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Kinetics and Mechanisms of Reactions of Gold^{III} Complexes. IV. Substitution Reaction by Diethylenetriamine in Tetrachloroaurate(III)

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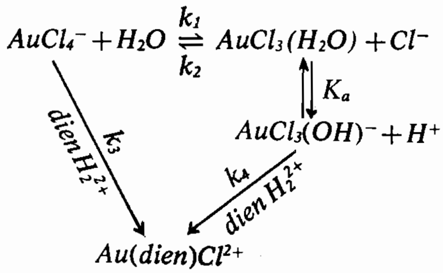
The reaction $AuCl_4^- + dien \rightarrow Au(dien)Cl^{2+} + 3Cl^-$ (dien = diethylenetriamine) in aqueous acid medium obeys the rate law

$$k_{obs} = \frac{k_3K'_a}{[H^+]} + \frac{k_1k_4K'_aK_a}{k_2[H^+]^2[Cl^-]}\ [dienH_3^{3+}],$$

derived from a consideration of the reaction scheme



where $dienH_3^{3+} \rightleftharpoons dienH_2^{2+} + H^+$ is the principle equilibrium between the amine species. The data were taken at various amine, hydrogen ions and chloride ion concentrations as well as different temperatures. The various rate constants at 25 °C have the values $k_3 = 7.3\ sec^{-1}\ M^{-1}$ and $k_4 = 1.2 \times 10^3\ sec^{-1}\ M^{-1}$. The activation parameters $\Delta H_3^* = 12.9$ kcal mol^{-1}, $\Delta H_4^* = 13.8$ kcal mol^{-1}, $\Delta S_3^* = -20.5$ e.u. and $\Delta S_4^* = +2$ e.u. were evaluated.

Introduction

The aqueous solution chemistry of gold(III) complexes is complicated by the presence of several solvolytic and acid-base equilibria[1] and the present study introduces the added feature of equilibrium between various protonated diethylenetriamine (dien) species. The marked paucity of detailed accounts of the reactions of gold(III) with polydentate ligands existing in the literature at present is to an extent being remedied by some recent work done in this laboratory[2] on the reaction of $AuCl_4^-$ with ethylenediamine and the work of Beran and Vlcek[3] on the similar system. The recent study by Teggins[4] on the reactions of $PtBr_4^{2-}$ with dien serves as a useful comparison for the study reported here.

This study has necessarily been confined to the pH region below 4.4 to ensure that the principle amine species present in solution were $dienH_3^{3+}$ and $dienH_2^{2+}$.[4] The system is shown to lend itself to selection of the principle reactions occurring and is characterised by a highly discriminative rate law. A second feature of the study is the presence of large amounts of free chloride[5] ions in the equilibrium reaction

$$AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3(H_2O) + Cl^-$$

even before the amine was allowed to react. The chloride concentration was expected to appear in the rate expression and was found to be invaluable in formulating the discussion that follows.

Experimental Section

$HAuCl_4$ solutions. The $HAuCl_4$ used was a Merck product. An approximately 10^{-3} *M* solution was made up in a 2 *M* NaCl (A.R. grade) medium to ensure that the principle gold species present were $AuCl_4^-$ and $AuCl_3(OH)^-$. The pH was adjusted with hydrochloric acid/sodium acetate buffer.

Buffer solutions were made according to the Tables given in the literature[6] from 1 *N* hydrochloric acid and 1 *N* sodium acetate.

Diethylenetriamine solutions. The diethylenetriamine used was a B.D.H. laboratory reagent, the purity of which was improved by distillation (boiling point 204-208°C),[7] crystallisation (as hydrochloride salt) in alcohol and recrystallisation in water-alcohol mixture. *Anal.* Calcd. for $C_4H_{16}N_3Cl_3$ C, 22.60; H, 7.59; N, 19.77. Found: C, 22.16; H, 7.34; N, 19.56. The

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[1] W. Robb, *Inorg. Chem.*, 6, 382 (1967).
[2] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 3, 29 (1969).
[3] P. Beran and A. A. Vlcek, Collection Czech. Chem. Commun., *24*, 3572 (1959).
[4] J. E. Teggins and T. S. Woods, *Inorg. Chem.*, 7, 1424 (1968).
[5] Usually the solvolysis released necleophile concentration is very low compared to that of the incoming group. CH. Lanford and H. B. Gray, « Ligand Substitution Processes », W. A. Benjamin, Inc., New York, 1965.
[6] A. I. Vogel, « Inorganic Analysis », Longmans, Green and Co., London, 1951, p. 869.
[7] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poë, *Inorg. Chem.*, 2, 921 (1963).

solution was buffered and made up in a 2 *M* NaCl medium as mentioned above.

pH Measurements were made with a Metrohm Model E300 pH meter.

Table I. 20°C μ = 2.2, 2.3 2 *M* NaCl

[dienH$_3^{3+}$] *M*	pH	k$_{obs}$ × 10^2 [a] sec^{-1}
0.067	3.9	17.8
0.05	3.9	15.2
0.04	3.9	11.3
0.0333	3.9	8.7
0.025	3.9	6.2
0.02	3.9	4.7
0.025	3.63	2.16
0.02	3.63	1.47
0.014	3.63	1.15
0.011	3.63	0.94
0.05	3.4	2.4
0.04	3.4	1.97
0.0333	3.4	1.71
0.025	3.4	1.18
0.02	3.4	0.9
0.067	2.9	1.44
0.05	2.9	0.85
0.04	2.9	0.64
0.0333	2.9	0.468
0.025	2.9	0.37
0.02	2.9	0.263
0.04	4.4	40.7
0.0333	4.4	30.0
0.025	4.4	24.5
0.02	4.4	17.3
0.067	3.77	10.7
0.06	3.77	10.1
0.05	3.77	8.1
0.04	3.77	6.3
0.0333	3.77	5.1
0.025	3.77	3.7
0.02	3.77	2.7
0.011	3.77	1.5
0.08	2.3	0.21
0.075	2.3	0.187
0.067	2.3	0.152
0.06	2.3	0.140
0.05	2.3	0.135
0.04	2.3	0.105
0.033	2.3	0.092
0.025	2.3	0.066
0.02	2.3	0.046
0.16	3.25	4.7
0.15	3.25	4.38
0.1333	3.25	3.56
0.12	3.25	3.46
0.1	3.25	2.95
0.08	3.25	2.16
0.0667	3.25	1.82
0.05	3.25	1.24
0.04	3.25	0.93
0.08	1.8	0.043
0.075	1.8	0.0372
0.0667	1.8	0.034
0.06	1.8	0.030
0.05	1.8	0.0257
0.04	1.8	0.0217
0.0333	1.8	0.0204
0.025	1.8	0.016
0.02	1.8	0.0107
0.05	4.1	26.1
0.04	4.1	22.7
0.0333	4.1	15.9
0.025	4.1	11.9
0.02	4.1	9.3

[a] Average of up to 10 values.

Kinetic experiments. The AuCl$_4^-$ and dien solutions were thermostated in a water-bath where temperatures were controlled to ±0.1°C. A measured aliquot of AuCl$_4^-$ solution was transferred to a cell housed in a constant temperature cell holder fitted to either a Cary 14 or 15 recording spectrophotometer. Working at a constant wave-length of 313 mμ, a measured amount of diethylenetriamine solution was injected or pipetted into the gold solution. The volume ratio of the two solutions was chosen so as to give the desired dien concentration. When an injection technique was used effective mixing was achived in not greater than 0.1 seconds, provided the volume ratio did not exceed 5:1. An excess of dien was used in order to achieve pseudo first-order conditions. A trace of the change in optical density with time was followed until no further change in optical density occurred whereupon the results were graphically analysed from plots of ln(OD$_t$–OD$_e$)[8] *vs.* time. The final spectrum was measured and compared with the published spectrum[7] of Au(dien)Cl^{2+}.

Results

Table I: k$_{obs}$ values measured at different [dien H$_3^{3+}$] and pH values.

Table II: The values measured for

$$\frac{k_3K'_a}{[H^+]} + \frac{k_1k_4K'_aK_a}{k_2[H^+]^2[Cl^-]} \qquad \text{(slope - equation (11))}$$

at different pH values.

Table III: Variation of slope (equation 11) with [Cl$^-$]. The slope is independent of ionic strength variation between 1.3 and 2.2.

Table IV: Slope values (equation 11) at different temperatures.

Table V: k$_3$ and k$_4$ values (equation 11) calculated from previous Tables, from which the activation parameters were calculated.

Table VI: Using k$_3$ and k$_4$ from Table V slope values were calculated at different pH values in order to draw up Figure 2.

Table II. 20 °C μ=2.2 2*M* NaCl.

pH	Slope sec^{-1} *M*$^{-1}$
3.9	2.784
3.63	0.85
3.4	0.49
2.9	0.16
4.4	9.37
3.77	1.596
2.3	0.025
3.25	0.28
1.8	0.0053
4.1	5.0

Table III. pH 3.6 20°C

[Cl$^-$] M	μ	Slope sec^{-1} *M*$^{-1}$
1.0	2.2	1.13
1.0	1.3	1.11
1.5	1.6	0.95
2.0	2.2	0.85

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(8) A. A. Forst and R. G. Pearson, « Kinetics and Mechanism », John Wiley and Sons, Inc., New York, N. Y., 1953.

Table IV.

pH	Temp. °C	μ	$[Cl^-], M$	Slope $sec^{-1} M^{-1}$
3.9	30	2.2	2	6.300
3.9	25	2.2	2	3.600
3.9	20	2.2	2	2.800
2.3	30	2.3	2	0.057
2.3	25	2.3	2	0.037
2.3	20	2.3	2	0.025

Table V.

	Temp. °C	k_3 $sec^{-1} M^{-1}$	k_4 $sec^{-1} M^{-1}$ 10^{-3}
From Table II	20	4.4	1.00
From Table III	20	6.0	0.76
From Table IV	25	7.3	1.20
From Table IV	30	11.1	2.00
E_a		13.5 kcal mol^{-1}	14.4 kcal mol^{-1}
ΔH^*		12.9 kcal mol^{-1}	13.8 kcal mol^{-1}
ΔS^*		—20.5 e.u.	+2 e.u.

Values used for constants in slope are:

$K_1 = 2.2 \times 10^{-2}$ }
$k_2 = 9.3$ } ref. 1
$K_a = 10^{-3}$ }
$K'_a = 2.45 \times 10^{-5}$ ref. 7

Table VI. 20°C $\mu = 2.2$ 2 M Cl^-

pH	Slope $sec^{-1} M^{-1}$ (calc.)
1.3	2.164×10^{-3}
1.7	5.444×10^{-3}
2.0	1.099×10^{-2}
2.3	2.242×10^{-2}
2.7	5.926×10^{-2}
3.0	1.292×10^{-1}
3.3	3.014×10^{-1}
3.7	1.0749
4.0	3.222
4.3	$1.0731 \times 10^{+1}$

Discussion

The main features of the results obtained in this study are

(i) the absence of a zero order dien path characteristic of solvent participation;

(ii) the apparent fractional order inverse hydrogen ion concentration dependence and;

(iii) the inverse Cl^- concentration dependence of the experimentally observed pseudo first-order rate constant.

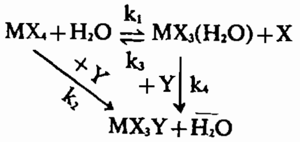
Before presenting a discussion and interpretation of these data, it is perhaps pertinent to the contents of this paper to examine the empirically established general rate law for substitution at a square planar molecule,[9] *viz.*

$$k_{obs} = k_s + k_y[Y] \qquad (1)$$

The equation applies to the general reaction

$$MX_4 + Y \rightarrow MX_3Y + X$$

where k_{obs} = pseudo first-order experimental rate constant; k_s = rate constant for solvent facilitated substitution by Y for X via the intermediate MX_3S; k_y = rate constant for direct substitution by Y for X. More specifically then, consider the reactions



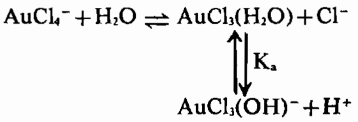
$k_4[Y]$ is considered to be much greater than $k_3[X]$ because usually to gain pseudo first-order experimental conditions $[Y] \gg [MX_4]$ and therefore $[Y] \gg [X]$. With this in mind it is a relatively simple matter to set up the differential equation, after making the usual steady-state assumptions regarding $[MX_3(H_2O)]$, describing $\frac{-d[MX_4]}{dt}$ which upon integration leads to the rate expression

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

Considering the ease in point, *viz.*

$$AuCl_4^- + dien \rightarrow \qquad (2)$$

it is necessary to take cognizance of several reactions that are known to occur in aqueous acid solutions containing $AuCl_4^-$. These are



$$\begin{array}{c} AuCl_4^- + H_2O \rightleftharpoons AuCl_3(H_2O) + Cl^- \\ \quad\quad\quad\quad\quad\quad\quad \updownarrow K_a \\ \quad\quad\quad\quad\quad\quad\quad AuCl_3(OH)^- + H^+ \end{array} \qquad (3)$$

and subsequent hydrolysis reactions of the chloro gold(III) complexes.[1] We chose to work at chloride ion concentration of 2 M and pH less than 4.4 at which value the principle species present are $AuCl_4^-$, $AuCl_3(H_2O)$ and $AuCl_3(OH)^-$ in the ratios of $1:10^{-3}: :10^{-2}$ at 25°C. At these pH values the principle amine species[10] present are $dienH_3^{3+}$ and $dienH_2^{2+}$. Under these conditions, knowing the value for k_1 and k_2[1], it can be calculated that the equilibration half-time for reaction (3) is considerably smaller than the observed half-time of reaction of dien[11] with $AuCl_4$ (eq. 2).

The distinct absence of a dien concentration independent path could indicate that the reaction measured was a direct substitution of chloride ligands in only $AuCl_4^-$, a result that is not imprecedented in Pt^{II} complex reaction studies.[12] The hydrogen ion concentra-

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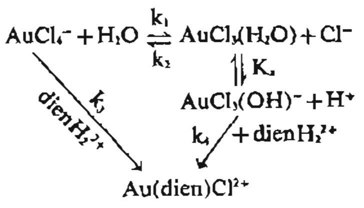
[9] F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reactions, » second edition, John Wiley and Sons. Inc., New York, N. Y., 1965.

[10] $[dienH_3^{3+}]:[dienH_2^{2+}] = 1.585:1$ (using values for pK_1 from ref. 7) at pH 4.4, and 4.070:1 at pH 2.

[11] At the highest concentration of $dienH_3^{3+}$ (0.4 M) and highest pH (4.4) the value for $t_{1/2} = 1.7$ sec. cf. to $t_{1/2} = 0.85$ sec. for equilibrium (eq. 3) at pH 4.3 and 2 M NaCl.

[12] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, *79*, 4055 (1957).

tion dependence of the reaction showed that the slope of the $[\text{dienH}_3^{3+}]$ *vs.* k_{obs} plot varied by more than a factor of 10, inversely, for each pH unit of change in experimental conditions. This fact could be accounted for if one considers in addition the likelihood of dienH^+ entering into the reaction even though it is present in very small amounts. The clear-cut inverse dependence of the slope of the plot of $[\text{dienH}_3^{3+}]$ *vs.* k_{obs} on the chloride ion concentration leads inevitably to the following mechanism;



Working under conditions of pH from 4.3 down to 1.8 and 2 *M* Cl^- the equilibria from $AuCl_4^-$ through $AuCl_3(H_2O)$ to $AuCl_3(OH)^-$ are rapidly established and continuously maintained throughout the course of the reaction.

It is possible to write the equation for the reaction as

$$\frac{d[\text{Au(dien)Cl}^{2+}]}{dt} = k_3[\text{AuCl}_4^-][\text{dienH}_2^{2+}] + k_4[\text{AuCl}_3(\text{OH})^-][\text{dienH}_2^{2+}] \tag{4}$$

$$= k_3[\text{AuCl}_4^-]\frac{K'_a}{[\text{H}^+]}[\text{dienH}_3^{3+}] + \frac{k_4k_1[\text{AuCl}_4^-]K_aK'_a[\text{dienH}_3^{3+}]}{k_2[\text{H}^+]^2[\text{Cl}^-]} \tag{5}$$

because

$$[\text{AuCl}_3(\text{OH})^-] = \frac{k_1K_a[\text{AuCl}_4^-]}{k_2[\text{H}^+][\text{Cl}^-]} \tag{6}$$

using the equilibrium relationships

$$K_a = \frac{[\text{AuCl}_3(\text{OH})^-][\text{H}^+]}{[\text{AuCl}_3(\text{H}_2\text{O})]} \tag{7}$$

$$k_1/k_2 = \frac{[\text{AuCl}_3(\text{H}_2\text{O})][\text{Cl}^-]}{[\text{AuCl}_4^-]} \tag{8}$$

and

$$K'_a = \frac{[\text{dienH}_2^{2+}][\text{H}^+]}{[\text{dienH}_3^{3+}]} \tag{9}$$

On the basis of the assumption that the system exists in a rapidly maintained equilibrium condition we can write

$$\frac{-d[\text{AuCl}_4^-]}{dt} = \frac{d[\text{Au(dien)Cl}^{2+}]}{dt} \tag{10}$$

and without further approximation integrate to the form

$$k_{obs} = \left[\frac{k_3K'_a}{[\text{H}^+]} + \frac{k_1k_4K'_aK_a}{k_2[\text{H}^+]^2[\text{Cl}^-]}\right][\text{dienH}_3^{3+}] \tag{11}$$

Equation 11 predicts that a plot of k_{obs} *vs* $[\text{dienH}_3^{3+}]$ should have a slope but no intercept (Figure 1). The values of the slopes of these plots, at constant $[Cl^-]$, plotted against the different values of $\frac{1}{[H^+]}$ should be non-linear, and are, as depicted by Figure 2. By utilising values for k_1, k_2, K_a, K'_a, k_{obs}, $[H^+]$ and $[Cl^-]$ for each set of experiments, values for k_3 and k_4, *viz.* 4.4 M^{-1} sec^{-1} and 1.0×10^3 M^{-1} sec^{-1} at 20°C were obtained from a non-linear least-squares curve fitting calculation done on the IBM 360 facility of the C.S.I.R.

A confirmatory set of values for the rate constants k_3 and k_4 were then obtained from those data taken at different Cl^- concentrations given in Table III, *i.e.*

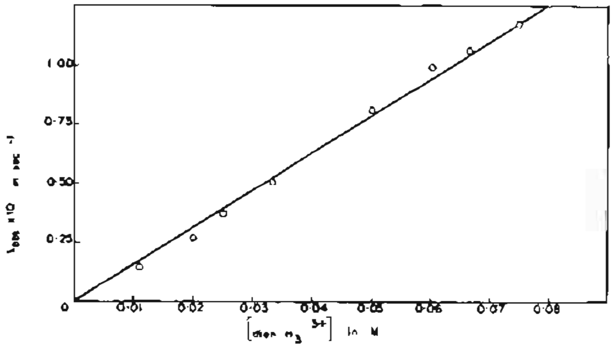


Figure 1. A typical plot of k_{obs} *vs.* $[\text{dienH}_3^{3+}]$

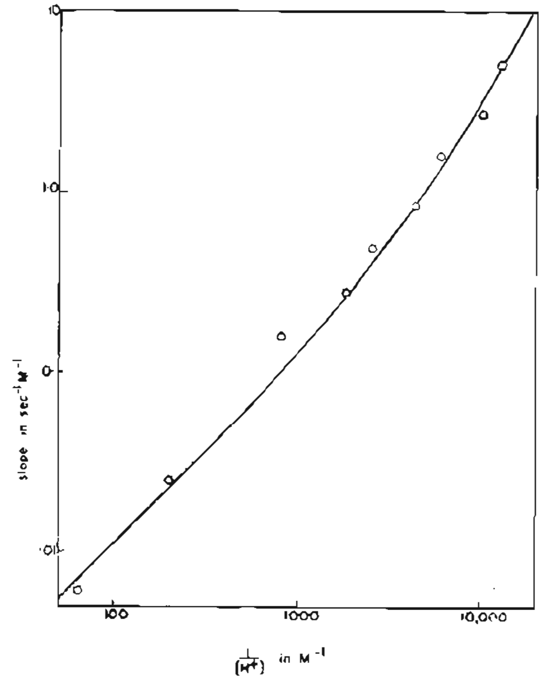


Figure 2. Deviation of experimental slope (equation 11) values at different pH values from calculated curve.

working at fixed $[H^+]$ and one of three $[Cl^-]$ whilst plotting k_{obs} *vs.* $[dienH_3^{3+}]$. Figure 3 shows the plot of the slopes *vs.* $\frac{1}{[Cl^-]}$. The values for the rate constants given in Table V show that fairly good agreement in values was obtained between the two methods of evaluating the rate constants k_3 and k_4 with the results from Table II being the more reliable.

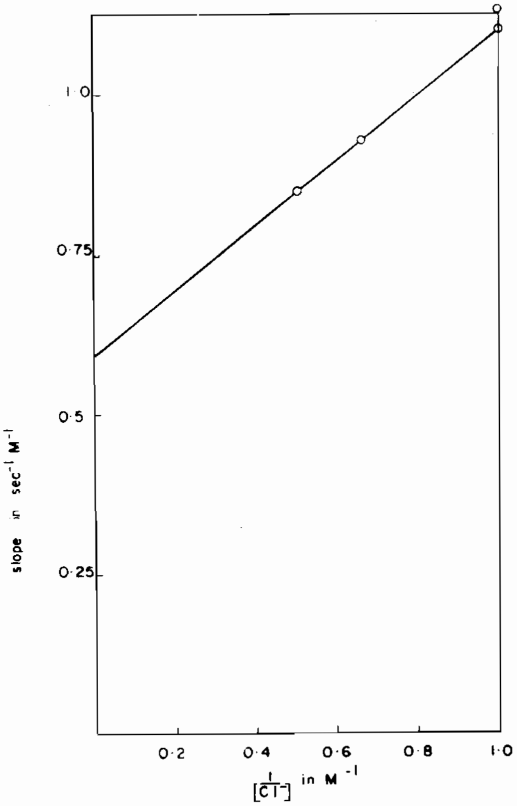
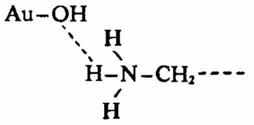


Figure 3. Plot of slope (equation 11) *vs.* $\frac{1}{[Cl^-]}$.

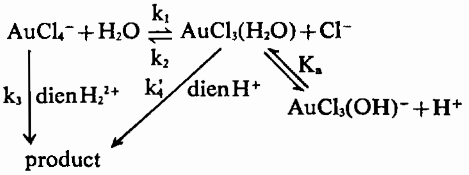
Some rather interesting differences are noted to exist between the results of this study and that of Teggins[4] *et al.* on the $PtBr_4^{2-} + dien \rightarrow$ reaction. They have considered the attack of dien, dien H^+ and H_2^{2+} on only $PtBr_4^{2-}$. The present study was confined to a lower pH range where dien and dien H^+ were not present to any extent. Interestingly, the results of Teggins *et al.* did show that the concentration of $PtBr_3(H_2O)^-$ species was varied with no effect on the rate of reaction. In the light of the present results it would seem that the extreme reactivity of $dienH_2^{2+}$ with the $AuCl_3(OH)^-$ as compared to $AuCl_4^-$ points to hydrogen bonding as a preliminary to activation as follows



whereupon water is expelled and the metal-nitrogen bond is formed. It has already been pointed and that the OH^- is a bad leaving group[13,14] for gold(III) complexes and hence in this way it is H_2O that becomes the leaving group. The kinetic rate expression does not allow for $AuCl_3(H_2O)$ to be the substrate describing the k_4 path because of the $\frac{1}{[H^+]^2}$ term.[15]

Although $dienH^+$ is present in very small amounts, the species cannot be excluded from the reaction mechanism. As already said $dienH^+$ is expected to be a better nucleophile than $dienH_2^{2+}$. In addition H_2O is a much better leaving group than OH^-. This might imply that the reaction $AuCl_3(H_2O) + dienH^+$ would be more likely to occur than the reaction $AuCl_3(OH^-) + dienH_2^{2+}$.

Bearing this in mind the mechanism will be:



The kinetic rate expression for this scheme is:

$$k_{obs} = \left[\frac{k_3 K'_a}{[H^+]} + \frac{k'_4 k_1 K'_a K''_a}{k_2 [H^+]^2 [Cl^-]} \right] [dienH_3^{3+}] \qquad (12)$$

where

$$K''_a = \frac{[dien\,H^+][H^+]}{[dien\,H_2^{2+}]} = 6.2 \times 10^{-10}$$ [7]

This rate expression is identical to equation 11, except that $k_4 K_a$ in the second term of equation 11 is replaced by $k'_4 K''_a$. The calculated value for k'_4 is 1.2×10^{10} $sec^{-1} M^{-1}$ which gives a ratio of $k_4 : k'_4 \simeq 1:10$.[7] Teggins *et al.*[4] found that the $dienH^+$ species is about 5 times more reactive than the $dienH_2^{2+}$ species. In the above mentioned mechanism there is a difference of a factor of 10^7 between the two species, which seems highly improbable, and so too is the extremely high rate constant $k'_4 = .2 \times 10^{10}$ sec^{-1} M^{-1} for a substitution reaction in an Au^{III} complex.

No doubt the rate law discussed in this paper should have a different form at pH values higher than 4.4, due to further hydrolyses of the chloro gold(III) complexes and also the presence of the less protonated dien ligands.

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(13) Reference 5, p. 34.
(14) Reference 9, p. 384.
(15) If dien H_2^{2+} reacts with $AuCl_3(H_2O)$ instead of $AuCl_3(OH)^-$ the differential equation integrates to the form:

$$k_{obs} = \left[\frac{k_3 K'_a}{[H^+]} + \frac{k_4 k_1 K'_a}{[H^+] k_2 [Cl^-]} \right] [dien\,H_3^{3+}].$$