base of Me_2dien $(CH_3)_2NCH_2CH_2NCH_2CH_2NH_2^-$
$MeEt_4dien$	4- methyl- 1,1 ,7,7 - tetra-ethyldiethylenetriamine $(C_2H_5)_2NCH_2CH_2N(CH_3)CH_2CH_2N(C_2H_5)_2$
Me_5dien	1,1 ,4,7,7 - pentamethyldi-ethylenetriamine $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$
Me_3dien	1,4,7- trimethyldiethylene-triamine $(CH_3)NHCH_2CH_2N(CH_3)CH_2CH_2NH(CH_3)$
Me_3dien_{-H}	the conjugate base of Me_3dien $(CH_3)NHCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)^-$

ABSTRACT

The alkyl substituted gold(III) complex $[Au(1,4,7\text{-}Me_3dien)Cl](PF_6)_2$ [where 1,4,7-Me$_3$dien represents $(CH_3)HNCH_2CH_2N(CH_3)CH_2CH_2NH(CH_3)$] has been synthesized. The cation of this compound differs from previously synthesized gold(III) complexes of similar structure since it can form a conjugate base only by loss of a hydrogen from a terminal nitrogen. Aqueous solution chemistry studies of this ion reveals that the Cl^- is hydrolyzed before loss of a proton from the ligand which is the reverse of the sequence observed with previously studied ions. Monobromo substitution rates are found to be slower than for the complex with no alkyl substitution but faster than for the completely methylated complex. A rate constant of $k_{B_r} = 17$ $\ell\text{-mole}^{-1}\text{-sec}^{-1}$ was obtained. The rate of chelate ligand unwrapping from the monobromo complex was also studied. This process was discovered to be second order in Br^- with a rate constant of $k = 15$ $\ell^2\text{-mole}^{-2}\text{-sec}^{-1}$.

INTRODUCTION

The square planar complexes of Pd(II) and Pt(II) have been extensively studied.[1] In particular, the kinetics indicate that substitution reactions proceed *via* a two step mechanism which is reagent dependent.

The substitution reaction:

$$MA_3X^{+n} + Y^- \xrightarrow{H_2O} MA_3Y^{+n} + X^-$$
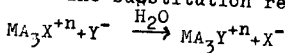
is believed to follow a bimolecular mechanism[2] represented as:
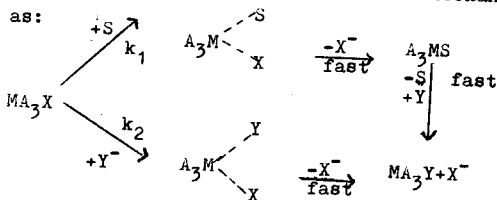
where S is the solvent, k_1 is the solvent path rate constant, Y^- is the substituting nucleophile, and k_2 is the reagent path rate constant.

The rate law for this mechanism would be:

$$\text{rate} = k_1[MA_3X^{+n}] + k_2[MA_3X^{+n}][Y^-]$$

which under first order conditions using excess Y^-[3] becomes:

$$\text{rate} = k_{obs}[MA_3X^{+n}]$$

where $k_{obs} = k_1 + k_2[Y^-]$

However, square planar complexes of Pd(II) and Pt(II) where the ligands are certain N-alkyl substituted diethylenetriamines undergo substitution reactions which

are nearly rate independent of reagent concentration.[4]
It has been suggested that steric hindrance due to
certain alkyl groups lying above and below the plane
of the ion inhibits the attack of the substituting
nucleophile.[5]

The aqueous solution chemistry of complexes of
Au(III) have shown the following acid-base equilibria:[6]

$$\left[Au(amine)X \right]^{+2} \xrightleftharpoons[+H+]{OH^-} \left[Au(amine_{-H})X \right] \xrightleftharpoons[+X^-]{+OH^-} \left[Au(amine_{-H})OH \right]^+$$
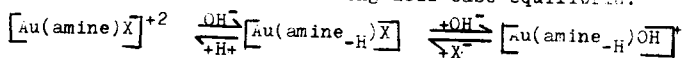
(where amine=dien,[6] 1,1-Me$_2$dien, 1,1-Et$_2$dien, 1,1,1,1
Me$_4$dien,[7] 1,1,7,7-Et$_4$dien,[4] X=Cl$^-$,Br$^-$).

These complexes also exhibit the following charac-
teristics: (a) Au(III) dien$_{-H}$ complexes undergo hydrolysis
in neutral solutions; (b) an excess of halide ion represses
hydrolysis in certain pH ranges; (c) the conjugate acids
of these complexes are stable in perchloric acid; and (d)
the conjugate acids of these complexes undergo decomposi-
tion in hydrohalic acids.[4,6]

These Au(III) complexes also have halide substitution
rates that are dependent on the extent of N-alkylation.
Thus, substitution of Br$^-$ for Cl$^-$ in $\left[Au(dien)Cl \right]^{+2}$ and
$\left[Au(dien_{-H})Cl \right]^+$ show a strong rate dependency on the con-
centration of Br$^-$.[8] However, $\left[Au(Me_5dien)Cl \right]^{+2}$,
$\left[Au(Et_4dien_{-H})Cl \right]^+$ and $\left[Au(MeEt_4dien)Cl \right]^{+2}$ undergo Br$^-$
substitution at rates which are practically independent
of the concentration of bromide ion.

Studies of a series of reactions of the type

$$[Au(amine_{-H})Cl]^+ + Br^- \longrightarrow [Au(amine_{-H})Br]^+ + Cl^-$$

using triamines of varying degrees of alkylation
have revealed that the experimental rate dependence
on bromide ion as a function of amine alkylation is
$dien_{-H} > Me_2dien_{-H} > Et_2dien_{-H} > Me_4dien_{-H} \gg Et_4dien_{-H}$.
However, on examination of space-filling molecular
models, it is observed that alkyl shielding of the
central Au(III) ion increases in the order: $dien_{-H} <$
$Me_2dien_{-H} < Me_4dien_{-H} < Et_2dien_{-H} \lessgtr Et_4dien_{-H}$. Therefore,
if only steric effects are involved, the rate dependence
should be $Me_4dien_{-H} > Et_2dien_{-H}$. [4,8]

To explain the difference between the molecular
model results and the observed kinetics for $[Au(Et_2dien_{-H})Cl]^+$
and $[Au(Me_4dien_{-H})Cl]^+$ it has been suggested that the
bromide substitution reaction of $[Au(Et_2dien_{-H})Cl]^+$
occurs via the following ring-opening mechanism: [7]
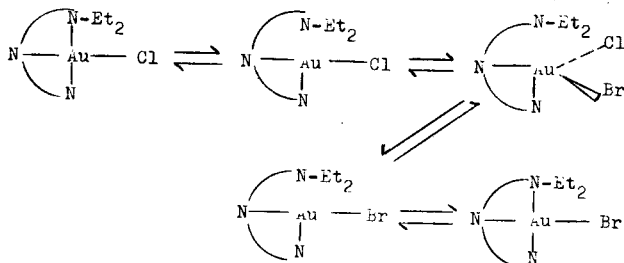
A similar ring-opening mechanism was suggested for the reaction of $[Au(Et_4dien_{-H})Cl]^+$ with N_3^-, [4] and for $[Pd(Et_4dien)SeCN]^+$ with Br^-. [10] The ring-opening mechanism was also invoked to explain the faster rate of bromide substitution of $[Au(MeEt_4dien)Cl]^{+2}$ whose $k_{Br}=.26M^{-1}sec^{-1}$ versus that of $[Au(Me_5dien)Cl]^{+2}$ whose $k_{Br}=.058M^{-1}sec^{-1}$. [9]

All of the Au(III) complexes discussed above fall into one of two possible groups. Either they contain no dissociable hydrogen atoms and consequently can not form a conjugate base (e.g. $[Au(Me_5dien)Cl]^{+2}$ and $[Au(MeEt_4dien)Cl]^{+2}$)or they most probably form such bases by loss of the hydrogen bonded to the central nitrogen of the diethylenetriamine chelate ligand. This hydrogen is expected to be the most acidic because of the inductive effects of the neighboring CH_2 groups. This study was undertaken to investigate the aqueous solution chemistry and the Br^- substitution rate of a complex which can only form a conjugate base by loss of a hydrogen from a terminal nitrogen of the chelate ring. In addition, the rate of the chelate ligand "unwrapping" reaction for the bromo complex was also investigated.

EXPERIMENTAL

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

Analyses: All gold analyses were performed in
triplicate. A small, accurately weighed amount of
synthesis product was placed in a 10ml beaker and
diluted to about 5ml volume with aqua regia. The
sample was then covered with a watch glass to prevent
mechanical loss and evaporated on a hot plate to
approximately 1ml. More concentrated HCl was added
and the evaporation continued. The procedure was
repeated until all nitrate was judged to be eliminated.
The solution was once more reduced to 1ml and
diluted in a flask to a volume of 100ml with 1MHCl.
The tetrachloroauric acid solutions so obtained had
final concentrations in the 10^{-4}M range. The
absorbance of these solutions was measured at
313nm, and the concentration of gold was read from
a previously prepared curve of absorbance versus
concentration of $HAuCl_4$. This calibration curve is
shown in Figure 1. The chloride analyses, also carried
out in triplicate, were performed by the Mohr method. [11]

FIGURE I

Absorbance of AuCl$_4^-$ _vs_ Au Concentration
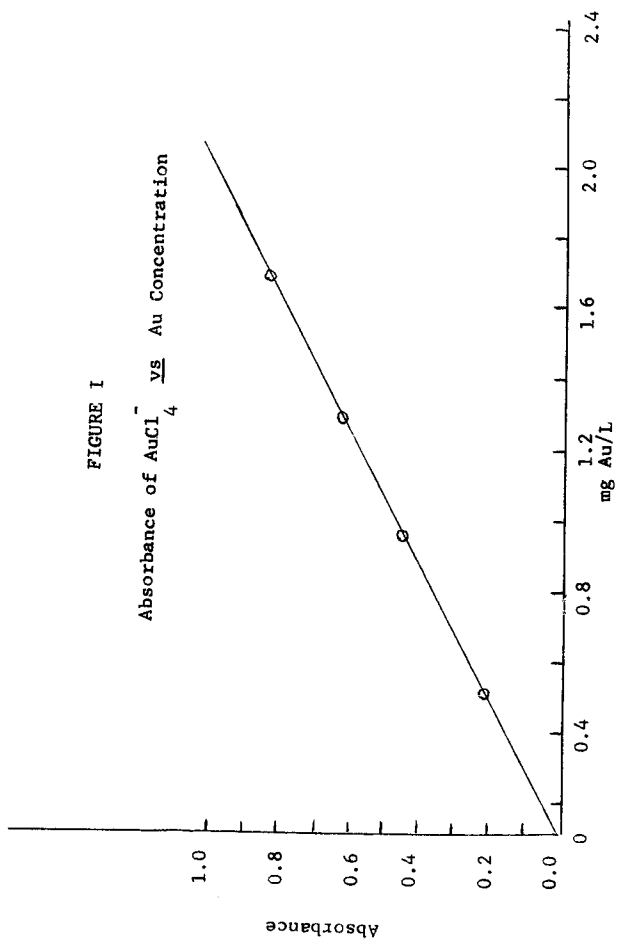
Preparation of Complex: Tetrachloroauric acid solutions were prepared as described above. When the volume was finally reduced to approximately 1ml and allowed to cool, hydrated crystals of $HAuCl_4 \cdot xH_2O$ were formed.

[Au(Me$_3$dien)Cl]Cl$_2$: $HAuCl_4 \cdot xH_2O$, equivalent to 1g (5mmoles) of gold, was dissolved in 100ml of H_2O. While mechanically stirring the solution, 5g of LiCl were added to inhibit hydrolysis, and the temperature of the solution was then reduced to $0^\circ C$.

A 1mmole solution of chelate ligand was prepared by diluting 1ml of pure 1,4,7-trimethyldiethylenetriamine to 6ml with H_2O. Five ml of this ligand solution were then added dropwise to the $HAuCl_4$ solution, at a rate that kept the pH of the solution below 5. Upon initial addition of the ligand solution , a yellow precipitate believed to be [Au(Me$_3$dien)Cl] [AuCl$_4$]$_2$ was immediately formed. To aid dissolution of this precipitate, and to increase conversion of [AuCl$_4$]$^-$ to [Au(Me$_3$dien)Cl]$^{+2}$, approximately 5.5ml (5.5mmoles) of 1M LiOH were added. The LiOH was also added at a rated which kept the pH below 5. When all of the LiOH had been added, the solution was filtered, and filtrate with an intense yellow color was obtained. Following the addition of 1g

of NH_4PF_6, the filtrate was frozen to an ice in liquid nitrogen. The frozen solution was attached to a rotary evaporator, where it was allowed to thaw under vacuum as the solvent was slowly removed. When the volume reached approximately 10-15ml, yellow crystals were visible. The solution was filtered and the crystals washed with ether. The crystals were redissolved in $10^{-3}M$ HCl, the solution frozen and the solvent again removed under vacuum. The resulting crystals were collected by filtration and stored in a refrigerated desiccator. A yield of 28% was obtained (based on the weight of gold used).

Analysis: Calculated for $[Au(Me_3dien)Cl]Cl_2$ Au, 44.0%; Cl, 23.4%; Found: Au, 44.5%; Cl, 22.7%.

Visible and Ultraviolet Spectra: Absorption spectra in these energy regions were measured on either a Cary 118 or a Perkin-Elmer Model 202 spectrophotometer using 1cm quartz cells.

Potentiometric Titrations: These were done in a jacketed beaker through which water was circulated by a Tamson constant temperature bath at $25.0 \pm .1^\circ C$. Magnetic stirring was employed, but stirring was stopped while taking readings. A Fisher Accumet Model 120pH Meter with a standard combination

electrode was used. This meter was standardized with
Beckman buffer solutions at pH's of 10.0, 7.0, and
4.0. A 5ml buret was used to add 0.2ml portions
of .0275M $HClO_4$, standardized with Na_2CO_3.

A 20mg sample of complex was dissolved in 20ml
distilled H_2O. The pH was adjusted to 9-10 with
between 0.1 and 0.2ml of 1M NaOH. This solution
was passed through a Dowex 1-X8 anion exchange
resin to make OH^- the only anion in solution.
The effluent was brought to a pH of 9-11 and diluted
to 160ml.

The total change in volume for the titration was
less than 10%. The time required for titration
was usually 45 minutes.

Conductometric Studies: The sample studied was
prepared as described above, and the effluent was
diluted to 160 ml.

The studies were performed in a tall form
beaker at ambient temperatures. Magnetic stirring
was employed as described above. A newly platinized
conductance electrode connected to an Industrial
Instruments Model RC-1B Conductance Bridge was used
to measure resistance at 0.2ml intervals of titrant.
The titrant, .0275M $HClO_4$, was introduced using
a 5ml buret. The time of these studies was usually
45 minutes.

RESULTS AND DISCUSSION

Hydrolytic Behavior of $[Au(Me_3dien)Cl]Cl_2$:

Complexes of the type $[Au(amine)Cl]^{+2}$ where amine is a diethylenetriamine ligand having a hydrogen on the central nitrogen atom hydrolyze according to the reaction sequence shown in Reaction R1. [6]

$$[Au(amine)Cl]^{+2} \underset{+H^+}{\overset{+OH^-}{\rightleftharpoons}} [Au(amine_{-H})Cl]^{+} \\ \underset{+H^+}{\overset{+OH^-}{\rightleftharpoons}} [Au(amine_{-H})OH]^{+} \qquad \text{R1}$$
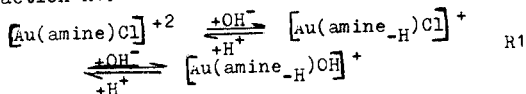
Studies show that these reactions are accompanied by smooth spectral transitions and well defined isosbestic points. The spectral features of these species indicate a maximum absorbance at 300-315nm for $[Au(amine)Cl]^{+2}$, a maximum absorbance at 370-400nm for $[Au(amine_{-H})Cl]^{+}$ and a maximum absorbance at 350-370nm for the complex $[Au(amine_{-H})OH]^{+}$. [7]

Where amine is a dien ligand with no hydrogens attached to nitrogens, the first step in the above mechanism obviously cannot occur. Such complexes decompose either before or shortly after substitution of hydroxide ion for chloride.

Since the complex $[Au(1,4,7-Me_3dien)Cl]^{+2}$ is different from both of the above examples, its hydrolytic behavior was of particular interest.

Eighteen mg of $[Au(Me_3dien)Cl]Cl_2$ were dissolved in 50ml of 0.1M HCl to produce a solution with a

concentration of 4×10^{-4}M. The solution was placed in a water jacketed beaker kept at $25^{\pm}$ .1°C. The pH, which was 1.0 at the start, was adjusted with NaOH. After each 0.5ml increment, a spectrum was obtained in the wavelength range of 270-400nm.

The spectral changes observed were different from those accompanying sequence R1. In this case, the absorbance initially decreased at all wavelengths as shown in Figure II. At more basic pH's, the absorbance increased to produce a broad band at 370nm, as shown in Figure III.

In order to more fully understand what was occuring, the removal of Cl$^-$ by ion exchange was undertaken. This process is described under "Potentiometric Titration" on pp 8 and 9. The resulting solution was acidified to a pH of 2 with $HClO_4$, and spectral changes were studied under the same set of conditions as previously described. These results are shown in Figures IV and V.

Curve A is $\left[Au(Me_3dien)H_2O\right]^{+3}$. Previous studies suggest that proton extraction from the dien ligand should result in a broad band in the 350-400nm region.[6] The spectral change leading to Curve B cannot involve this process, and most probably involves proton extraction from H_2O as shown in R2.

$$\left[Au(Me_3dien)H_2O\right]^{+3} + OH^- \rightleftharpoons \left[Au(Me_3dien)OH\right]^{+2} + H_2O \quad R2$$

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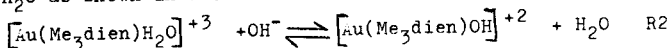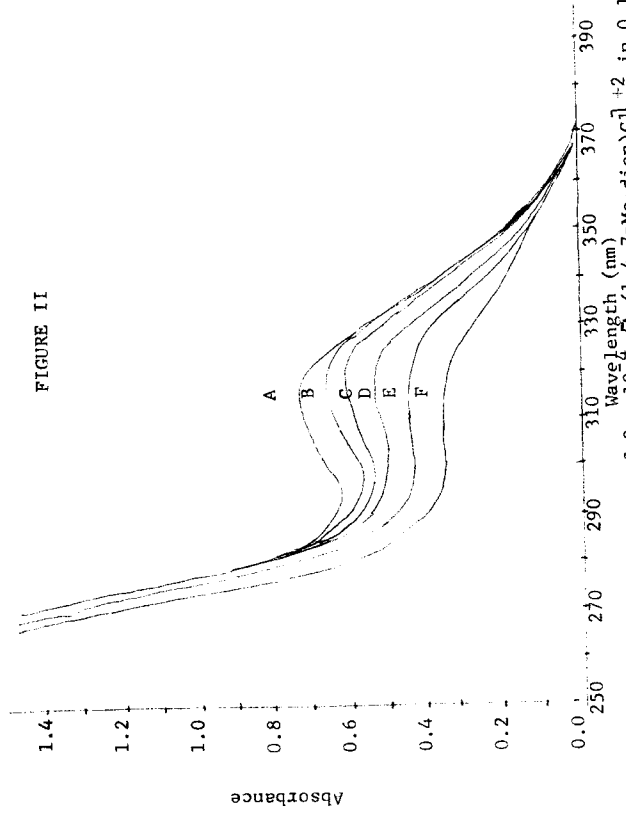
FIGURE II

Absorption spectra of 8×10^{-4} [Au(1,4,7-Me$_3$dien)Cl]$^{+2}$ in 0.1 M Cl$^-$ as a function of pH at 25°C. A. pH = 1.0; B. pH = 1.5; C. pH = 2.5; D. pH = 4.7; E. pH = 5.6; F. pH = 6.2.

FIGURE III
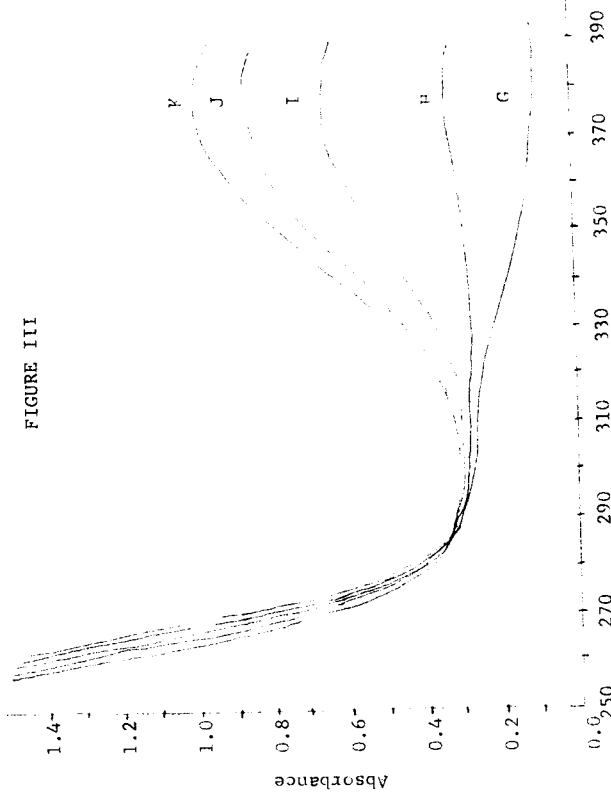
Absorption spectra of 8×10^{-4} M [Au(1,4,7-Me$_3$dien)Cl]$^{+2}$ in 0.1 M Cl$^-$ as a function of pH at 25°C. G. pH = 6.7; H. pH = 7.3; I. pH = 7.8; J. pH = 8.2; K. pH = 8.8-9.5.

FIGURE IV

Absorption spectra of 4.5×10^{-4} M $[Au(1,4,7\text{-Me}_3\text{dien})H_2O]^{+3}$ as a function of pH at 25°C. A. pH = 2.0; B. pH = 6.2; C. pH = 7.1.

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FIGURE V

Absorption spectra of 4.5×10^{-4} M $[Au(1,4,7-Me_3dien)H_2O]^{+3}$ as a function of pH at 25°C. C. pH = 7.1; D. pH = 7.7; E. pH = 8.2; F. pH = 8.7; G. pH = 10.1; H. pH = 11.8.
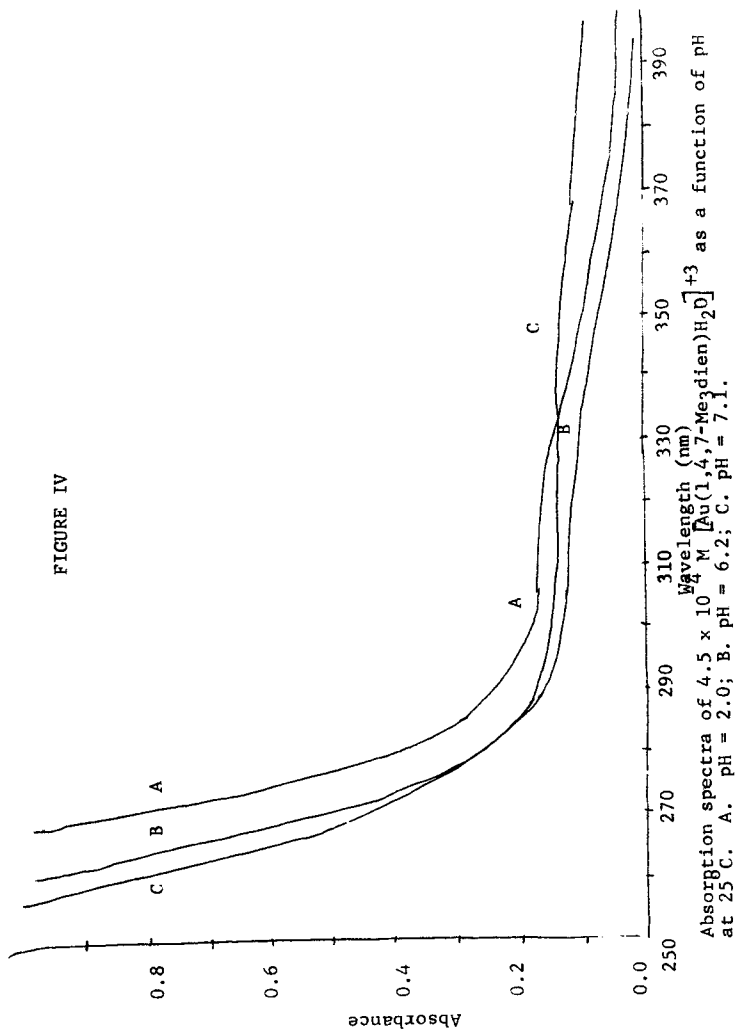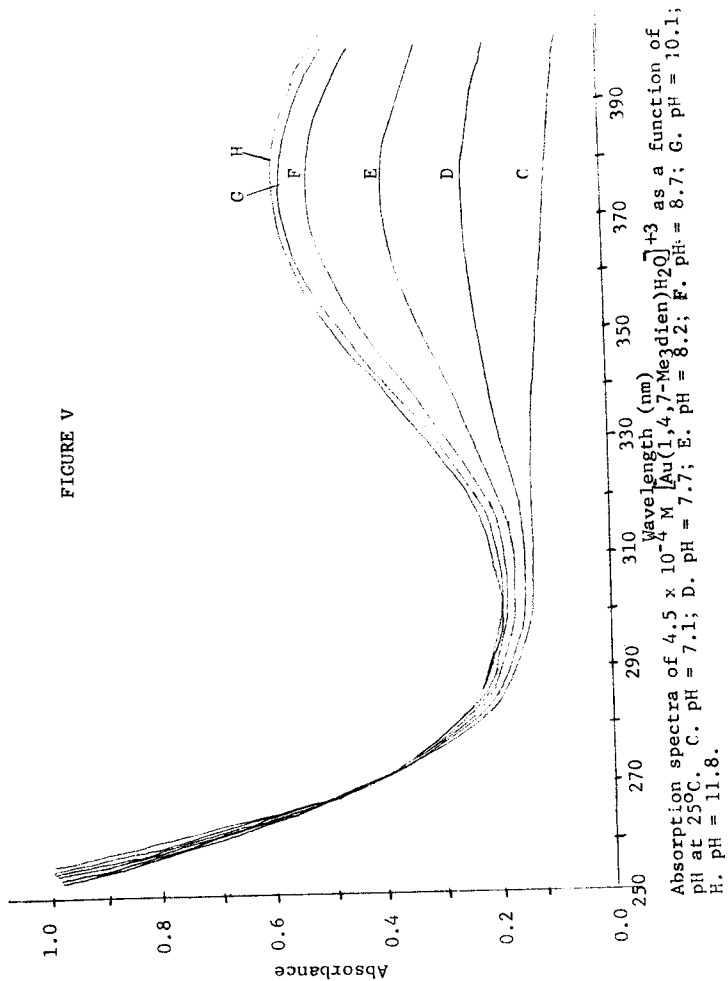
It is obvious that more than two species must be present in going from Curve B to Curve C since no isosbestic points were observed. The final product in Figure V (Curve H) must be $[Au(Me_3dien_{-H})OH]^+$ since there is no Cl^- in solution. Therefore, reaction R3 occurs in the pH range of 7.1-11.8.

$$[Au(Me_3dien)OH]^{+2} + OH^- \rightleftharpoons [Au(Me_3dien_{-H})OH]^+ + H_2O \qquad R3$$
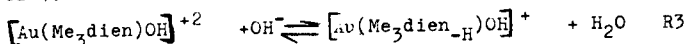
Support for these conclusions is apparent in the potentiometric and conductometric titrations whose results are shown in Figure VI. The results of the potentiometric titrations indicate two distinct equilibria: one in a pH range of 9.5 to 7.0, and the other in the range 7.0 to 4.0. These can be assigned to reactions R4 and R5.

$$[Au(Me_3dien_{-H})OH]^+ + H^+ \xrightarrow{pH\ 9.5-7.0} [Au(Me_3dien)OH]^{+2} \qquad R4$$
$$[Au(Me_3dien)OH]^{+2} + H^+ \xrightarrow{pH\ 7.0-4.0} [Au(Me_3dien)H_2O]^{+3} \qquad R5$$
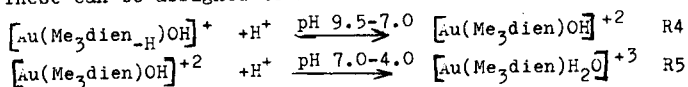
The conductometric titration curve can be explained as follows. The initial decrease in conductance is due to neutralization of OH^-. The first break is the result of Reaction R4 taking place. The conductance increases because a +1 ion is being converted to a +2 ion. The second break is the result of Reaction R5 taking place. The rate of increase in conductance is less because a +2 ion is being converted to a +3 ion. At the end of the curve, a sharp increase in conductance occurs, due to the increased

FIGURE VI

Specific Conductance (ohms^{-1} -cm^{-1})

Potentiometric and conductometric titrations of 0.044 moles of $[Au(1,4,7-Me_3dien-_H)OH]^+$ with 0.0275 M HClO$_4$ at 25°C.
———Potentiometric curve. ----Conductometric curve.

presence of the mobile hydrogen ion. These results suggest hydrolysis of $\left[\text{Au}(\text{Me}_3\text{dien})\text{Cl}\right]^{+2}$ proceeds by the sequence shown in reaction R6, rather than by sequence R1.

$$\left[\text{Au}(\text{Me}_3\text{dien})\text{Cl}\right]^{+2} \underset{+\text{H}^+}{\overset{+\text{OH}^-}{\rightleftharpoons}} \left[\text{Au}(\text{Me}_3\text{dien})\text{OH}\right]^{+2}$$
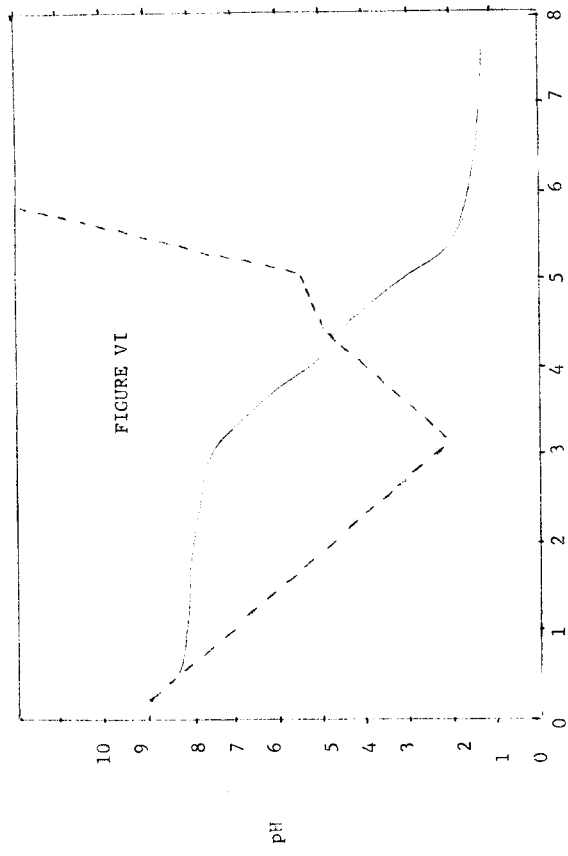
$$\underset{+\text{OH}^-}{\overset{+\text{H}^+}{\rightleftharpoons}} \left[\text{Au}(\text{Me}_3\text{dien}_{-\text{H}})\text{OH}\right]^{+}$$

R6
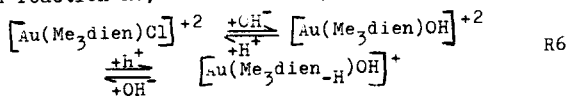
This is supported by results shown in Figure VII. Curve A is $\left[\text{Au}(\text{Me}_3\text{dien})\text{H}_2\text{O}\right]^{+3}$, prepared as described earlier. Curves B-F illustrate conversion of this ion to $\left[\text{Au}(\text{Me}_3\text{dien})\text{Cl}\right]^{+2}$. These results show that the process is complete when the ratio of $\left[\text{Cl}\right]/\left[\text{Au}\right] = 1$.

Reaction sequences R2 through R5 seem to suggest the relatively weak acidity of the hydrogens on the terminal nitrogens of the ligand. This lends support to the belief that when complexes of the type $\left[\text{Au}(\text{dien})\text{X}\right]^{+2}$ are hydrolyzed, it is the hydrogen on the central nitrogen which is most easily removed. This can be explained if one looks at the sigma bond structure along the H-N-Au-Cl axis. It is apparent that Cl would draw electron density toward itself, thereby polarizing Au, which would in turn polarize N, drawing the electron pair between H and N closer to N. This polarization along this axis would facilitate loss of H^+.

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FIGURE VII

Absorption spectra at 25°C. of 4.5×10^{-4} M $[Au(1,4,7\text{-Me}_3\text{dien})H_2O]^{+3}$ at pH = 2.0 as a function of added Cl^-. Ratio of moles Cl^- to moles complex: A. 0; B. 0.11; C. 0.33; D. 0.44; E. 0.67; F. 0.78-1.00.
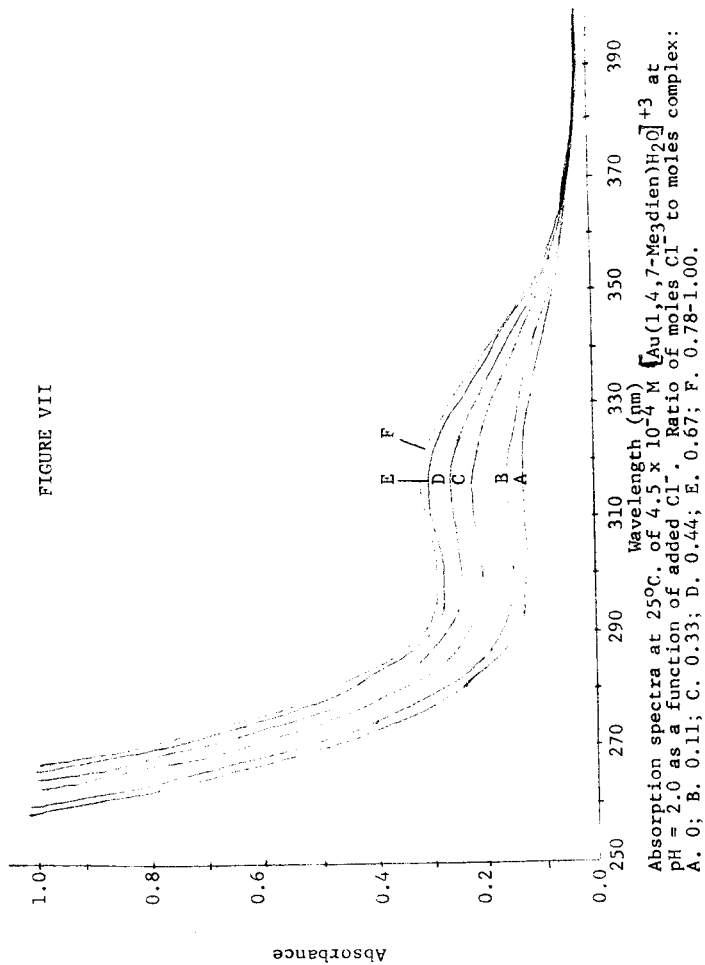
Ligand Replacement Kinetics:

Studies of the hydrolytic behavior of $[Au(Me_3dien)Cl]^{+2}$ indicate that the kinetics of replacement of Cl^- by Br^- should be observed at low pH. The relative stability of $[Au(Me_3dien)Br]^{+2}$ and $[AuBr_4]^-$ was determined. Figure VIII shows a stable complex formed from $[Au(Me_3dien)H_2O]^{+3}$ containing one Br per Au (Curve H). However, $[Au(Me_3dien)H_2O]^{+3}$ in a large excess of Br^- does not result in Curve H. Rather, a product was formed having an intense band at 380nm with a molar absorptivity of 3200. This result was observed by all solutions over a 24 hour period. The same product was formed when $[Au(Me_3dien)Cl]Cl_2$ was dissolved in a solution containing excess Br^-. These results indicate that at a pH of 2.0, reactions R7 and R8 occur in sequence.

$$[Au(Me_3dien)Cl]^{+2} + Br^- \longrightarrow [Au(Me_3dien)Br]^{+2} + Cl^- \qquad R7$$
$$[Au(Me_3dien)Br]^{+2} + 3Br^- \longrightarrow [AuBr_4]^- + Me_3dien \qquad R8$$
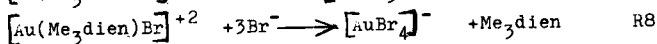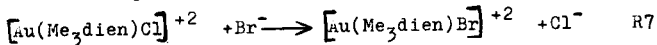
However, reaction R7 is much faster than reaction R8 so that all of the monochloro salt is converted to the monobromo species before any appreciable amount of $[AuBr_4]^-$ is formed. To further understand these reactions, the kinetics of reactions R7 and R8 were studied.

The kinetics of reaction R7 will be discussed first. A solution of 4×10^{-4} M $[Au(Me_3dien)Cl]Cl_2$ was prepared in 0.1M $HClO_4$. Kinetic studies for R7 were run by

FIGURE VIII
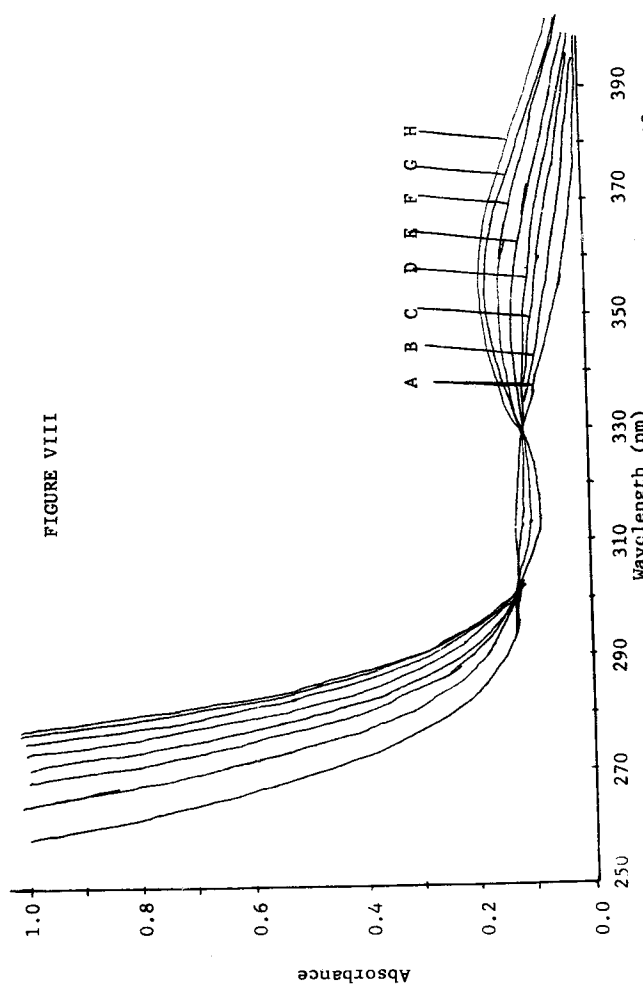
Absorption spectra at 25°C. of 4.5×10^{-4} M $[Au(1,4,7-Me_3dien)H_2O]^{+3}$ at pH = 2 as a function of added Br^-. Ratio of moles of Br^- to moles of complex: A. 0; B. 0.11; C. 0.22; D. 0.34; E. 0.45; F. 0.56; G. 0.67; H. 0.78-1.34.

allowing the solution to react with an equal volume
of a solution containing various bromide ion concentrations.
The bromide solution contained enough $NaClO_4$ to produce,
after mixing, a total ionic strength of 0.15.

Rates were dertermined using an Aminco-Morrow Stopped
Flow Apparatus in conjunction with a monochromator from
a Beckman D.U. The photomultiplier tube was connected
through an Aminco-Morrow High Performance Kinetic
Photometer to the vertical input of a Tektronix 3A1
Storage Oscilloscope. The traces of change in transmittance
percentage versus time were recorded using a Polaroid
Oscilloscope Camera. A typical trace is presented in
Figure IX.

All reactions were run at a temperature of $25 \pm .1^{\circ}C$.
The wavelength of interest was 313nm. Bromide concentra-
tions varied from .01 to .05M. Each run was performed in
quadruplicate. Reproducibility was better than 2% trans-
mittance.

The transmittance values obtained from these traces
were converted to absorbance at time "t" (A_t), and at
the completion of the reaction(A_∞). The log of their
difference was then plotted versus time, for each
concentration of bromide ion. A typical plot is
shown in Figure X. From the linear plots so obtained,
the psuedo first order rate constant, which is equal to

FIGURE IX
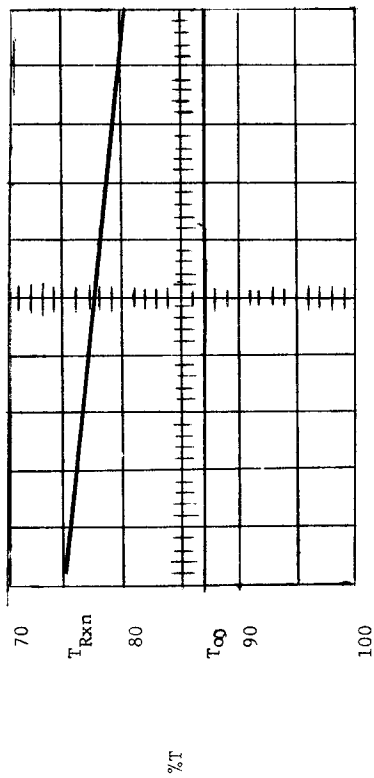
Typical Oscilloscope Trace for Reaction of [Au(1,4,7-Me3dien)Cl]+ with Br−. T_{100} = 100% Transmittance; T_{Rxn} = Transmittance of reaction; T_∞ = Reaction transmittance at infinite time.

FIGURE X
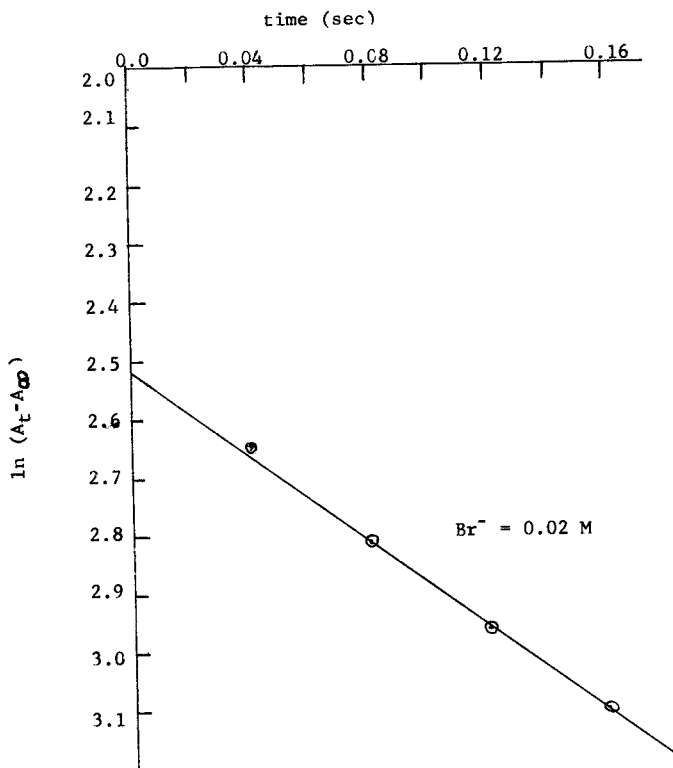
Typical Plot of $\ln(A_t-A_\infty)$ vs time for the Reaction
of $[Au(1,4,7-Me_3dien)Cl]^{+2}$ with Br^- at 25° C.

the slope, was calculated for each bromide concentration used. Table I is a list of k_{obs} for each bromide ion concentration studied. Plots of quadruplicate runs yielded slopes which agreed within 15%. A plot of these observed rate constants versus Br^- concentration yielded a straight line. The intercept equals k_1, the solvent path rate constant, and the slope is equal to k_2, or the bromide path rate constant. Figure XI illustrates the plot of the data given in Table I. From the plot it can be found that $k_1=0.25sec^{-1}$ and $k_{Br}=170M^{-1}-sec^{-1}$.

A comparison of these results with those of other $[Au(dien)X]^{+2}$ complexes is shown in Table II.

As seen in Table II, the k_{Br} for the Cl^- substitution reaction for the complex $[Au(dien)Cl]^{+2}$ is $380M^{-1}sec^{-1}$, and the k_{Br} for the same reaction of $[Au(Me_5dien)Cl]^{+2}$ is $0.058M^{-1}sec^{-1}$. The fact that the k_{Br} for the complex $[Au(Me_3dien)Cl]^{+2}$ falls in between these two extreme cases, indicates the strong effect of steric hindrance on reaction rates. The faster rate of $[Au(MeEt_4dien)Cl]^{+2}$ ($k_{Br}=0.26M^{-1}sec^{-1}$) as opposed to the rate of $[Au(Me_5dien)Cl]^{+2}$ has been attributed to a ring-opening mechanism.[9]

The rates for reaction R8 were determined using a Perkin-Elmer 202 Ultraviolet-Visible spectrophotometer

TABLE I

Psuedo First Order Rate Constants For:

$$\left[\text{Au}(\text{Me}_3\text{dien})\text{Cl}\right]^{+2} + \text{Br}^- \longrightarrow \left[\text{Au}(\text{Me}_3\text{dien})\text{Br}\right]^{+2} + \text{Cl}^-$$
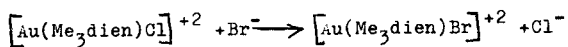
$$\mu = 0.15 \text{ with NaClO}_4$$

Br^- Concentration	k_{obs}
0.05 M	8.3 sec^{-1}
0.04 M	7.6 sec^{-1}
0.03 M	5.5 sec^{-1}
0.02 M	3.4 sec^{-1}
0.01 M	1.9 sec^{-1}

FIGURE XI

Observed **Rate** Constant for $[Au(1,4,7-Me_3dien)Cl]^{+2}$ **vs** Bromide Concentration @ 25.0°C.
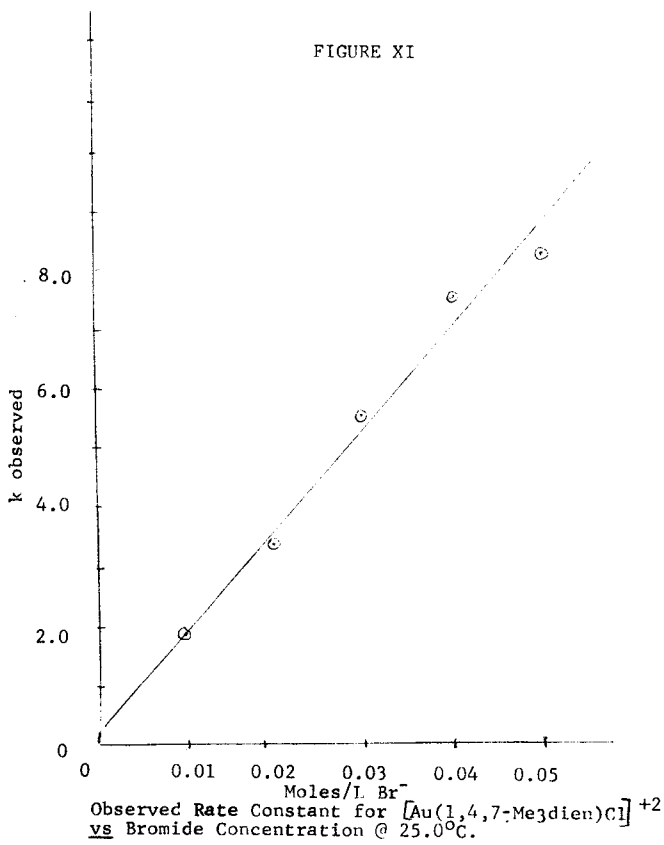
TABLE II

Rate Constants for the Reaction:

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

Complex	$k_1(sec^{-1})$	$k_2(M^{-1}sec^{-1})$	Ref.
$[Au(Me_3dien)Cl]^{+2}$	0.2	170	this work
$[Au(dien)Cl]^{+2}$	0.0	380	8
$[Au(dien_{-H})Cl]^+$	0.6	190	8
$[Au(Me_2dien_{-H})Cl]^+$	0.2	44	7
$[Au(Me_5dien)Cl]^{+2}$	0.002	0.058	9
$[Au(MeEt_4dien)Cl]^{+2}$	0.01	0.26	9

in conjunction with a Hewlett-Packard Model 17501A
Strip Chart Recorder. The chart measured absorbance
versus time.

A solution of the complex was prepared as previously
described. The solution was brought to a pH of 1 with
$HClO_4$ whereupon a solution of Br^- equivalent to one
mole Br^- per mole Au(III) was added to convert the
complex to $\left[Au(Me_3dien)Br\right]^{+2}$.

Equal amounts of the above solution and a solution
containing Br^- ion were simutaneously pipetted into
the cell of the spectrophotometer.. The Br^- solution
contained enough $NaClO_4$ to produce an ionic strength
of 0.15 after mixing. All reactions were carried out
at $25^{\pm}$ .1°C at a wavelength of 380nm. Bromide
concentrations varied from 0.01 to 0.05M.

The data obtained was treated in the same manner
as previously described. When k_{obs} was plotted versus
$\left[Br^-\right]$ a curve was obtained (Figure XII). However,
when the observed rate constants were plotted versus
$\left[Br^-\right]^2$ a straight line was obtained, where the
second order rate constant was equal to the slope
(Figure XIII). A list of k_{obs} versus $\left[Br^-\right]$ is
shown in Table III. The third order rate constant
was determined to be 15 l^2-$mol^2$$sec^{-1}$.

The fact that the ligand unwrapping reaction is

FIGURE XII

Observed Rate Constants for the Reaction:
$[Au(1,4,7-Me_3dien)Br]^{+2} + 3Br^- \longrightarrow AuBr_4^-$
vs Bromide Concentration.

FIGURE XIII

Observed Rate Constants for the Reaction:
$[Au(1,4,7-Me_3dien)Br]^{+2} + 3Br^- \rightarrow AuBr_4^-$
vs $[Br^-]^2$ @ 25°C.

TABLE III

Psuedo First Order Rate Constants For:

$$\left[\text{Au(Me}_3\text{dien)Br}\right]^{+2} + 3\text{Br}^- \longrightarrow \text{AuBr}_4^- + \text{Me}_3\text{dien}$$

$$\mu = 0.15 \text{ with NaClO}_4$$

Br⁻ Concentration	$k_{obs} \times 10^2$
0.05 M	3.6 sec⁻¹
0.04 M	2.3 sec⁻¹
0.03 M	1.3 sec⁻¹
0.02 M	0.51 sec⁻¹
0.01 M	0.085 sec⁻¹

second order in Br^- was surprising. Earlier studies on the stabilities of the acidic forms of complexes of the type $[Au(amine)Cl]^{+2}$ in excess Cl^- have indicated that only those complexes having ethyl groups attached to the nitrogens decomposed to $[AuCl_4]^-$ at low pH's.[9] Stevens also maintains that the complexes $[Au(Me_5dien)Br]^{+2}$ and $[Au(MeEt_4dien)Br]^{+2}$ decompose to $[AuBr_4]^-$ at low pH's; the latter being less stable than the first.[9] However, this work is the first attempt to obtain rate data for the ligand unwrapping reaction.

The second order kinetics of the reaction: $[Au(Me_3dien)Br]^{+2} \longrightarrow [AuBr_4]^-$ illustrates two things: a) the breaking of the second Au-N bond is rate determining and b) these bidentate species are actually four coordinate. A mechanism which would explain the ligand unwrapping reaction is Reaction R 9.

The rate of formation becomes:

$$\frac{d\left[AuBr_4\right]^-}{dt} = k_3 \left[I\right]\left[Br^-\right]$$

but $K_{eq_2} = \dfrac{\left[I\right]}{\left[Br^-\right]\left[R\right]}$

therefore, $\left[I\right]= K_{eq_2}\left[R\right]\left[Br^-\right]$

then $\dfrac{d\left[AuBr_4\right]^-}{dt} = k_3 \cdot K_{eq_2}\left[R\right]\left[Br\right]^2$

Under excess $\left[Br^-\right]$, psuedo first order conditions exist such that

$$\frac{d\left[AuBr_4\right]^-}{dt} = k_{obs}\left[R\right] \text{ where } k_{obs} = k_3 \; K_{eq_2}\left[Br^-\right]^2$$

This implies that an intermediate similar to (I) was involved in the $\left[Au(Me_3dien)Cl\right]^{+2} + Br^- \longrightarrow \left[Au(Me_3dien)Br\right]^{+2} + Cl^-$ reaction. Thus, in a large excess of $\left[Br^-\right]$ the general mechanism as shown in reaction R 10 would be:

$$\left[CH_3 - N - \underset{\overset{|}{NH}}{\overset{NH}{Au}} - Cl \right]^{+2} \xrightarrow[K_{eq(1)}]{+Br^-} \left[\underset{CH_3}{\overset{CH_3}{N}} \underset{H}{\overset{NH}{Au}} \overset{Br}{\underset{Cl}{}} \right]^{+}$$

k_2

$$\left[CH_3 - N - \underset{\overset{|}{N-CH_3}}{\overset{NH}{Au}} - Br \right]^{+2} \xrightarrow[K_{eq2}]{+Br^-} \left[\underset{H--N}{\overset{N-CH_3}{Au}} \overset{Br'}{\underset{Br}{}} \right]^{+}$$

$+Br^-$ k_3 R10
$+Br^-$

$$\left[Br - \underset{\overset{|}{Br}}{\overset{Br}{Au}} - Br \right]^{-} + \; 1,4,7, - Me_3 \; dien$$
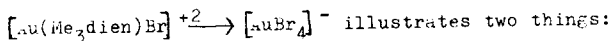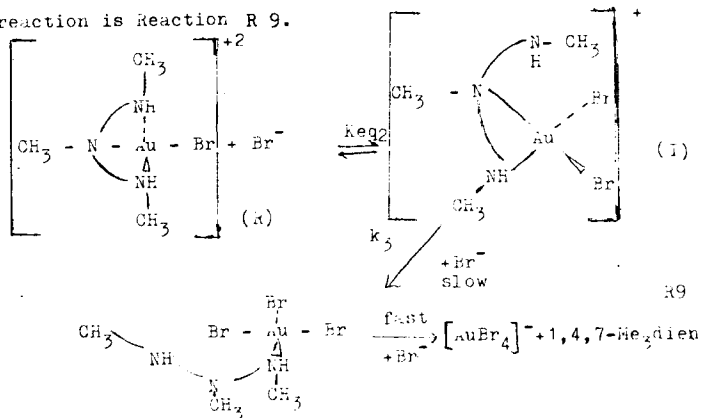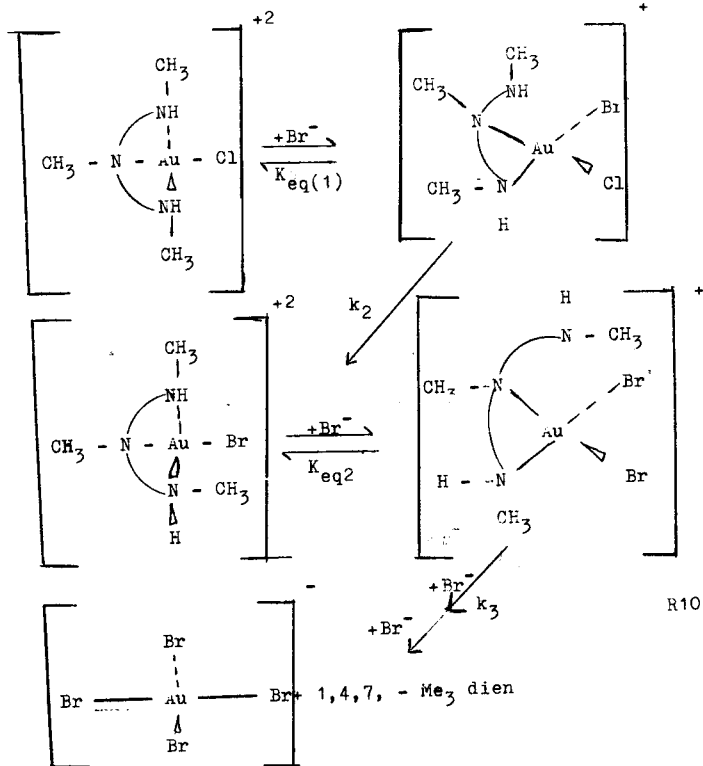
with $k_2 >> k_3$. Therefore, k_{Br} for the Cl^- substitution reaction is actually equal to $k_2 \, K_{eq(1)}$ while k_{Br} for the ligand unwrapping reaction is equal to $k_3 \, K_{eq(2)}$. This further suggests that it is the breaking of the $Au - Cl$ bond which is rate determining in the substitution reaction. When insufficient Br^- is present, the reaction does not go much beyond the formation of the monobromo complex.

As mentioned previously, it has been suggested that ethyl substituted ligands undergo Cl^- substitution via the "dangling" end type of intermediate. However, the results of this study show that this intermediate also exists when the central nitrogen is methylated. Therefore, the faster rate of $\left[Au(MeEt_4dien)Cl\right]^{+2}$ over $\left[Au(Me_5dien)Cl\right]^{+2}$ may be due to the combined effects of the substitution, leading to a greater concentration of the "dangling end species", and methyl substitution on the central nitrogen, leading to weaker $N - Au$ bonds.

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