

TABLE III
 KINETIC DATA AND ACTIVATION PARAMETERS, $\mu = 1.00$ (NaCl)

Reaction	Rate constant, $M^{-1} \text{ sec}^{-1}$ (298°K)	ΔH^* , kcal/mole	ΔS^* , gibbs/mole
$(\text{NC})_5\text{FeNO}_2^{3-} + \text{OH}^- \xrightarrow{k_{12}} (\text{NC})_5\text{FeNO}_2\text{H}^{3-}$	0.55 ± 0.01	12.6 ± 0.2	-17.5 ± 0.7
$(\text{NC})_5\text{FeNO}_2^{4-} + \text{H}_2\text{O} \xrightarrow{k_{23}} (\text{NC})_5\text{FeOH}_2^{3-} + \text{NO}_2^-$	$(1.4 \pm 0.2) \times 10^{-4}$	21.6 ± 0.9	-3.6 ± 3.0
$\text{NO}_2^- + (\text{NC})_5\text{FeOH}_2^{3-} \xrightarrow{k_{32}} (\text{NC})_5\text{FeNO}_2^{4-} + \text{H}_2\text{O}$	0.46 ± 0.07^a	9.3 ± 1.1^a	-28.3 ± 3.7^a

^a Values obtained from activation-parameters for k_{23} , and ΔS° and ΔH° for equilibrium 2.

the same and the enthalpy of activation is about 5 kcal/mole smaller for the bisulfide reaction. A complete kinetic and thermodynamic investigation of the system is presently being carried out.

From the data obtained it is possible to comment on other reactions in which nitroprusside takes part. Cambi¹⁰ has made observations on the reaction between nitroprusside and acetone. It is clear from our preliminary experiments that acetone does not react with the products of the hydroxide-nitroprusside reaction, $(\text{NC})_5\text{FeNO}_2^{4-}$ and $(\text{NC})_5\text{FeH}_2\text{O}^{3-}$. Therefore

(10) L. Cambi, *Chem. Zent.*, **I**, 1756 (1913); *ibid.*, **II**, 1109 (1914).

the enolate form of acetone must be competing with hydroxide for the site on nitroprusside, the product in the acetone-nitroprusside reaction being $(\text{NC})_5\text{FeNO}(\text{C}_3\text{H}_5\text{O})^{3-}$. This species can then aquate as $(\text{NC})_5\text{FeNO}_2^{4-}$ does in the hydroxide-nitroprusside reaction. In general base-nitroprusside reactions will involve equilibria of the type in reaction 1, and the species formed will depend on the competitive equilibria between the bases in the system for the site on nitroprusside. Reactions between bases and nitroprusside may provide an interesting route in the preparation of some unique compounds.

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The Aqueous Solution Chemistry and Kinetic Behavior of a Pseudo-Octahedral Complex of Gold(III)

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The pseudo-octahedral complexes, $[\text{Au}(\text{Et}_4\text{dien-H})\text{X}]\text{PF}_6^2$ ($\text{X} = \text{Cl}, \text{Br}$) have been synthesized and their aqueous solution chemistry investigated. Evidence is presented for hydrolytic and acid-base equilibria. In addition, rate constants for the reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with Br^- and OH^- and half-lives for the isotopic exchange of this substrate and its conjugate acid with Cl^- are reported. The rate of chloride ion replacement is almost independent of the nature and the concentration of the reagent. Other reagents such as N_3^- , I^- , and SCN^- replace not only the chloride ion but also the triamine to yield complexes of the type AuX_4^- .

Introduction

The rates of substitution reactions of square-planar metal complexes are usually dependent on the nature and concentration of the reagent.³ Octahedral complexes in aqueous solution generally react at rates that do not depend on the entering ligand, except for anation reactions.⁴ The square-planar, low-spin, d^8 complex $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ has been found to react like an octahedral substrate.⁵ This anomalous result was ascribed to the structure of this ion and suggests the

difference in behavior between octahedral and square-planar complexes is due in part to steric considerations. Because it behaves like an octahedral complex, the complex was designated a pseudo-octahedral complex.

Investigations of some reactions of $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ in aqueous solution show that these proceed almost entirely by the path that is first order in reagent.⁶ Because of this strong dependence of the rate of reaction on the entering ligand, it seems of interest to test the importance of steric factors using the analogous sterically hindered system. This paper reports the results of such a study on the complex ions $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ and $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$.

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(2) dien = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, $\text{Et}_4\text{dien} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, $\text{Et}_4\text{dien-H} = (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$.

(3) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(4) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, Chapter 3.

(5) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

(6) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

Experimental Section

Materials.—Fine gold powder was obtained from Engelhard Industries, Inc., and 1,1',7,7'-tetraethyldiethylenetriamine, purchased from Ames Laboratories, Inc., was used without further purification. All other chemicals used were reagent grade.

Analyses.—Attempts to analyze for gold content by ignition of a small quantity of the compound in a microcrucible failed to give reproducible results, presumably due to the presence of PF_6^- . Consequently, a quantity of the compound (ca. 100 mg) was dissolved in 1 ml of warm 0.1 *M* HCl and 0.5 ml of hot 5% hydroquinone was added. Under these conditions precipitation of metallic gold is quantitative.⁷ The precipitate was collected by filtration through weighed sintered glass crucibles, washed with CH_3OH , and dried at 110°, and the weight of Au was determined by difference.

The chloride ion content was determined by treating an aqueous solution of ca. 50 mg of the compound with a few drops of 1 *M* NaOH and warming until reduction to metallic Au was complete. The residue was removed by filtration and the chloride ion titrated with $\text{Hg}(\text{NO}_3)_2$ at pH 3.0–3.5 using diphenylcarbazone–bromophenol blue as indicator.⁸

Preparation of Complexes.—The HAuCl_4 (or HAuBr_4) starting material was prepared by allowing a weighed quantity of gold powder to dissolve in a few milliliters of a mixture of concentrated HCl (or HBr) and concentrated HNO_3 . This solution was evaporated to a small volume, more concentrated HCl (or HBr) was added, and the evaporation was repeated. Upon cooling the HAuCl_4 (or HAuBr_4) crystallized.

[Au(Et₄dien-H)Cl]PF₆.—A 20-ml aqueous solution of HAuCl_4 containing 2 g (10 mg-atoms) of Au was added dropwise with stirring to 8 ml (32 mmoles) of 1,1',7,7'-tetraethyldiethylenetriamine in 50 ml of H_2O at 0°. When the yellow precipitate which formed initially was completely dissolved and the resulting orange solution had begun to darken, the pH of the reaction mixture was adjusted with concentrated HCl to a value of ca. 6. After filtration to remove metallic Au, an excess of 0.25 *M* NH_4PF_6 was added. The dark red precipitate of the complex was collected by filtration. This was dissolved in 150 ml of a 30% acetone–70% absolute ethanol solution and filtered. The filtrate was evaporated to ca. 20 ml in a rotary evaporator. The product was collected on filter paper, washed with alcohol and ether, and dried *in vacuo* over P_2O_5 . A yield of 32% (based on the weight of Au) was obtained.

Anal. Calcd for $\text{AuC}_{12}\text{H}_{28}\text{N}_3\text{ClPF}_6$: Au, 33.3; Cl, 6.0. Found: Au, 33.4; Cl, 6.3.

In an attempt to isolate the acid form of this complex, 0.450 g of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]\text{PF}_6$ was dissolved in 10 ml of acetone and 50 ml of 2 *M* H_2SO_4 in absolute ethanol was added. Evaporation to ca. 20 ml in a rotary evaporator failed to produce any significant crystallization.

[Au(Et₄dien-H)Br]PF₆.—The procedure was similar to that employed for the analogous chloro complex with HAuBr_4 and HBr used in place of HAuCl_4 and HCl. However, the reaction was slow and it was necessary to allow the reaction mixture to warm to room temperature before complete solution of the initial precipitate occurred. A yield of 29% (based on the weight of Au) was obtained.

Anal. Calcd for $\text{AuC}_{12}\text{H}_{28}\text{N}_3\text{BrPF}_6$: Au, 31.0. Found: Au, 30.7.

Although these compounds were stored in the absence of light, they slowly darkened and became gummy. It was necessary to recrystallize them after about 30 days.

Spectrophotometric Measurements.—Ultraviolet absorption spectra were measured with Beckman DU and Cary Model 14 spectrophotometers using 1-cm quartz cells.

pH Measurements.—A Beckman Model G pH Meter with a glass electrode was used. This was standardized at pH 4 (Fisher

Scientific standard buffer solution) and pH 7 (Beckman buffer solution).

Buffers.—Buffer solutions of pH 6.3 and 7.7 were prepared from 50 ml of 0.1 *M* KH_2PO_4 plus the required amount of 0.1 *M* NaOH and distilled water. Buffer concentrates which when diluted 10-fold produced solutions of pH 7.3 were prepared by dissolving 34.05 g of KH_2PO_4 or 34.52 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ + 175 ml of 1.00 *M* NaOH in distilled water and diluting to 500 ml.

Kinetic Studies.—The compound $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]\text{PF}_6$ is only moderately soluble and dissolves very slowly in H_2O . Since it dissolves readily in acetone, solutions for kinetic study were prepared by dissolving a weighed amount of the compound in 1 ml of acetone and diluting to 100 ml with distilled H_2O . A freshly prepared solution was used for each run, except when checking to see if the hydrolysis product had any effect on the reaction rate.

Reactions of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with Br^- and N_3^- .—These reactions were followed spectrophotometrically at 320 and 330 μm . The concentrations of Br^- and N_3^- were always large enough to ensure pseudo-first-order conditions. In some experiments the reagent solution was buffered by dissolving the NaBr or NaN_3 in a buffer solution of the desired pH. In other experiments buffering of the reagent solution was achieved by adding buffer concentrate to a concentrated solution of the reagent and diluting by a factor of 10. Rate constants were computed from the slope of a plot of $-\log(A_\infty - A_t)$ vs. t .

For the reaction with Br^- isosbestic points were observed to occur at 300 and 366 μm and the absorption spectrum of the product was shown to be identical with the spectrum of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Br}]\text{PF}_6$.

No isosbestic points were observed for the reaction with N_3^- , the absorptivity increasing at all wavelengths over the region scanned. Since gold azide compounds are known to be explosive, no attempt was made to isolate the product of this reaction. The possible products are considered in the Results and Discussion section.

The Reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with OH^- .—Attempts to follow this reaction spectrophotometrically using buffered solutions of pH >8 always resulted in reduction, as evidenced by a visual darkening of the solution. However, fairly good isosbestic points were observed during the first 60–80 min of reaction. In an effort to circumvent reduction, the reaction was studied using a Radiometer TTT-1 titrator functioning as a pH-Stat. All solutions were prepared from CO_2 -free demineralized water and reactions were carried out under N_2 . The titrator was standardized at pH 7 and 10 using Beckman standard buffer solutions. In a typical run 15 ml of 0.20 *M* NaClO_4 was introduced into a jacketed beaker through which water circulated from a constant temperature bath at $25.0 \pm 1^\circ$. Standard 0.0105 *M* NaOH was added with stirring until the pH value previously set on the titrator was achieved. This solution was allowed to stand for several minutes to check the constancy of the pH. The reaction was then initiated by addition from a syringe of 1 ml of a 4.0×10^{-3} *M* solution of the complex.

Some reduction of the complex during reaction was observed to occur. Plots of $\log(V_\infty - V_t)$ vs. time, where V_∞ = volume of 1 equivalent of NaOH and V_t = volume of base added at time t , were linear only over the first 60–80 min of reaction. Consequently, pseudo-first-order rate constants were calculated from the slope of such plots over the first 60 min of reaction. The product of this reaction was not identified, but was assumed to be $[\text{Au}(\text{Et}_4\text{dien-H})\text{OH}]^+$.

Isotopic Exchange Studies.—The radioactive compound $[\text{Au}(\text{Et}_4\text{dien-H})^{36}\text{Cl}]\text{PF}_6$ was prepared by dissolving a few tenths of a gram of the unlabeled compound in a small volume of acetone and diluting to ca. 100 ml with absolute alcohol. Approximately 0.4 ml (ca. 100 μcuries) of a H^{36}Cl solution obtained from the Oak Ridge National Laboratory was neutralized with NaOH. The solutions were mixed, allowed to stand overnight, and evaporated to a few milliliters in a rotary evaporator. The $[\text{Au}(\text{Et}_4\text{dien-H})^{36}\text{Cl}]\text{PF}_6$ was recovered by filtration.

The solution of $[\text{Au}(\text{Et}_4\text{dien})^{36}\text{Cl}]^{2+}$ was prepared by dis-

(7) F. E. Beamish, J. J. Russel, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 174 (1937).

(8) F. E. Clark, *Anal. Chem.*, **22**, 553 (1950).

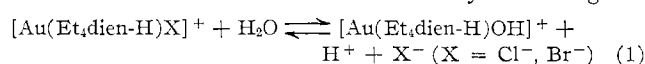
solving a weighed amount of $[\text{Au}(\text{Et}_4\text{dien-H})^{36}\text{Cl}]\text{PF}_6$ in 1 ml of acetone and diluting to 100 ml with 1.0 *M* HClO_4 . Equal volumes of 5.0×10^{-4} *M* solutions of $[\text{Au}(\text{Et}_4\text{dien})^{36}\text{Cl}]^{2+}$ and NaCl (dissolved in 1.0 *M* HClO_4) were mixed, wrapped in aluminum foil, and placed in a thermostated bath at the desired temperature. At recorded intervals 2-ml aliquots were withdrawn and allowed to pass through separate columns of Dowex 50W-X8 exchange resin, 100–200 mesh, *ca.* 2 cm in height and 8 mm in diameter. Under these conditions the complex was retained on the resin and the free chloride ion passed through. Complete removal of free chloride ion was ensured by rinsing the column with 4–6 ml of 1 *M* HClO_4 . One milliliter of 0.20 *M* NaCl was added to the total effluent from each separation. The solutions were neutralized with 4 *M* NaOH , made acid with 1 ml of 0.1 *M* HNO_3 , and heated almost to boiling. Excess 1 *M* AgNO_3 was added to precipitate AgCl . The precipitates were coagulated by heat and collected on 21-mm diameter filter paper circles supported by a sintered glass disk equipped with a removable chimney. Care was taken to obtain an even distribution of the precipitate. These filter paper circles were cemented to aluminum counting trays and their activity measured with the aid of a Tracerlab TGC-2 Geiger tube connected to a Tracerlab Super-scaler, Model SC-18A.

The exchange half-life, $(t_{1/2})_{\text{ex}}$, was evaluated from the slope of a plot of $-\log(1 - F)$ vs. t where F is the fraction exchanged at time t . Pseudo-first-order rate constants were calculated from the expression $k_1 = 0.693b/(a + b)(t_{1/2})_{\text{ex}}$ where a is the concentration of complex and b is the concentration of NaCl .

For the isotopic exchange of $[\text{Au}(\text{Et}_4\text{dien-H})^{36}\text{Cl}]^+$, the reaction solution was prepared as before except that 0.25 *M* NaClO_4 was used instead of 1.0 *M* HClO_4 . The reaction was quenched by discharging 2-ml aliquots of the reaction mixture into 2 ml of 2 *M* HClO_4 . Thereafter the procedure was identical with the above.

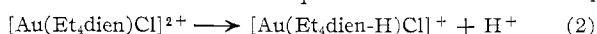
Results and Discussion

Equilibria Studies.—The complexes $[\text{Au}(\text{dien})\text{X}]^{2+}$ have been shown to exhibit both acid–base and hydrolytic equilibria in aqueous solution.⁹ Thus, it was expected that the complexes prepared in this study would hydrolyze in solution according to eq 1. That this reaction did occur was confirmed by observing the



absorption spectra of freshly prepared solutions of the complexes in water and in 0.20 *M* NaX ($\text{X} = \text{Cl}, \text{Br}$). No change in the absorption spectrum of the halide ion solution was observed to occur over a 24-hr period. However, during the first 60 min after preparation a slight shift in the absorption peaks toward shorter wavelengths was observed to occur when no excess halide ion was present. The total shift was small, suggesting the hydrolysis equilibrium favored the left side of eq 1. Attempts to push the equilibrium farther to the right by addition of OH^- and by the preparation of the solution in a pH 10 buffer resulted in eventual reduction of the complex.

An attempt to determine the $\text{p}K_a$ of the reaction represented by eq 2 by potentiometric titration of *ca.* 10^{-3} *M* solutions of the amido complex with standard HClO_4



produced a titration curve with no discernible end point. The limited solubility of the complex prohibited the use of more concentrated solutions.

(9) W. H. Baddley, F. Basolo, H. B. Gray, C. Nolting, and A. J. Poë, *Inorg. Chem.*, **2**, 921 (1963).

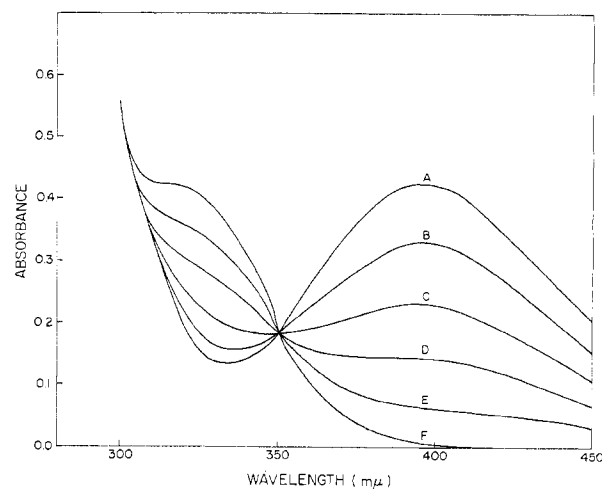


Figure 1.—Absorption spectra of 2.5×10^{-4} *M* $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]\text{PF}_6$ as a function of pH: A, in 0.20 *M* NaCl , pH 6.7; B, in 0.20 *M* NaCl , pH 3.0; C, in 0.20 *M* NaClO_4 , pH 2.5; D, in 0.20 *M* NaClO_4 , pH 2.0; E, in 0.20 *M* NaClO_4 , pH 1.5; F, in 1.0 *M* HClO_4 . All solutions contain 1% acetone.

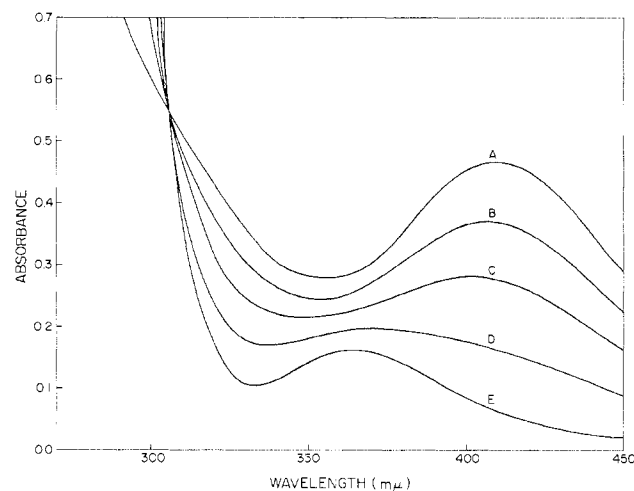


Figure 2.—Absorption spectra of 2.5×10^{-4} *M* $[\text{Au}(\text{Et}_4\text{dien-H})\text{Br}]\text{PF}_6$ as a function of pH: A, in 0.20 *M* NaBr , pH 6.8; B, in 0.20 *M* NaClO_4 , pH 3.11; C, in 0.20 *M* NaClO_4 , pH 2.54; D, in 0.20 *M* NaClO_4 , pH 2.02; E, in 1.0 *M* HClO_4 . All solutions contain 1% acetone.

A spectral study of a 0.10 *M* NaClO_4 solution of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]\text{PF}_6$ as a function of pH revealed an isosbestic point at 352 $\text{m}\mu$ in the pH range 0–3. The failure to observe this isosbestic point at $\text{pH} > 3$ was presumably due to hydrolysis of the complex. No further change in the spectrum was observed to occur when the acidity was increased beyond 1 *M* H^+ . A similar spectral study in 0.10 *M* NaCl revealed an isosbestic point at the same wavelength in the pH range 6.7–2.5. Below pH 2.5 the complex began to break down and a peak at 313 $\text{m}\mu$ characteristic of AuCl_4^- appeared.

A value of $\text{p}K_a = 2.2$ was obtained for the reaction illustrated by eq 2 from the spectral changes shown in Figure 1. Absorbances at 320 and 400 $\text{m}\mu$ were used to compute this value. Application of this method to the analogous bromo complex resulted in a value of $\text{p}K_a = 2.5$. The spectral changes used to obtain this value

are shown in Figure 2. Absorbances at 350 and 410 $m\mu$ were used in the computation.

For the ion $[\text{Au}(\text{dien})\text{Cl}]^{2+}$, Baddley, *et al.*,⁹ reported pK_a values of 4.0 in 0.5 M NaClO_4 and 4.7 in 0.5 M NaCl . In studies of the change in the absorption spectrum of this ion as a function of pH, isosbestic points at different wavelengths were observed in the two solutions. These differences in pK_a values and spectra were attributed to a reduced positive charge on the central ion in chloride ion solutions due to axial interaction of the chloride ions above and below the planar $[\text{Au}(\text{dien})\text{Cl}]^{2+}$. It appears that no such interaction should be possible with the present complexes because of the shielding by the ethyl groups. This is supported by the fact that the isosbestic point occurs at the same wavelength in both 0.1 M NaCl and 0.1 M NaClO_4 .

One other point of interest is that the tetraethyl derivative $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$ is a much stronger acid than is the unsubstituted complex $[\text{Au}(\text{dien})\text{Cl}]^{2+}$. That the replacement of N-H hydrogens by alkyl groups results in the alkyl derivative being a stronger acid is fairly common. For example, $[\text{Pt}(\text{NH}_3)_6]^{4+}$ has a pK_a^{10} of 7.9 compared with a value of 5.5 for $[\text{Pt}(\text{en})_3]^{4+}$ and $(\text{CH}_3)_3\text{NCH}_2\text{COOH}^+$ is a stronger acid than $\text{H}_3\text{NCH}_2\text{COOH}^+$ by a factor of three.¹¹ This effect of alkyl substitution on relative acidities has been explained¹² in terms of a decrease in energy of solvation. The suggestion being that the more positive acid is more solvated than its less positive conjugate base, and as a result for analogous systems the greater the energy of solvation, the weaker the acid. An additional effect for the complex $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$ vs. $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ is perhaps that in the latter complex two molecules of water can interact with Au(III) by weakly coordinating along the Z axis. This interaction may permit a partial dissipation of charge resulting in a less effective positive charge on Au(III) than that for the sterically hindered system where much less of such interaction with the solvent is possible. Thus, the larger effective positive charge on Au(III) may in part be responsible for the greater acidity of the tetraethyl derivative relative to the unsubstituted complex.

Kinetic Studies.—It is convenient to report these results and discuss them under three separate headings. The first two deal with the replacement of the chloro group from the complex, which is the point of primary interest in this investigation. The last topic has to do with reactions leading also to the replacement of the coordination triamine.

Reactions of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with Br^- , OH^- , and Cl^- .—Rate data for the replacement of chloride ion in the complex $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with three different reagents are recorded in Table I. The results show that the rates of reaction are all very similar, being largely independent of the nature and concentration of the reagent. This is in accord with previous observations and the suggestion that the four ethyl groups

TABLE I
RATE CONSTANTS AT 25° FOR THE REACTION^a
 $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+ + \text{Y}^- \xrightarrow{\text{H}_2\text{O}} [\text{Au}(\text{Et}_4\text{dien-H})\text{Y}]^+ + \text{Cl}^-$
[Y⁻], M $k_{\text{obsd}} \times 10^4, \text{sec}^{-1}$
 $\mu = 0.25$ with NaClO_4

0.005 Br^-	1.2
0.010 Br^-	1.3 ^b
0.010 Br^-	1.3 ^c
0.033 Br^-	1.4 ^c
0.050 Br^-	1.7
0.050 Br^-	1.6 ^c
0.050 Br^-	1.6 ^d
0.100 Br^-	2.0
0.100 Br^-	2.0 ^e
$2.5 \times 10^{-4} \text{Cl}^-$	0.75 ^f

$\mu = 0.20$ with NaClO_4

pH 8.0 (OH^-)	1.3
pH 8.5 (OH^-)	1.6
pH 9.0 (OH^-)	1.3
pH 10.2 (OH^-)	1.4

^a Concentration of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+ = 2.5 \times 10^{-4} M$.
^b Values of $k_{\text{obsd}} \times 10^4 \text{sec}^{-1}$ at 18° = 0.62 and at 35° = 3.6.
 $\Delta H^* = 18 \text{ kcal/mole}$ and $\Delta S^* = -17 \text{ eu}$. ^c No inert salt added.
^d Solution of complex was allowed to reach hydrolysis equilibrium before adding NaBr . ^e In pH 7.3 buffer. ^f $(t_{1/2})_{\text{ex}} = 77 \text{ min}$.

on the triamine efficiently shield the metal from nucleophilic attack.⁵ It is particularly significant that this is also observed with the Au(III) complex, because experiments have shown that the analogous sterically unhindered complex $[\text{Au}(\text{dien-H})\text{Cl}]^+$ reacts almost exclusively by the direct reagent displacement path.⁵

Substitution reactions of square-planar low-spin d^8 metal complexes generally follow the two-term rate law given by eq 3. At present, the only known ex-

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{reagent}] \quad (3)$$

ceptions to this are complexes of the type $[\text{M}(\text{Et}_4\text{dien-X})]^{2+}$ where $\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{II}),$ and $\text{Au}(\text{III})$. These systems appear to provide the final stage of steric retardation which is known to occur for reactions of square-planar complexes.¹³ The results in Table I suggest that the reagent path, k_2 of eq 3, must make at most only a very small contribution to the over-all rate of reaction. However, the data do show a slight, but consistent, increase in rate of reaction with increasing concentration of bromide ion for its reaction with $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$. This increasing trend was not observed for the analogous reaction of the Pd(II) system.⁵ The increase in rate for the Au(III) reaction may be due to its having a marked tendency to react by the reagent path, such that even with these adverse steric conditions the direct displacement makes a slight contribution to the total rate of reaction. An alternative explanation might be that the dynamic opening and closing of the chelate ring can permit a direct displacement by bromide ion when the chelate ring is in an open position. That such a mechanism is possible follows from the discussion given in the last section on the reaction of this complex with azide ion.

(10) Reference 4, p 388.

(11) A. Neuberger, *Proc. Roy. Soc. (London)*, **A158**, 68 (1937).

(12) Reference 4, p 392.

(13) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

Since the rates of hydrolysis (Table I) are the same, within experimental error, as the rates of reaction with bromide ion this suggests that the rate-determining steps for the two reactions are the same. There is no information on the detailed mechanism but it may resemble the solvent-assisted dissociation process suggested for aquation reactions of octahedral cobalt(III) complexes.¹⁴ In such a case the rate-determining step would be that of the reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with water to give $[\text{Au}(\text{Et}_4\text{dien-H})\text{OH}]^+$, which in turn would rapidly react with Br^- to form the product $[\text{Au}(\text{Et}_4\text{dien-H})\text{Br}]^+$. A less likely alternative process is that of slow dissociation to yield $[\text{Au}(\text{Et}_4\text{dien-H})]^{2+}$, followed by the fast formation of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Br}]^+$. That the rate of chloride ion exchange with $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$, in one experiment, was found to be less than its rate of hydrolysis or of reaction with bromide ion seems to be due to the experimental difficulties of the exchange studies.

Exchange of Cl^- with $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$.—Kinetic data on the isotopic exchange reaction of $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$ are reported in Table II. Unfortunately, only equimolar concentrations of chloride ion and the complex could be used. Higher chloride ion concentrations caused destruction of the complex with subsequent formation of AuCl_4^- . Attempts to investigate the replacement of chloride ion by bromide ion also failed, because at these acid conditions the complex dissociates to give AuBr_4^- .

TABLE II
RATE CONSTANTS AND ACTIVATION
PARAMETERS FOR THE ISOTOPIC EXCHANGE REACTION
 $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+} + \text{Cl}^- \rightleftharpoons [\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2-} + \text{Cl}^*$

Temp, °C	$(t_{1/2})_{\text{exchange}}$, hr	$k_1 \times 10^6$, sec ⁻¹
25	50	1.9
30	31	3.1
35	17	5.5
ΔH^*_{298}		19 kcal/mole ⁻¹
ΔS^*_{298}		-22 eu

Since other $[\text{M}(\text{Et}_4\text{dien})\text{X}]^{n+}$ complexes react at rates that do not depend on the entering reagent, it seems plausible that the rate of exchange of chloride ion with $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$ would not depend on the concentration of chloride ion. On the basis of this assumption, it is of interest to compare the data in Table II with those in Table I. The results show that the conjugate base $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ reacts faster than its parent acid $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+}$. This is a significant observation, since it provides direct evidence that an amido complex reacts more rapidly than its corresponding amine complex. The result is in agreement with the conjugate base mechanism proposed for the base hydrolysis of certain metal amines.¹⁵ That the amido Au(III) complex reacts only approximately seventy times faster than its amine parent resembles the smaller effect of hydroxide ion on the hydrolysis of Cr(III) and

Rh(III) complexes rather than the much larger effect found for Co(III) and Ru(III) systems.¹⁶ Several factors have been discussed in an attempt to explain these differences between rates of acid and base hydrolysis for different M(III) complexes. One point made was that the rate of base hydrolysis may tend to correlate the ease of reduction of M(III) to M(II), because the amido group has a tendency to force higher electron density on M(III). This does parallel the rapid rates of hydrolysis of Co(III) and Ru(III) with the ease of reduction of these metal ions to M(II), compared to the slower rates for Cr(III) and Rh(III), which are more difficult to reduce. On this basis the Au(III) system would also be expected to show a relatively small difference in reactivity between the amido and amine complexes, because Au(II) is not a readily available oxidation state for gold.

One other comparison that can be made of the data in Table II is summarized in Table III. The rate constants and activation parameters for the replacement of chloride ion in $[\text{M}(\text{Et}_4\text{dien})\text{Cl}]^{n+}$, where M = Pd(II), Pt(II), and Au(III), are compared. These results show that the rates of reaction decrease in the order Pd(II) > Au(III) > Pt(II) and that the difference in rate is largely due to a difference in enthalpy of activation. Since these reactions are almost independent of

TABLE III
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR
SOME RELATED REACTIONS OF Pd(II), Au(III), AND Pt(II)

Reaction	Temp, °C	k_{obsd} , sec ⁻¹	ΔH^* , kcal/mole ⁻¹	ΔS^* , eu
$[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+ + \text{I}^-^a$	25	2×10^{-8}	16 ± 1	-19 ± 3
$[\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{2+} + \text{Cl}^-$	25	1.9×10^{-6}	19 ± 1	-22 ± 3
$[\text{Pt}(\text{Et}_4\text{dien})\text{Cl}]^+ + \text{I}^-^b$	80	5.6×10^{-6}	24 ± 1	-15 ± 3

^a W. H. Baddley, Doctorate Thesis, Northwestern University, Evanston, Ill., 1964. ^b R. Wanguo, Masters Thesis, Northwestern University, Evanston, Ill., 1964.

reagent, it appears that the most important factor in the energy of activation is that of breaking the M-Cl bond. Therefore, the activation energies might be expected to parallel the M-Cl bond strengths. Unfortunately, there is no direct information on bond strengths in these systems but it is generally believed that the Pd-Cl bond is weaker than the Pt-Cl bond.¹⁷ Thus, it was no surprise to find a lower activation energy for the reaction of the Pd(II) system compared with that of Pt(II). What could not be anticipated was the relative activation energies for the reactions of the Au(III) and Pt(II) complexes. If one considers only the separation of charges, then it should require more energy to separate a Cl^- from Au(III) than from Pt(II). Furthermore, the logarithm of the total formation constant¹⁸ in water solution for AuCl_4^- has a value of 21 compared with 16 for PtCl_4^{2-} . On this

(16) J. A. Broomhead, F. Basolo, and R. G. Pearson, *ibid.*, **3**, 826 (1964).

(14) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964); C. H. Langford, *ibid.*, **4**, 265 (1965).

(15) Reference 4, p 124; R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, **4**, 433 (1965).

(17) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(18) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, pp 284, 288.

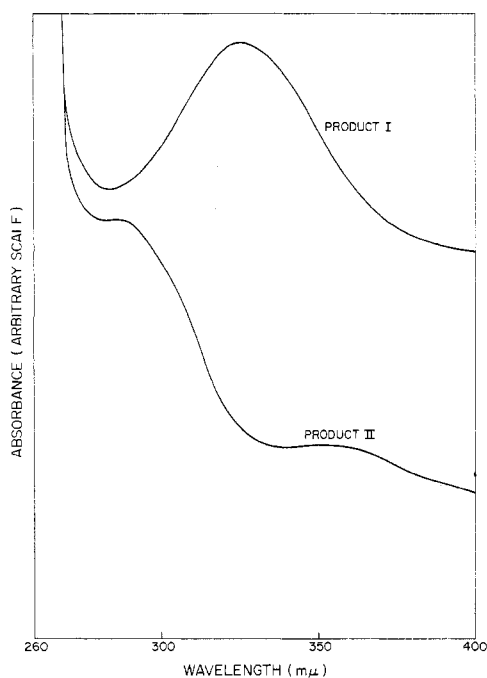


Figure 3.—Absorption spectra of products resulting from the reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]\text{PF}_6$ with NaN_3 : product I = $[\text{Au}(\text{N}_3)_4]^-$; product II = $[\text{Au}(\text{Et}_4\text{dien-H})(\text{N}_3)_2]$; see text.

basis one would have expected a larger activation energy for the reaction of the Au(III) complex compared with that of Pt(II). The results obtained are contrary to this and pose an anomaly that, at present, is not understood. The results could be explained if the Pt-Cl bond strength in this system were greater than that of Au-Cl. However, this is not in accord with the conclusion reached previously.⁶ Perhaps the reason for this anomaly is that water plays a greater role in the solvent-assisted dissociation of the Au(III) complex than it does in the reaction of the Pt(II) complex.

Reaction of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ with N_3^- .—The reaction between N_3^- and $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ produced two different products depending on the concentration of the azide ion and on the acidity of the reaction mixture. The spectra of these two products are shown in Figure 3. Product I is formed more readily, the higher the concentration of azide ion and/or the lower the pH of the solution. For example, a buffered solution at a pH of 6.3 containing 0.1 M N_3^- yields product I, whereas at 0.05 M N_3^- product II predominates. The absorption spectrum of product I is identical with that obtained by the addition of excess N_3^- to a solution of AuCl_4^- . Therefore, product I is assumed to be $[\text{Au}(\text{N}_3)_4]^-$. Reactions of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ that result in the formation of product I appear to involve the intermediate formation of product II.

No attempt has been made to isolate and characterize product II, because of the danger that the azide compound would explode. However, there is reason to suspect that the complex is $[\text{Au}(\text{Et}_4\text{dien-H})(\text{N}_3)_2]$, where the triamine behaves as a bidentate ligand. One reason is that this species represents the first step in the removal of the tridentate ligand to yield $[\text{Au}(\text{N}_3)_4]^-$,

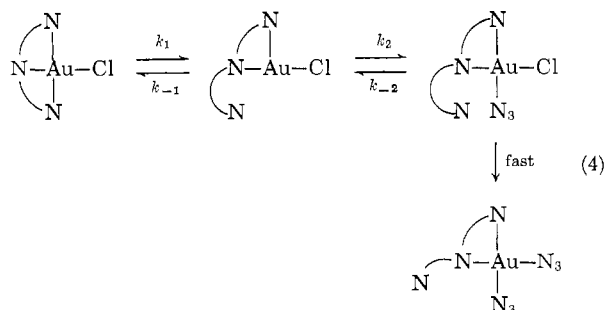
and spectral changes of such reaction mixtures show that product II is an intermediate in this process. Another reason is provided by the data in Table IV, which show that its rate of formation depends on the concentration of azide ion. Because of the steric hindrance in such systems, experiments show that the replacement of the monodentate ligand does not depend on the entering group. It is most unlikely that N_3^- would differ that much from Br^- , if the two were undergoing the same reaction with $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ of chloride ion replacement.

TABLE IV
RATE CONSTANTS AT 25° FOR THE REACTION^a
 $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+ + 2\text{N}_3^- \rightarrow [\text{Au}(\text{Et}_4\text{dien-H})(\text{N}_3)_2] + \text{Cl}^-$

$[\text{NaN}_3], M$	$k_{\text{obsd}} \times 10^4, \text{sec}^{-1}$
No inert salt added	
0.010	3.6 ^b
0.040	9.9 ^b
0.050	12 ^c
0.050	13 ^d
0.080	16 ^b
0.100	18 ^b
0.100	24 ^d
$\mu = 0.25$ with NaClO_4	
0.005	1.9
0.010	2.6
0.050	8.1
0.100	16
0.100	16 ^b
$\mu = 1.0$ with NaClO_4	
0.500	52
1.00	115

^a Concentration of $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+ = 2.5 \times 10^{-4} M$.
^b In pH 7.3 buffer. ^c In pH 6.3 buffer. ^d In pH 7.7 buffer.

The dependence of this reaction on the concentration of azide ion is readily explained on the basis of reaction 4. Since the chelate ring once opened can reclose with rate constant k_{-1} or react with azide ion, $k_2[\text{N}_3^-]$, it follows that the rate of formation of product must depend on the concentration of azide ion. This mechanism requires that at high concentrations of azide ion, where $k_2[\text{N}_3^-] \gg k_{-1}$, a limiting rate corresponding to k_1 be reached. The data in Table IV show that this



limiting rate was not reached at 1.0 M N_3^- . A plot of the k_{obsd} vs. $[\text{N}_3^-]$ is linear and has a nonzero intercept with a value of $1.5 \times 10^{-4} \text{sec}^{-1}$, in good agreement with the rate constant obtained for the reaction of the complex with Br^- or OH^- . Thus, this represents that portion of the reaction which proceeds by a dissociation

tion mechanism, k' in eq 7, without opening of the chelate ring. Applying the steady-state approximation to that portion of the reaction which proceeds by path 4, its rate constant $k_{(4)}$ can be represented by eq 5.

$$k_{(4)} = \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1} + k_2 [\text{N}_3^-]} \quad (5)$$

Under the experimental conditions used the reaction goes to completion and therefore k_{-2} is ignored. Also at these conditions the rate of reaction is first order in $[\text{N}_3^-]$, after correcting for k' , which means that $k_{-1} \gg k_2 [\text{N}_3^-]$. Because of this eq 5 simplifies to eq 6. This

$$k_{(4)} = \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1}} \quad (6)$$

means that the values of k_{obsd} in Table IV are related to the rate constants for the over-all reaction by eq 7.

$$k_{\text{obsd}} = k' + \frac{k_1 k_2 [\text{N}_3^-]}{k_{-1}} \quad (7)$$

Mechanisms of this type are fairly common for the removal of chelate ligands from metal complexes.¹⁹

(19) Reference 4, pp 154, 200; R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, **86**, 3983 (1964).

Furthermore, recent kinetic studies²⁰ show that the reaction of $[\text{Pd}(\text{dien})\text{Cl}]^+$ in acid solution containing chloride ion readily forms $[\text{Pd}(\text{dien})\text{Cl}_2]$ and then more slowly yields PdCl_4^{2-} . This result is analogous to the reaction sequence proposed here for the reaction between $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ and azide ion. Similar qualitative observations were made for the reaction with iodide ion and with thiocyanate ion. The reactions seem to proceed in two steps and to yield the corresponding AuX_4^- complex. That under similar conditions neither chloride nor bromide ions replace the triamine from the complex is because the chloro and bromo complexes of gold(III) are less stable than the analogous azido, iodo, and thiocyanato complexes.

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(20) A. J. Poë, private communication.

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Monohalide Displacements of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ in Dipolar Aprotic Solvents

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Kinetic data for monohalide displacement of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ with various nucleophiles in acetone and dimethyl sulfoxide are reported. From a comparison of these rate data with the rates of the corresponding reactions in methanol, it appears that the nucleophilic reactivity order remains the same regardless of the nature of the solvent. The reactivity order parallels the polarizability order of the entering groups. Saturated carbon substrates present a reverse reactivity order as well as a large shift of the reactivity of halide ions in going from protic to dipolar aprotic solvents, depending on the anion solvation. However, in the $\text{S}_\text{N}2$ reactions at soft centers, which generally enhance the polarizability of the nucleophiles, the nucleophilic order and the reactivity are practically unaffected when the solvent is changed. In accordance with the reagent solvation, the nucleophilic discrimination factor of *trans*- $[\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}_2]$ is greater in protic than in dipolar aprotic solvents.

Introduction

Most of the rate measurements on platinum(II) complexes refer to reactions in hydroxylic solvents such as methanol and water. In these solvents the order of reactivity of the entering groups is found to be the same for different Pt(II) substrates.^{1,2} In dipolar aprotic solvents, the only available data concern the chloride exchange of *trans*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$.³

(1) For a review and references see: (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964); (c) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(2) F. Basolo, "Mechanisms of Inorganic Reactions," Summer Symposium of Inorganic Chemistry of the American Chemical Society, Kansas, 1964, p 82.

(3) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

The most important factors recognized to influence the nucleophilic reactivity toward saturated carbon (for which a large amount of data is available) are the following: geometrical factors including steric hindrance⁴ or steric acceleration,⁵ ion aggregation,⁶ M basicity,⁷ M–Y bond strength,⁸ polarizability, and H basicity.⁹ Moreover, it has been recently pointed out

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