Kinetics and Mechanism of Reactions of Gold(III) Complexes. VI. Substitution Reactions by Methyl Substituted Diethylenetriamines in Tetrachlorogold(III)

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The reaction $AuCl_4^- + am \rightarrow AuCl(am)^{2+} + 3Cl^-$ where $am = 1,1,4$-trimethyldiethylenetriamine in aqueous acid medium obeys the rate law

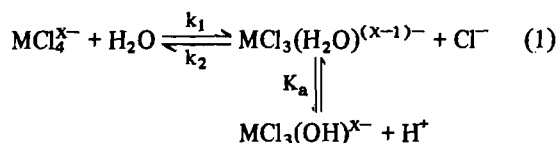$$k_{obsd} = \left[\frac{k}{[H^+]} + \frac{k'}{[H^+]^2[Cl^-]}\right][amH_3^{3+}]$$

where k and k' are constants. When $am = 1,1,7,7$-tetramethyldiethylenetriamine or $1,1,4,7,7$-pentamethyldiethylenetriamine the rate law changes to

$$k_{obsd} = \left[\frac{k''[Cl^-]}{[H^+]} + \frac{k'''}{[H^+]^2}\right][amH_3^{3+}]$$

where k'' and k''' are constants. Ion pair formation between the latter protonated amines and chloride ions not only explains the change in the rate laws mentioned above but also the observation of an "extra" chloride ion term in the rate laws for the displacement of chelated amines by Cl^- from four-coordinate d^8 complexes.

Introduction

The substitution reactions of tetrachlorogold(III) [1] and tetrachloropalladium(II) [2] in aqueous solutions are normally studied in the presence of relatively high concentrations of chloride and hydrogen ions in order to prevent hydrolyses of these complexes [3]. The principle species present in solution under these conditions are:

$$MCl_4^{x-} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MCl_3(H_2O)^{(x-1)-} + Cl^- \quad (1)$$

$$\Big\Vert K_a$$

$$MCl_3(OH)^{x-} + H^+$$

(For M = Pd, x = 2 and M = Au, x = 1)

For M = Pd $K_a \sim 10^{-7}$ [4] and the deprotonation step can be deleted. Studies on the reactions of chelating nucleophiles like ethylenediamine (en) or

diethylenetriamine (dien) with tetrachlorogold(III) [1] showed that the rate determining step was the entering of the first nitrogen, with the ring closing step(s) being fast. The rate law found for this type of system is:

$$k_{obsd} = \left[\frac{k}{[H^+]} + \frac{k'}{[Cl^-][H^+]^z}\right][amH_n^{n+}] \quad (2)$$

(For am = en, n = 2; am = dien, n = 3; M = Pd, z = 1; M = Au, z = 2).

However, as soon as the chelates become heavily sterically strained by methylation of the nitrogens [1], the [Cl⁻] term migrates to above the line of the first term in equation 3:

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

This phenomena has been explained in terms of ion pair formation between $amH_{\{n-1\}}^{\{n-1\}+}$ and Cl^- [1, 2].

It is very interesting to note that in the studies on dechelation of chelated Au^{III} [5] and Pd^{II} [6] complexes by HCl and "extra" [Cl⁻] term was found in the rate laws and in one case this was attributed to an ion pair formation of the type $[Cl_4Pd-N-NH^+\cdot Cl^-]^{2-}$ [6].

The aim of this study is to determine whether the methylsubstituted diethylenetriamines also react as ion pairs with $AuCl_4^-$ and to attempt to rationalise all of the above data in terms of one mechanism.

Experimental

The materials and solutions were prepared and purified as previously described [1]. In addition the same kinetic procedure was followed. The pK_a values for the substituted diethylenetriamines listed in Table I were obtained by titrating the hydrochloride salts of the amines used with a 0.1N NaOH aqueous solution.

TABLE I. pK$_a$ Values of Tridentate Amines in Aqueous Solution at 25 °C and μ = 0.1.

| Ligand	pK$_{a1}$	pK$_{a2}$
en[b]	7.1	9.9
dien[c]	4.6	–
tri-dien[a]	~4.0	9.0
tetra-dien	3.3	9.0
penta-dien	~2.5	9.0

[a]Values estimated.   [b]Reference 1(a).   [c]Reference 1(b).

TABLE II. Slope Values (k$_{obsd}$ vs. [amH$_3^{3+}$], Equation 7 and 8) for the Reaction 4 at 25 °C, μ = 1.0 M.

pH	[Cl$^-$], M	Slope (equations 7 and 8), s^{-1} M^{-1}
am = Tri-dien		
3.0	1.0	0.125
3.5	1.0	0.32
3.8	1.0	0.5
4.3	1.0	1.5
4.0	1.0	0.725
4.0	0.8	1.43
4.0	0.5	2.00
4.0	0.2	5.00
am = Tetra-dien		
2.4	1.0	0.2
2.8	1.0	0.525
2.92	1.0	0.61
2.95	1.0	0.73
3.15	1.0	1.2
3.4	0.5	1.9
3.4	1.0	2.5
3.4	1.5	3.29
3.54	1.0	5.0
4.0	1.0	40.0
4.3	1.0	95.0
4.5	1.0	280.0
am = Penta-dien		
2.8	1.0	0.18
3.1	1.0	0.46
3.4	1.0	0.8
3.4	0.2	0.24
3.7	1.0	1.46

Results and Discussion

All the methylsubstituted diethylenetriamine ligand substitution reactions studied

$$AuCl_4^- + am \rightarrow AuCl(am)^{2+} + 3Cl^- \tag{4}$$
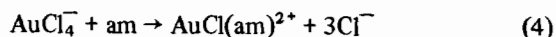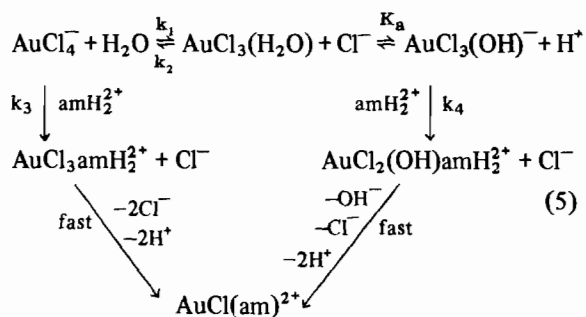
(am = 1,1,4-trimethyldiethylenetriamine (tri-dien),

TABLE III. Rate and Equilibrium Constants[a] for Reaction 4 at 25 °C and μ = 1.0 M.

am	k$_3'$	k$_4' \times 10^{-2}$	Data Source
Tri-dien	0.7	–	slope vs. $\dfrac{1}{[H^+]}$
	0.35	0.4	slope vs. $\dfrac{1}{[Cl^-]}$
Tetra-dien	1.6	–	slope vs. $\dfrac{1}{[H^+]}$
	1.1	1.5	slope vs. [Cl$^-$]
	–	2.0	slope [H$^+$] vs. $\dfrac{1}{[H^+]}$
Penta-dien	0.1	–	slope vs. $\dfrac{1}{[H^+]}$
	0.09	0.2	slope vs. [Cl$^-$]

[a]For am = tri-dien, k$_3'$ = k$_3$ s^{-1} M^{-1} and k$_4'$ = k$_4$ s^{-1} M^{-1}. For am = tetra-dien or penta-dien, k$_3'$ = k$_3$K$_{ip}$ s^{-1} M^{-2} and k$_4'$ = k$_4$K$_{ip}$ s^{-1} M^{-2}.

1,1,7,7-tetramethyldiethylenetriamine (tetra-dien) and 1,1,4,7,7-pentamethyldiethylenetriamine (penta-dien)) showed only one reaction. A linear dependence of k$_{obs}$ on [am], with no intercept was observed in all cases. The values of these slopes at different H$^+$ and Cl$^-$ concentrations are given in Table II, from which it is clear that a greater than first order inverse dependence on [H$^+$] exists.

For am = tri-dien an inverse [Cl$^-$] dependence was found similar to the en and dien systems [1a, b, d, 2a] (equation 2). As has been shown previously, this can be accommodated by the reaction scheme;

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

$$k_3 \downarrow amH_2^{2+} \qquad\qquad amH_2^{2+} \downarrow k_4$$

$$AuCl_3amH_2^{2+} + Cl^- \qquad\qquad AuCl_2(OH)amH_2^{2+} + Cl^-$$

$$fast \diagdown \begin{matrix} -2Cl^- \\ -2H^+ \end{matrix} \qquad \begin{matrix} -OH^- \\ -Cl^- \end{matrix} fast \qquad (5)$$

$$-2H^+$$

$$AuCl(am)^{2+}$$

where the principle amine species present in solution at pH < 4 are controlled by the equilibrium:

$$amH_3^{3+} \overset{K_{a1}}{\rightleftharpoons} amH_2^{2+} + H^+ \tag{6}$$
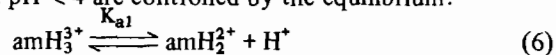
The rate law derived from reaction scheme 5 is

$$k_{obsd} = \left[\frac{k_3 K_{a1}}{[H^+]} + \frac{k_4 k_1 K_a K_{a1}}{k_2 [H^+]^2 [Cl^-]}\right][amH_3^{3+}] \tag{7}$$

TABLE IV. Average Rate Constants[b] for Reaction 4 at 25 °C, $\mu = 1.0\ M$.

Ligand	k_3'	k_4'	pK_{a1}
en	466	676	7.1[a]
MED	110	9000	7.07[a]
DMED(symm)	126	970	7.11[a]
DMED(asymm)	52	1596	6.55[a]
tri-MED	24	600	6.43[a]
TMED	5.6	114	5.92[a]
dien	7.3	1200	4.61[a]
tri-dien	5.3	40	~4.0
tetra-dien	1.4	150	3.3
penta-dien	0.1	20	~2.5

MED = N-methylethylenediamine
DMED(symm) = N,N'-dimethylethylenediamine
DMED(asymm) = N,N-dimethylethylenediamine
tri-MED = N,N,N'-trimethylethylenediamine
TMED = N,N,N',N'-tetramethylethylenediamine

[a]Reference 1c. [b]For en, dien and tri-dien, $k_3' = k_3\ s^{-1}\ M^{-1}$, $k_1' = k_4\ s^{-1}\ M^{-1}$. For MED, DMED(symm), DMED-(asymm), tri-MED, TMED, tetra-dien and penta-dien, $k_3' = k_3 K_{ip}\ s^{-1}\ M^{-2}$, $k_4' = k_4 K_{ip}\ s^{-1}\ M^{-2}$.

Values calculated for k_3 and k_4 using equation 7 (all the other constants are known) appear in Table III.

For am = tetra-dien or penta-dien a direct [Cl⁻] dependence similar to the methylsubstituted ethylenediamine systems [1c, 2b] was found. This has previously been explained by the amines reacting as ion pairs [1, 2],

$$amH_2^{2+} + Cl^- \underset{\longleftarrow}{\overset{K_{ip}}{\longrightarrow}} amH_2^{2+} \cdot Cl^-$$
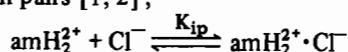
the rate law 7 therefore changing to

$$k_{obsd} = \left[\frac{k_3 K_{a1} K_{ip}[Cl^-]}{[H^+]} + \frac{k_4 k_1 K_a K_{a1} K_{ip}}{k_2[H^+]^2} \right] [amH_3^{3+}] \quad (8)$$

The $k_3 K_{ip}$ and $k_4\ K_{ip}$ values calculated on the basis of equation 8 are also given in Table III. The average rate constants for all the substituted ethylenediamines [1] and diethylenetriamines [1] as well as their pK_a values are listed in Table IV.

The one big question arising here is whether the lowest or highest methylated nitrogen deprotonates first in the amH_n^{n+} species (en, n = 2; dien, n = 3). Previously [1c] it was argued that on the basis of comparing the order of basicity of monodentate amines with the order of the pK_{a1} values of the substituted ethylenediamines, the lower substituted nitrogens looses its proton first. On steric grounds, one therefore expects the reactivities of the methyl-substituted ethylenediamines to be MED ~ DMED-(asymm) > DMED(symm) ~ tri-MED > TMED which is more of less the case (see Table IV). It must howev-

er be kept in mind that these rate constants incorporates K_{ip} values which may vary drastically and therefore leave these comparisons worthless.
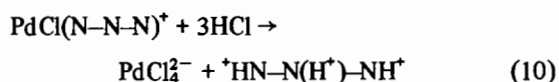
In changing from en to dien the question of which nitrogen deprotonates and therefore binds first with Au(III) becomes more difficult. Assuming that the lowest methylated nitrogen deprotonates first, the reactivities of dien and tri-dien (methylated in the 1,1,4 positions) would be more or less the same provided that the unmethylated nitrogen in tri-dien deprotonates first. It is evident that this is more or less the case for k_3, but not for k_4. It may once again [1c] be due to the fact that hydrogen bonding between the oxygen of $AuCl_3(OH)^-$ and a hydrogen on one of the ammonium groups, results in deprotonation of this ammonium group followed by substitution of water (a much better leaving group than OH^-) by the resultant deprotonated amine group. This will mean that the methylated nitrogen participates in the bond formation step for am = tri-dien and therefore a drastic decrease in reactivity from dien to tri-dien results.

In going from tetra-dien to penta-dien a more than ten fold drop in reactivity was found as is shown by the $k_3\ K_{ip}$ and $k_4\ K_{ip}$ values. This implies that the central nitrogen of tetra-dienH_3^{3+} and penta-dienH_3^{3+} deprotonates first and is therefore the first nitrogen to bond, if the K_{ip} values for the two amines are more or less the same.

The answer to the ion pair formation behaviour of the substituted ethylenediamines and diethylene-triamines will most probably also have to be found in hydrogen bonding. In these long chain ligands it can be envisaged that the orientation of the chain may be very important and alignment may have to be such that the unprotonated nitrogen must be directed towards the empty p_z orbital perpendicular to the plane of the complex in order to achieve bonding. If however hydrogen bonding between a hydrogen of an ammonium group and the negative charge on the metal is formed, the orientation of the chelate group may be very unfavourable for nucleophilic attack of the unprotonated nitrogen. Ion pair formation between this ammonium group of the chelate and a free chloride ion may now have the effect of neutralising the one end of the long amine chain and therefore enables favourable orientation for a nucleophilic attack of the unprotonated nitrogen. If however the least methylated nitrogen of the chelate amine deprotonates first, then one would not expect a difference in behaviour between en and MED or DMED(asymm) as has been found, unless ion pair formation is encouraged with methylation of the nitrogens. It is known that spherical symmetry encourages ion pair formation. On the other hand, if the highest methylated nitrogen deprotonates first, the reactivity of this nitrogen may be so drastically reduced that ion pair formation with a free chloride ion is needed

in order to facilitate the reaction. The fact that only N,N,N′,N′-tetramethylethylenediamine of all the N- and N′-methylsubstituted ethylenediamines reacts as an ion pair towards palladiumtetrachloride, may be due to the fact that palladium(II) is much more reactive than gold(III) and therefore only the most sterically strained chelate needs activation from ion pair formation. This is however once again in support of the least methylated nitrogen being the first to deprotonate, otherwise N,N,N′-trimethylethylenediamine and N,N-dimethylethylenediamine should also react as ion pairs towards palladiumtetrachloride.

Poë and Vaughan [6] studied the reverse of the above reactions:

$$PdCl_2(N{-}N) + 2HCl \rightarrow PdCl_4^{2-} + {}^+HN{-}NH^+ \qquad (9)$$

$$PdCl(N{-}N{-}N)^+ + 3HCl \rightarrow$$
$$PdCl_4^{2-} + {}^+HN{-}N(H^+){-}NH^+ \qquad (10)$$

(N–N = en; N–N–N = dien, Et_4 dien)

These reactions proceed in two steps, both of which were studied kinetically for N–N = en, while only the second step could be followed for reaction (10). They found the rate of the first step to be directly dependent on [Cl⁻] while the [H⁺] dependence was limiting. The second step was found to be first order in both [H⁺] and [Cl⁻] at high acid concentrations, whereas a greater than first order dependence on [Cl⁻] was found at low [H⁺]. These observations were rationalized as follows:

FIRST STEP


$$(11)$$

SECOND STEP

$$(12)$$
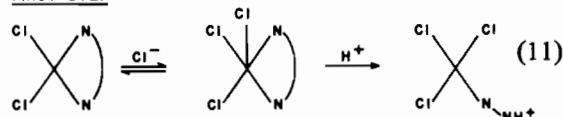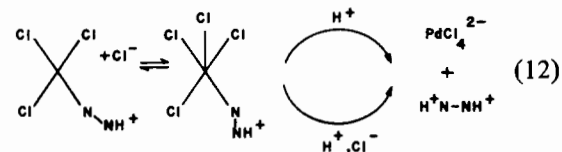
The mechanism thus proceeds via the formation of a five-coordinate intermediate, followed by an electrophilic attack by a hydrogen ion on the coordinated nitrogen. For the second step there is, however, an additional path needed in order to incorporate an additional chloride ion. It is very interesting that it was suggested that hydrogen bonding to a free chloride ion could occur so as to form an ion pair of the type $[Cl_4Pd{-}N{-}NH^+{\cdot}Cl^-]^{2-}$ which might be more susceptable to electrophilic attack by a hydrogen ion at the coordinated nitrogen atom. For N–N = 2,2′-bipyridyl (bipy) and central metal ion = Au [5] only one reaction step was observed with the empirical rate law being

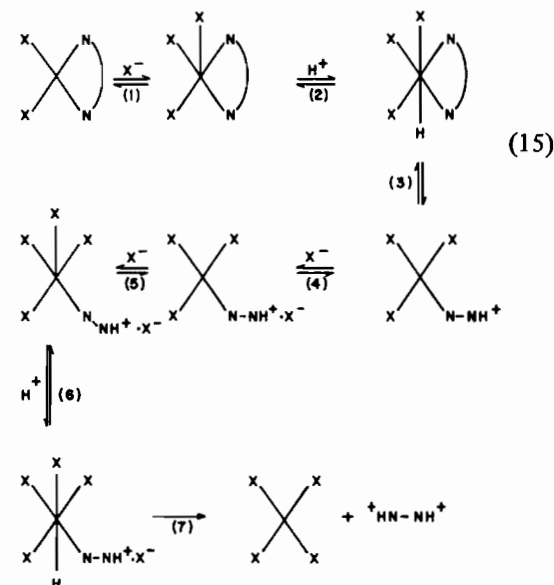$$k_{obsd} = k[X] + k'[H^+][X] + k''[H^+][X]^3 \qquad (13)$$

(X = Cl, Br)

The proposed reaction scheme was

$$(14)$$
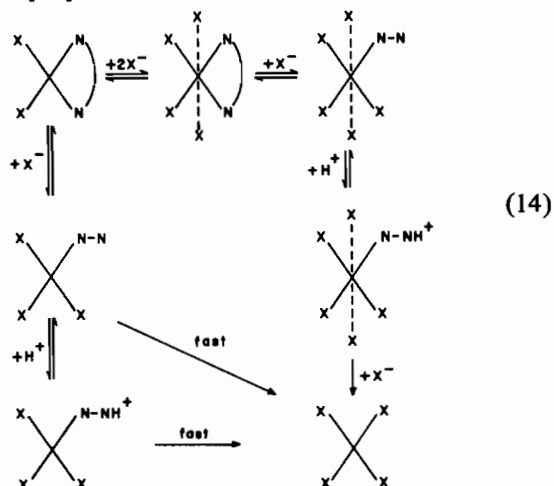
With the present knowledge of oxidative addition reactions it is most probably easier to explain the above dechelation results for reactions 11 and 12 as follows:

$$(15)$$

If the species inbetween step 1 and 2 is in steady state while step 3 is the rate determining step, it will explain the direct [Cl⁻] and limiting [H⁺] dependence found for the first step. Steps 4 to 7 can accommodate the greater than first order dependence on [Cl⁻] and direct [H⁺] dependence. Steps 2 and 6 are oxidative addition reactions while steps 3 and 7 are reductive elimination. The species inbetween these steps are therefore Pd^{IV}. Reaction sequence 15 combined in one detectable reaction step with steps 6

and 7 being fast, is also in agreement with the k'' [H⁺][Cl⁻]³ term in empirical rate law 13. This however implies that Au^V intermediate species are involved, which is not very likely. A more suitable reaction scheme is the following:
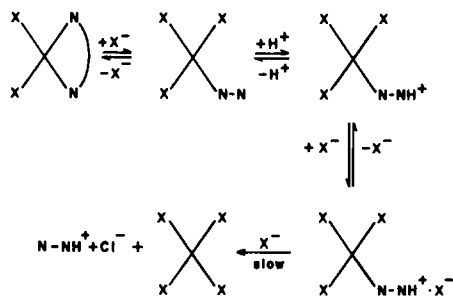
The "extra" [Cl⁻] term can thus be accounted for by introducing ion pair formation. The reason why ion pair formation is needed in these cases may once again be due to the fact that hydrogen bonding plays a very important role in the reactivity of these long chain ligands. Therefore once the one nitrogen is dislodged from the complex and protonated, this proton may form a hydrogen bond with a coordinated halide. It may thus be very difficult to replace the second (and third) nitrogen due to this "chelate" effect. Once the protonated nitrogen is "neutralized" by ion pair formation with a free chloride, the chelate ligand is more easily replaced. Hydrogen bonding and ion pair formation therefore seems to play an important role in both chelation and dechelation reactions of metal complexes.

References

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