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Kinetics and Mechanisms of Reactions of Gold(III) Complexes. V. Substitution Reactions by Methyl Substituted Ethylenediamines in Tetrachloroaurate(III)

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The reaction,

$$AuCl_4^- + am \rightarrow AuCl_2am^+ + 2Cl^-$$

where am = xN, yN′–(x+y)methylethylenediamine (x = 1, 2; y = 0, 1, 2) in aqueous acid medium obeys the rate law

$$k_{obs} = \left[\frac{k\,[Cl^-]}{[H^+]} + \frac{k'}{[H^+]^2}\right][amH_2^{2+}]$$

where k and k′ are constants. The formation of ion pairs between the protonated amines and chloride ion is considered as a possibility for explaining this rate law.

Data were taken at different amine, hydrogen, and chloride ion concentrations and temperatures.

Introduction

This paper reports further results obtained in the study of complex formation between various polyamines and tetrachloroaurate(III) and its hydrolysis products.[1,2,3] A series of N- and N,N′-methyl substituted ethylenediamines were used in the study, viz., N-methylethylenediamine (MED), N,N′-dimethylethylenediamine (DMED symm.), N,N-dimethylethylenediamine (DMED asymm.), N,N,N′-trimethylethylenediamine (tri-MED) and N,N,N′,N′-tetramethylethylenediamine (TMED).

Some remarkable differences were observed in the rate law pertaining to these data as compared to the previously published report on the reaction between diethylenetriamine (dien) and tetrachloroaurate(III).[2] It was reported that for the reaction,

$$AuCl_4^- + dienH_2^{2+} \rightarrow$$

in acetate buffered medium, a rate law of the form

$$k_{obs} = \left[\frac{k}{[H^+]} + \frac{k'}{[H^+]^2\,[Cl^-]}\right][dienH_3^{3+}]$$

accounted for all observations and a mechanistic scheme was put forward in which the principle reactions were between $AuCl_4^-$, its hydrolysis product $AuCl_3(OH)^-$, and $dienH_2^{2+}$. This rate law has now been shown to be applicable to ethylenediamine (en) as well,[3] but when N-alkyl substituted ethylenediamines are used the rate law is changed to the form

$$k_{obs} = \left[\frac{k\,[Cl^-]}{[H^+]} + \frac{k'}{[H^+]^2}\right][amH_2^{2+}]$$

This latter form of the rate law holds for all of the five N- and N,N′-alkyl substituted ethylenediamine ligands used in the complex formation studies. Furthermore, we have also observed such a change to take place in the rate law when the central metal atom featured is palladium(II).[4]

Experimental

Preparation and Purification of Materials and Solutions

The amines used were Koch-Light laboratory products, the purity of which was improved by crystallization of the hydrochloride salt from ethanolic solutions. The salts were recrystallized from water and analysed for C, H and N content. These salts were used to make up the amine reaction solutions which were buffered by acetic acid/acetate and made up to a specified sodium chloride ion concentration.

The preparation of the buffered $HAuCl_4$ solutions, the pH measurements and kinetic experiments were done in the same manner as previously described.[1,2]

Conductance Experiments

All the conductance measurements were recorded on a YSI model 31 conductivity bridge (cell No. 3402, cell constant 0.1).

The chloride ion concentration in the pure sodium chloride plot (Figure 3) was obtained by continuously diluting 2*M* and 0.1*M* sodium chloride solutions by half. Two different sodium chloride concentration solutions were used to obtain one plot because of the relatively big error arising after five dilutions.

The sodium chloride concentration in the presence of 0.1*M* en and TMED with or without 0.2*M* acetic acid, were obtained by adding small amounts of sodium chloride to the amine solutions. The conductance of the pure amine solutions were subtracted from the values obtained with sodium chloride present, thus the effective conductance due to free sodium chloride is calculated.

pK_a *Measurements*[5]

0.1*M* am·2HCl solutions were titrated with 0.1*N* NaOH solutions on a Radiometer pH meter 25, Titrator II.

Results

In the reactions

$AuCl_4^- + am \rightarrow$

only the least sterically hindered amine used viz. MED, was found to coordinate two molecules to the gold complex. However, the optical density change of the second step was very small, hence resulting in inaccurate values which are not reported here.

TABLE I. $[H^+]$ Dependence of slope k_m (equation 1) at 25° C, μ = 2.3 and 2*M* NaCl.

Ligand	pH	Slope in M^{-1} sec^{-1}
N-methylethylenediamine	4.22	0.800
	3.40	0.080
	3.27	0.057
	2.92	0.025
	3.50	0.105
	4.00	0.400
N,N-dimethylethylenediamine	2.25	6.10×10^{-3}
	3.15	5.30×10^{-2}
	4.37	1.26
	4.65	3.00
	3.88	0.34
N,N′-dimethylethylenediamine	3.35	4.60×10^{-2}
	4.76	1.80
	2.77	1.06×10^{-2}
	5.05	4.30
	4.50	0.86
	4.07	0.28
N,N,N′-trimethylethylenediamine	4.00	0.27
	4.53	1.06
	4.58	1.27
	3.46	0.07
	4.36	0.64
N,N,N′,N′-tetramethylethylenediamine	4.70	0.756
	4.00	0.149

All of the polydentate ligand substitution reactions showed a linear relationship between k_{obs} and [am], which yielded no intercept.

$$k_{obs} = k_m[am]; \qquad [H^+], [Cl^-] \text{ constant} \qquad (1)$$

From Tables I and II, the slope of equation 1, k_m, has a functional dependence on $[H^+]$ and $[Cl^-]$ which can be formulated as

$$k_m = \frac{C_1}{[H^+]} + \frac{C_2}{[H^+]^2}; \qquad [Cl^-] \text{ constant} \qquad (2)$$

and

$$k_m = C_3 + C_4[Cl^-]; \qquad [H^+] \text{ constant} \qquad (3)$$

respectively.

TABLE II. $[Cl^-]$ and temperature dependence of slope k_m, (equation 1) at μ = 2.3.

Ligand	pH	Temp. °C	$[Cl^-]$ in *M*	Slope in M^{-1} sec^{-1}
N-methyl en	4.0	20	0.2	0.112
	4.0	25	0.2	0.176
	4.0	30	0.2	0.250
	4.0	20	2.0	0.266
	4.0	25	2.0	0.400
	4.0	30	2.0	0.570
N,N-dimethyl en	2.25	30	2.0	9.4×10^{-5}
	2.25	25	2.0	6.1×10^{-3}
	2.25	20	2.0	3.8×10^{-3}
	3.88	30	2.0	0.5
	3.88	25	2.0	0.34
	3.88	20	2.0	0.21
	2.25	25	0.2	3.84×10^{-3}
N,N′-dimethyl en	4.07	30	2.0	0.432
	4.07	25	2.0	0.276
	4.07	20	2.0	0.166
	4.55	25	0.2	0.33
	4.53	25	1.5	0.71
	4.55	25	1.0	0.56
	4.5	25	2.0	0.86
	4.76	20	2.0	1.1
	3.35	25	2.0	.046
	3.35	30	2.0	.073
N,N,N′-trimethyl en	4.0	30	2.0	0.3
	4.0	25	2.0	0.214
	4.0	20	2.0	0.128
	4.0	25	0.2	0.093
	4.0	20	0.2	0.062
	4.0	30	0.2	0.14
N,N,N′,N′-tetramethyl en	4.7	20	2.0	0.52
	4.7	25	2.0	0.756
	4.7	30	2.0	1.0
	4.0	30	0.2	0.072
	4.0	25	0.2	0.044
	4.0	20	0.2	0.029
	4.0	25	2.0	0.149

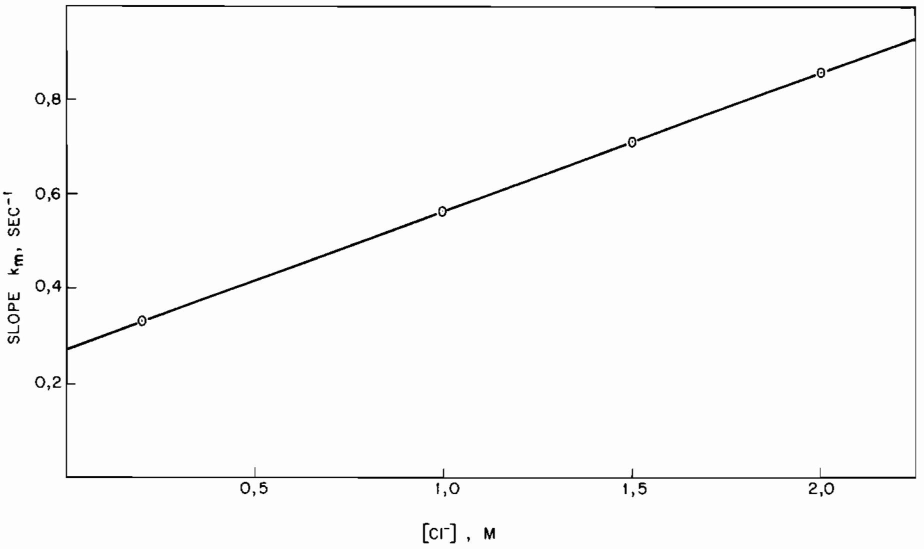


Figure 1. [Cl$^-$] dependence of the slope k_m, (equation 1) with DMED (symm.) as ligand.

The contribution of the $C_2/[H^+]^2$ term in equation 2 is very small in the pH range in which the data were taken. Unfortunately the reactions become immeasurably fast at the higher pH values where this term will dominate the overall equation. However, the curvature away from linearity at the higher pH values suggests that the pH dependence is the same as found for ethylenediamine[1,3] and diethylenetriamine.[2] Because of a favourable pK_a value in the latter case, the $C_2/[H^+]^2$ term is prominent at a relative low pH value.

The reaction rate also becomes immeasurably fast as the pH is increased much sooner than is expected for a linear pH relationship.

Exactly the same behaviour was found for the ethylenediamine reaction and therefore the quadratical inverse hydrogen ion concentration dependence was overlooked[3] in the initial study.[1]

Figure 1 shows the [Cl$^-$] dependence of the slope, k_m, with DMED (symm) as ligand.

The combination of equations 2 and 3 with 1 leads to an expression that accommodates all of the experimental data and is given by equation 4.

$$k_{obs} = \left[\frac{k\,[Cl^-]}{[H^+]} + \frac{k'}{[H^+]^2}\right][amH_2^{2+}] \qquad (4)$$

Table III lists the rate constants and activation parameters. The rate constants $k_3' = (k_3\,K_{ip})$ and $k_4' = (k_4\,K_{ip})$ are incorporated into k and k′ respectively, and are simply calculated from these values as described in the discussion.

This rate law was further confirmed by the independent calculation of k and k′ from the [H$^+$] and [Cl$^-$]

TABLE III. Rate constants and activation parameters for the reaction $AuCl_4^- + am \rightarrow$.

	Temp. °C	k_3' M^{-1} sec^{-1} [a] × 10^{-2}	k_4' M^{-1} sec^{-1} [b] × 10^{-3}
N-methylethylenediamine			
From Table I	25	0.7	10.4
From Table II	25	1.47	7.5
From Table II	20	1.01	6.39
From Table II	30	2.12	9.33
E_a kcal mol^{-1}		13.1	6.9
ΔH^* kcal mol^{-1}		12.5	6.3
ΔS^* eu		–7.7	–20
ΔF^* kcal mol^{-1}		14.8	12.2
N,N-dimethylethylenediamine			
From Table I	25	0.696	0.937
From Table II	25	0.250	1.71
From Table II	25	0.604	2.14
From Table II	20	0.379	1.67
From Table II	30	0.929	2.35
E_a kcal mol^{-1}		17.8	6.0
ΔH^* kcal mol^{-1}		17.2	5.4
ΔS^* eu		+8.7	–25
ΔF^* kcal mol^{-1}		15	13
N,N′-dimethylethylenediamine			
From Table I	25	1.46	0.77
From Table II	25	1.07	1.17
From Table II	20	0.83	0.8
From Table II	25	1.27	1.7
From Table II	30	2.04	2.11

[a] $k_3' = k_3\,K_{ip}$. [b] $k_4' = k_4\,K_{ip}$.

TABLE III (Cont.)

	Temp. °C	k_3' M^{-1} sec^{-1} [a] × 10^{-2}	k_4' M^{-1} sec^{-1} [b] × 10^{-3}
E_a kcal mol^{-1}		15.6	16.9
ΔH^* kcal mol^{-1}		15.0	16.3
ΔS^* eu		+1.3	+11
ΔF^* kcal mol^{-1}		14.6	13
N,N,N′-trimethylethylenediamine			
From Table I	25	0.29	0.344
From Table II	25	0.23	0.854
From Table II	20	0.098	0.846
From Table II	25	0.18	0.91
From Table II	30	0.24	1.2
E_a kcal mol^{-1}		15.8	6.8
ΔH^* kcal mol^{-1}		15.2	6.2
ΔS^* eu		−2	−24
ΔF^* kcal mol^{-1}		15.7	13.4
N,N,N′,N′-tetramethylethylenediamine			
From slope vs. 1/[H$^+$] graph	25	0.062	–
From slope vs. [Cl$^-$] graph	25	0.044	0.106
From slope vs. 1/[H$^+$] graph	30	0.0829	0.18
From slope vs. 1/[H$^+$] graph	25	0.0627	0.123
From slope vs. 1/[H$^+$] graph	20	0.0432	0.093
From slope x[H$^+$] vs. [Cl$^-$] graph	30	0.059	–
From slope x[H$^+$] vs. [Cl$^-$] graph	25	0.049	–
From slope x[H$^+$] vs. [Cl$^-$] graph	20	0.035	–
E_a kcal mol^{-1}		11.3	11.3
ΔH^* kcal mol^{-1}		10.7	10.7
ΔS^* eu		−19	−13
ΔF^* kcal mol^{-1}		16.4	14.6

[a] $k_3' = k_3 K_{ip}$. [b] $k_4' = k_4 K_{ip}$.

data (equations 2 and 3). The two sets of values obtained agreed within experimental error.

If one looks at the rate constants presented in Table III, it is clear that the experimental error is relatively big. This is due to the small contribution of the second term in equation 2 as stated above.

The dependence of the observed rate constant on the [am] and [H$^+$] is exactly the same as that found for the reactions of the gold(III) substrates with en and dien.[2,3] There is, however, a surprising difference in [Cl$^-$] dependence, since this was found to be indirect with the latter ligands. The rate law had the form given by equation 5.

$$k_{obs} = \left[\frac{k''}{[H^+]} + \frac{k'''}{[H^+]^2[Cl^-]}\right][amH_n^{\,n+}] \qquad (5)$$

TABLE IV. pK_a values of 0.1*M* am·2HCl solutions and pH values of 0.05*M* am·2HCl solutions at 25° C.

Ligand	pH (calc.)	pH (measured)	pK_{a1}	pK_{a2}
dien	–	–	4.61[9]	–
en	4.05	4.2	7.10	9.92
MED	4.04	4.05	7.07	10.04
DMED (symm)	4.05	4.12	7.11	10.03
DMED (asymm)	–	–	6.55	9.65
tri-MED	–	–	6.43	9.78
TMED	3.46	3.43	5.92	9.17

TABLE V. Slope values of Λ vs. $\sqrt{[Cl^-]}$ graphs.

	Slope ohms^{-1} cm^2 M^{-1}
NaCl	59
NaCl + en (pH 11.3)	59
NaCl + TMED (pH 10.8)	59
NaCl + en + HAc	40
NaCl + TMED + HAc	33
NaCl + en·2HCl	56
NaCl + TMED·2HCl	40

In order to account for the change in the role of the [Cl$^-$], the possibility of ion pair formation between Cl$^-$ and amH_2^{2+} was studied by testing the validity of the Onsager equation with respect to a NaCl solution in the presence and absence of the amines.

$$\Lambda = \alpha\Lambda_0 - \alpha^{3/2}(A + B\Lambda_0)\sqrt{C} \qquad (6)$$

Λ = equivalent conductance
Λ_0 = equivalent conductance at infinite dilution
A and B = constants
C = concentration
α = degree of dissociation

The results are shown in Figures 2 and 3, and the slope values are listed in Table V.

Since the pK_a values of the am·2HCl ligands were needed a 0.1*M* solution of the hydrochloride salt of the amines was titrated with 0.1*N* NaOH.[5] The pK_a values are listed in Table IV, together with pH values of some 0.05*M* am·2HCl aqueous solutions.

Discussion

Comparison of the two rate laws, 4 and 5, draws attention to the fact that Equation 4 can be transformed to 5 by multiplying the slope, k_m, by [Cl$^-$]. Practically, this effect can be seen as a chloride ion participation in the rate determining step of the reaction mechanism, either coupled to the complex or to the ligand. Since it is assumed that no change in mechanism occurs in going

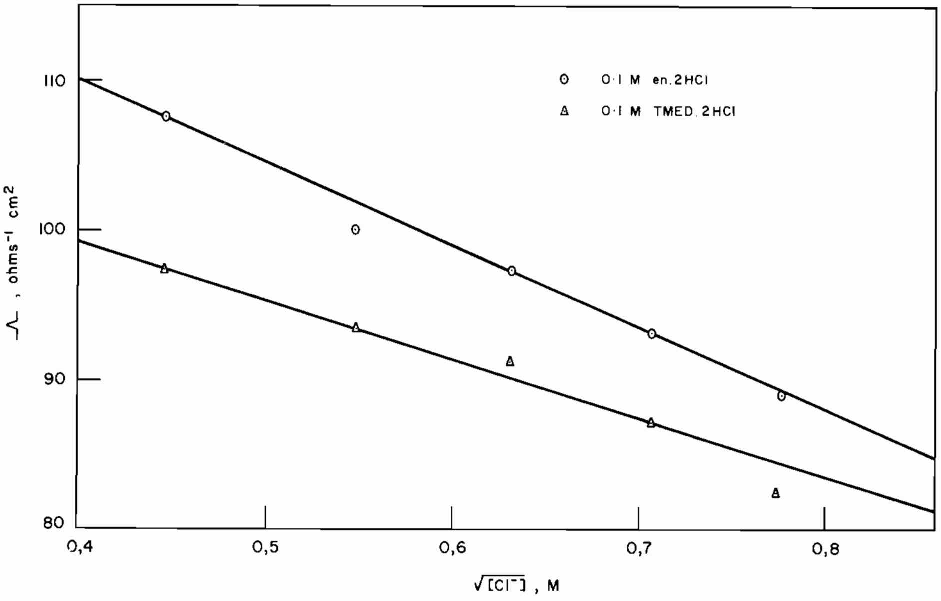


Figure 2. $\sqrt{[\mathrm{Cl}^-]}$ dependence of the equivalent conductance of 0.1*M* en·2HCl and TMED·2HCl aqueous solutions.

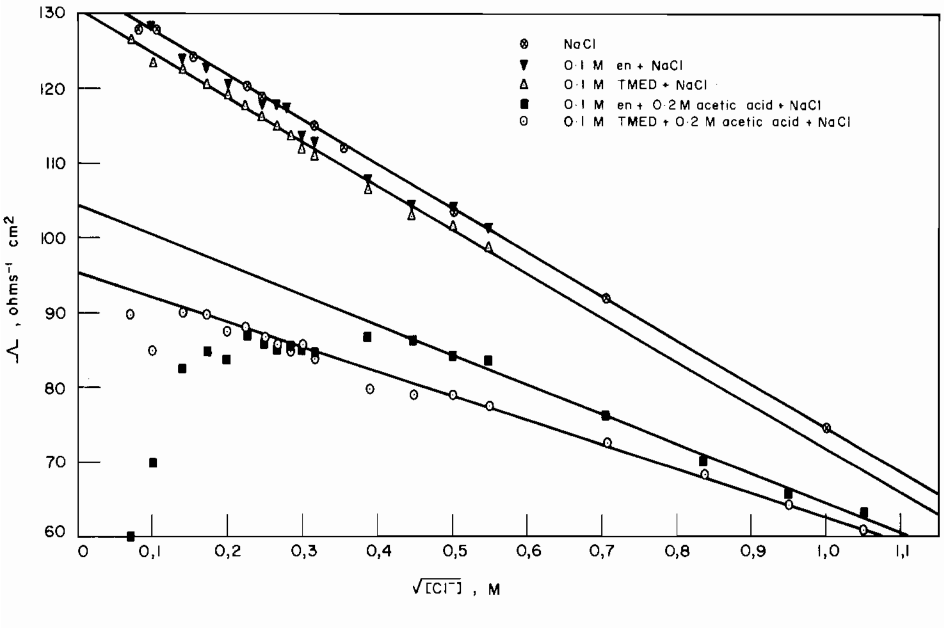


Figure 3. $\sqrt{[\mathrm{Cl}^-]}$ dependence of the equivalent conductance of an aqueous NaCl solution with protonated or unprotonated amines present and absent.

from en or dien to the N-alkyl substituted amines, the role of the chloride ion needed further explanation.

Two possibilities spring to mind in seeking an explanation and must be viewed as the chloride ion associating with the complex substrate or with the chelating diamine. Either of these eventualities would produce the desired transformation in the rate law.

Because no shift in the 313 nm peak of $AuCl_4^-$ occurred when raising the chloride ion concentration of the solution, the second possibility, namely ion pair formation between amH_2^{2+} and Cl^- presented itself as a likely explanation of events.

It is therefore worth while spending some time discussing the aqueous solution chemistry of the bidentate amines. Firstly the difference in pK_{a1} and pK_{a2} values and the effect of methylation on the pK_a values warrant some comment. The pK_{a2} values are about in line with those of primary amines[6] and can thus be considered as a true indication of the softness of this nitrogen. However, the pK_{a1} values are unusually low. This is most probably due to the electrostatic repulsion in the doubly charged molecule.

It is well known that the order of basicity of monodentate amines is $NH_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$ because of the mutual opposition of inductive and steric effects. The same order is found in the pK_{a2} values of en, MED and DMED (asymm.), while the respective pK_{a1} values follow the order en >MED >DMED (asymm.). This points to the unsubstituted end of the amine chain as being the first nitrogen to lose its proton, very likely because of steric influence from the substituted side in this molecule. It may thus be generally accepted that the lower substituted nitrogen loses its proton first.

The fact that the equivalent conductance of TMED $\cdot$ 2HCl is lower than that of en $\cdot$ 2HCl (Figure 2) regardless of the much lower pH of the former solution (Table IV) is very promising as far as ion-pair formation at the substituted amines is concerned. Figure 3 shows that there is practically no difference in the slope (Table V) and intercept of the NaCl plots in both the absence and presence of unprotonated amines, but the slope value drops drastically when NaCl is in the presence of protonated amines. This, as well as the initial curve in the latter plots is expected when ion pair formation occurs, since α (Equation 6) is a variable which is much more sensitive to $[Cl^-]$ change in the lower $[Cl^-]$ region. Both these factors suggest that ion pair formation favours TMED more and generally favours the more heavily substituted amine.

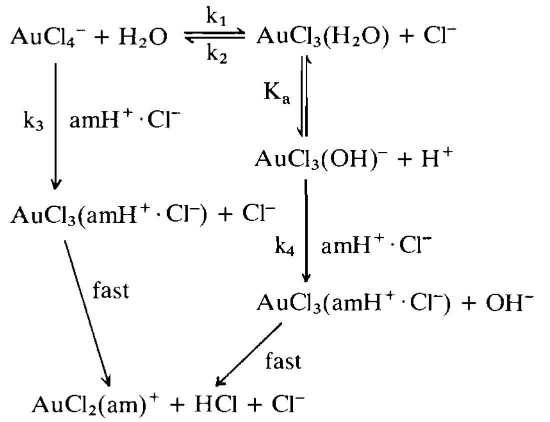
If the above mentioned ion pair is brought in as the only change from the reaction scheme proposed for the reactions between $AuCl_4^-$ and en or dien,[1,2,3] the equilibrium

$$amH^+ + Cl^- \underset{}{\overset{K_{ip}}{\rightleftharpoons}} amH^+ \cdot Cl^-$$

will account for the change of the rate law to 7 if $amH^+ \cdot Cl^-$ is taken as the incoming ligand.

$$k_{obs} = \left[\frac{k_3\, K_{a1}\, K_{ip}\, [Cl^-]}{[H^+]} + \frac{k_4\, k_1\, K_a\, K_{a1}\, K_{ip}}{k_2[H^+]^2}\right] [amH_2^{2+}] \qquad (7)$$

Equation 7 can be derived from the reaction scheme:[2]



k and k′ from equation 4 now becomes $k_3\, K_{a1}\, K_{ip}$ and $k_4\, k_1\, K_a\, K_{a1}\, K_{ip}/k_2$ respectively. Since k_1, k_2, K_a and K_{a1}[7] are known, $k_3\, K_{ip}$ and $k_4\, K_{ip}$ can be calculated. Unfortunately K_{ip} is not known, therefore the k_3 and k_4 values can not be isolated unless the K_{ip} values are calculated theoretically as Rorabacher did to overcome this difficulty in the $Ni(H_2O)_6^{2+}$ + am system.[8] For the sake of picking up trends in the series, these values were taken to calculate the activation parameters. As a result of this the only possible comparisons will be amongst the amines used in this report.

From the values listed in Table III it can be seen that there is a satisfactory agreement between the values calculated for $k_3\, K_{ip}$ or $k_4\, K_{ip}$ by using the two different approaches given by Equations 2 and 3.

The reason why the gold(III) substrate should discriminate so sharply between en or dien and the substituted amines with respect to the nature in which the ligand (ion pair or not) participates in these reactions is rather puzzling, and needs some further investigation.

The $k_3\, K_{ip}$ values are constantly smaller than the $k_4 \cdot K_{ip}$ values, as was found to be the case for k_3 and k_4 with the en and dien systems.[2,3] Again this points to $AuCl_3(OH)^-$ as being a more reactive complex than $AuCl_4^-$.

Although there is a definite retardation in the reactions as more heavily substituted amines are used, the relative importance of steric hindrance as opposed to basicity can not be evaluated, firstly because the pK_{a1} values are not an indication of the basicity, and secondly because k_3 or $k_4\, K_{ip}$ are not separable. It is therefore also impossible to decide, on the basis of rate constants, which nitrogen coordinates first, or for that matter, deprotonates first. However, the fact that only one molecule coordinates around the gold(III) metal (except for MED), indicates that steric hindrance in these ligands is not small.

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