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An Investigation into the Mechanisms of the Substitution Reactions by Ethylenediamine and Diethylenetriamine in Tetrachlorogold(III)

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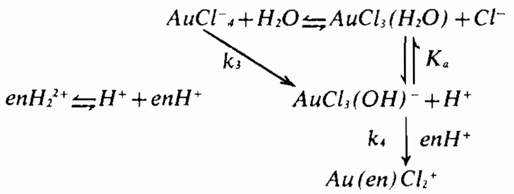
It is shown that the reaction

$$AuCl_4^- + enH^+ \rightarrow$$

(en = ethylenediamine) in aqueous acid medium obeys the same rate law as the reaction with the diethylenetriamine ligand viz.

$$k_{obs} = \left\{ \frac{k_3K_a'}{[H^+]} + \frac{k_4k_1K_aK_a'}{k_2[Cl^-][H^+]^2} \right\} [enH_2^{2+}]$$

which is derived from the reaction scheme



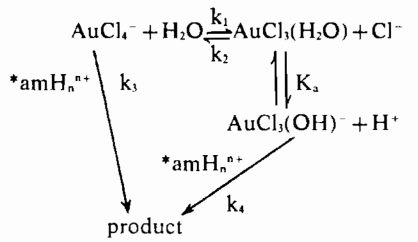
Introduction

This laboratory reported the reaction of ethylenediamine and tetrachlorogold(III) in acid buffered medium.[1] On the basis of the data that were available a rate law of the form

$$k_{obs} = \frac{kK_a'[enH_2^{2+}]}{[H^+]} \tag{1}$$

was established and the results were interpreted in terms of a mechanism involving the reaction of $AuCl_3(OH)^-$ and enH^+.

A subsequent more detailed study of the reaction between $AuCl_4^-$ and diethylenetriamine (dien) led to what we believe to be a complete description of the events that occur when an unsubstituted polyamine reacts with the gold(III) substrate.[2] These were presented in reference 2 as being



(2)

The rate law conforming to this scheme, and established by experimentation, is;

$$k_{obs} = \left\{ \frac{k_3K_a'}{[H^+]} + \frac{k_4k_1K_aK_a'}{[H^+]^2[Cl^-]k_2} \right\} [amH_n^{n+}]$$

It would appear that our report on the reaction between ethylenediamine and the gold(III) substrate overlooked the other term in the general equation,[3] and made the wrong assignment for the reactive gold (III) substrate. This paper reports the complete study and makes some further observations in the comparison of en and dien as chelating ligands.

Experimental Section

The experimental conditions were exactly the same as previously described[1], except that the ethylenediamine solutions were 0.1 – 2.0*M* with respect to the chloride ion concentration, and the ionic strength made up to 2.3 by sodium perchlorate.

Results

The results of the experiments reported here will show that the term $\frac{1}{[H^+]^2[Cl^-]}$, in equation 3 does in fact manifest itself at low chloride ion concentrations, when the first reaction of ethylenediamine with the gold(III) substrate is considered. Thus, it is shown in Tables I and II that a tenfold decrease in the chloride ion concentration leads to an experimental rate law of the form

$$k_{obs} = \left(\frac{k}{[H^+]} + \frac{k'}{[H^+]^2[Cl^-]} \right) [amH_n^{n+}] \tag{3}$$

(*) $K'_a = amH_{n+1}^{+(n+1)} \overset{K'_a}{\rightleftharpoons} amH_n^{n+} + H^+$.

(1) W.J. Louw and W. Robb, *Inorg. Chim. Acta*, 3, 29 (1969).

(2) W.J. Louw and W. Robb, *Inorg. Chim. Acta*, 3, 303 (1969).

(3) The Chemical Society, Special Publication No. 6, "Stability Constants. Part 1: Organic Ligands." Metcalfe and Copper Ltd., London, p. 5 (1957) (K_a value at 25°C and 1*M* KNO_3).

Considering the reaction scheme to be the same as that postulated for the diethylenetriamine system, it is possible to evaluate the constants k_3 and k_4 of equation 3. The values of k_1 and k_2 as well as K_a were taken from reference 5. The results are given in Table III.

Table I(a). k_{obs} values for the reaction $AuCl_4^- + enH^+ \longrightarrow$ at pH 4.3, $\mu = 2.3$, 25°C, and $0.2M[Cl]$.

$[enH_2^{2+}] \times 10^2$ M	$t_{1/2}$ sec	$k_{obs} \times 10^2$ sec^{-1}
6.6	23	3.0
6.0	26	2.62
5.0	35	1.98
4.0	43	1.61
3.3	55	1.27
2.5	70	0.99
2.0	93	0.77

Table I(b). k_{obs} values for the reaction $AuCl_4^- + enH^+ \longrightarrow$ at pH 4.3 $\mu = 2.3$, 25°C, and $0.5M[Cl^-]$.

$[enH_2^{2+}] \times 10^2$ M	$t_{1/2}$ sec	$k_{obs} \times 10^2$ sec^{-1}
1.0	202	0.34
2.0	102	0.68
3.0	68	1.02
4.0	51	1.36
5.0	41	1.70

Table II. Slopes (eq. 2) dependence on $[Cl^-]$ at 25°C, $\mu = 2.3$ and pH 4.3

$[Cl^-]$ in M	Slope in $M^{-1}sec^{-1}$
2.0[a]	0.31
1.0[a]	0.32
0.5	0.34
0.3[a]	0.366
0.2	0.40
0.15[a]	0.43
0.10[a]	0.50

[a] Full tables of values for k_{obs} *vs.* $[Cl^-]$ are omitted for the sake of brevity.

Table III. k_3 and k_4 values (eq. 2) at 25°C.

	k_3 in $M^{-1}sec^{-1}$	k_4 in $M^{-1}sec^{-1}$
From rate law 1	473[a]	—
From rate law 2	460	676
Rate constants for dien[2]	4.3	1200

[a] k_1 in eq. 1 (equivalent to k_3 in eq. 2)

Discussion

These additional data serve to illustrate that the general mechanism proposed for the complex formation reaction of the terdendate ligand, diethylenetriamine[2], with the chlorogold(III) substrate is equally pertinent to the ethylenediamine reaction with the same substrate. This means that the previously reported second-order rate constant for reaction of ethylenediamine[1], which has a value of 473 M^{-1} sec^{-1} must correspond to the rate constant k_3 in the general scheme given in equation 3. The constant was measured at high chloride ion concentrations *i.e.* $2M$ and thus caused the second term in equation 3 to be rather small *i.e.* $\frac{k_3K'_a}{[H^+]} \gg \frac{k_4k_1K_aK'_a}{[H^+]^2[Cl^-]k_2}$ and therefore resulting in a rate expression given in equation 1. The results given in Table III show that the rate constant, k_3 value is in very good agreement with the earlier reported value.

Using the values for k_3 and k_4 reported here form the extended study it is easily shown that at pH 4.3 and $[Cl^-] = 2M$ the term containing k_4 contributes a mere 3% of the observed reaction rate. A tenfold decrease in the chloride ion concentration at the same pH increases the contribution from this term to 25% of the total and hence it becomes kinetically detectable. The reason for the immediately obvious form of the exxperimental rate law in the case of diethylenetriamine is simply found when one compares the values of K'_a, the first deprotonation constants, of ethylenediamine[3] and diethylenetriamine[4] *viz.*, $3.3 \times 10^{-8}M$ and $2.5 \times 10^{-5}M$, respectively, and also the relative magnitudes of k_3 and k_4. Thus both terms are detectable over a wide range of chloride ion concentrations and pH values.

Table III also gives the rate constants previously reported for the dien system and will be used in the discussion that follows. There is a striking difference in k_3 values for the two polyamines yet the k_4 values for the two polyamines yet the k_1 values differ only by factor of two. Linear free-energy relationships have been drawn up for the reactions of $AuCl_4^-$ with various pyridine bases in methanol[6] according to the Bronsted equation

$$\log k = \alpha pK_a + \text{constant}$$

α (0.15) was taken as a measure of the discriminating ability of $AuCl_4^-$. A similar LFER is found for the reaction between $AuCl_4^-$ and methyl substituted ethylenediamines in water[7] with a α value of 1.5. Viewing the k_3 values for en and dien in this fashion a value of $\alpha = 0.5$ in water was computed. This value for α would imply that $AuCl_4^-$ has lost some of its discriminatory powers when reacting with primary amines having vastly differing pK_a values as compared to the substituted ethylenediamines. Since linear free-energy relationships can only be expected if no steric effects are operating it would appear that the small α value arises from the likelihood that it is the centre nitrogen of dien, which is really a secondary amine, that is the first to bond to the gold in going to the five-coordinated intermediate. Of the several arguments that lead to he conclusion that it is the centre nitrogen that deprotonates first in $dienH_3^{3+}$ *viz.*: (i) electrostatic repulsion by protons on the nitrogens, (ii) increased solvation of terminal nitrogens stabilizing the

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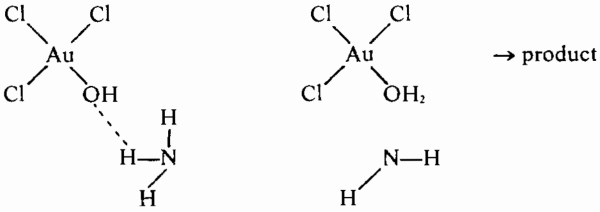
(4) W.H. Baddley, F. Basolo, H.B. Gray, C. Nölting and A.J. Poë, *Inorg. Chem.*, *2*, 921 (1963).
(5) W. Robb, *Inorg. Chem.*, *6*, 382 (1967).
(6) L. Cattalini, M. Nicolini and A. Orio, *Inorg. Chem.*, *5*, 1674 (1966).
(7) To be published.

charge and (iii) a steric effect encouraging deprotonation, it is the latter that provides an explanation for the $\alpha = 0.5$ value.

A glance at the relative values of k_4, *i.e.* the reaction of the amines with $AuCl_3(OH)^-$ substrate raises the question of why only a factor of two differences occurs between enH^+ and $dienH_2^{2+}$ in their reactivity. A reasonably simple explanation is forthcoming if one considers the protonated nitrogen to attach itself via a hydrogen bond to the OH group on the gold leading then to the formation of water, a good leaving grup as compared to hydroxide, and the metal nitrogen bond[2] as shown below:



A statistical factor 2 would neatly explain the difference between $K_4(enH^+) = 676\,M^{-1}\,sec^{-1}$ and $k_4(dienH_2^{2+}) = 1200\,M^{-1}\,sec^{-1}$.