# Displacement of Chelate Ligands from Planar Four-co-ordinate Complexes. Part II.[1] Preparation and Substitution Reactions of Dichloro(*NNN'N'*-tetramethylethylenediamine)- and Dichloro(*NNN'N'*-tetraethylethylenediamine)-gold(III) Complexes

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The kinetics of nucleophilic displacement of the chelate ligands *NNN'N'*-tetraethylethylenediamine (teen) and *NNN'N'*-tetramethylethylenediamine (tmen) from the complexes $[Au(teen)Cl_2]^+$ and $[Au(tmen)Cl_2]^+$ have been studied in 5% water–methanol solutions at 25 °C. At constant $[H^+]$ the reaction rate is second order in the chloride-ion concentration for low values of $[Cl^-]$ and tends to a first-order dependence as $[Cl^-]$ increases. On the other hand, at constant $[Cl^-]$ the rate is first order in acid concentration for low values of $[H^+]$ and approaches a limiting value as $[H^+]$ increases. The kinetic data fit a rate law for a mechanism in which displacement of the two donor atoms of the bidentate ligand occurs in two consecutive steps, each proceeding through the normal associative nucleophilic attack known for planar complexes. The intermediate in which the ligand is half bonded undergoes reversible protonation at the unco-ordinated nitrogen atom. The low value of the rate constant calculated for the protonation process is explained on the basis of slow interconversion from '*gauche*' to '*trans*' configurations of the half-bonded ligand. The rate constant for opening of the chelate ring has also been estimated and compared with substitution rates of unidentate amines in gold complexes.

IN Part I we reported a kinetic study on the displacement of 2,2'-bipyridyl from $[Au(bipy)X_2]^+$ (X = Cl or Br) by excess of halide ion in an acidic water–methanol medium.[1] In the reaction mechanism, axial interaction of two halide ions above and below the planar substrate with formation of a six-co-ordinate intermediate was postulated in order to account for a third-order dependence of the reaction rate on the concentration of the entering halide. In order to ascertain if this mechanism is a common feature in displacement of chelate ligands from square-planar gold(III) complexes, we have now studied the kinetics of displacement of *NNN'N'*-tetramethylethylenediamine (tmen) and *NNN'N'*-tetraethylethylenediamine (teen) from $[Au(L)Cl_2]^+$ cations by chloride ion. In this case the five-membered ring obtained by co-ordination of the substituted en ligand (L) to the metal atom cannot have any aromatic character, as was suggested in the bipy case.[2] Furthermore, in the teen complex the steric hindrance due to the ethyl groups significantly decreases the extent of axial interaction with the halogen ions. The results of this investigation are reported in the present paper and discussed in relation to the displacement of analogous ligands from other square-planar complexes.

## EXPERIMENTAL

The salt $H[AuCl_4],3H_2O$ was obtained from Johnson, Matthey and Co.; lithium chloride, lithium perchlorate, perchloric acid, *NNN'N'*-tetramethylethylenediamine (tmen) and *NNN'N'*-tetraethylethylenediamine (teen) were all reagent grade products.

*Preparation of Complexes.—Dichloro*(NNN'N'*-tetramethylethylenediamine*)*gold*(III) *perchlorate.* A solution of tmen (0·23 g) in water (20 cm³) was cooled in a ice-bath and treated with the stoicheiometric amount of $Na[AuCl_4]$ dissolved in water (10 cm³). A gelatinous compound first precipitated, but after stirring for 20 min at 0 °C this dissolved completely giving a pale yellow solution. Addition of $LiClO_4$ (3·0 g in 5 cm³ $H_2O$) and $HClO_4$ (few drops of concentrated solution) precipitated the pale yellow complex which was separated, washed with water, ethanol, and diethyl ether, and dried over silica gel under vacuum. The complex was characterized through i.r. and conductivity measurements and elemental analysis {Found: C, 14·6; H, 3·2; Cl, 21·5; N, 5·6. $[Au(tmen)Cl_2]ClO_4$ requires C, 14·9; H, 3·3; Cl, 22·0; N, 5·8%}.

Dichloro(*NNN'N'*-tetraethylethylenediamine)gold(III) perchlorate was prepared similarly. The stoicheiometric amount of $Na[AuCl_4]$ in water was added to a solution of teen (3·5 g in 20 cm³ $H_2O$) cooled in an ice-bath. The initial precipitate dissolved after shaking, giving a pale yellow solution which was filtered and treated with excess of $LiClO_4$ and a few drops of concentrated $HClO_4$. The resulting pale yellow solid was separated and characterized {Found: C, 22·4; H, 4·6; Cl, 19·4; N, 5·2. [Au-

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[1] Part I, G. Annibale, L. Cattalini, A. A. El Awady, and G. Natile, *J.C.S. Dalton*, 1974, 802.

[2] P. Haake and P. A. Cronin, *Inorg. Chem.*, 1963, **2**, 879.

(teen)$Cl_2$]$ClO_4$ requires C, 22·3; H, 4·5; Cl, 19·7; N, 5·2%}.

The solid complexes are unstable at room temperature, slowly changing to dark coloured materials which probably contain gold(0); they were therefore stored in dry-ice. Their solutions, however, were sufficiently stable for the kinetics to be followed, provided freshly prepared solutions were used. At the concentrations used for the kinetic runs, the extent of decomposition was *ca.* 50% after 1 d. Separate solutions of the complex and reagents were prepared in methanol containing 5% water. The concentrations of chloride and perchloric acid were determined by standard titrimetric methods. Preliminary experiments showed that all absorbing species closely obeyed Beer's law in the solvent used. The kinetics were followed by observing absorption changes in the u.v. region of the spectrum at a constant temperature. The reagent solutions were thermostatted separately for at least 30 min before the reaction was initiated by rapidly mixing them. All reaction mixtures contained lithium perchlorate to give a constant ionic strength ($I$ = 1·7M).*

All kinetic runs were carried out with excess of the entering reagent. First-order rate constants were calculated from plots of log ($A_\infty - A_t$) against time, where $A_t$ and $A_\infty$ are absorbances at time $t$ and after at least six half-lives respectively. These plots were linear for at least three half-lives. The experimentally determined rate constants $k_{obs}$ ($s^{-1}$) are summarized in Tables 1 and 3. From the values of $k_{obs}$ the parameters $B_0$, $B_1$, and $B_1'$ shown in Tables 2 and 4 were calculated by least-squares methods. The constants $r$, $s$, and $t$ (see text) were derived from these parameters using an unweighted least-squares program and the error in their values was derived from the standard deviations of $B_0$, $B_1$, and $B_1'$ using the formula for indirect error.

## RESULTS

*Reaction of* [Au(teen)$Cl_2$]$ClO_4$.—The spectroscopic course of this reaction showed the presence of two well defined isosbestic points at 295 and 352 nm, clearly indicating that the reaction occurs in only one step. The final spectrum showed an intense peak with a maximum at 310 nm (ε 5·75 × $10^3$ l $mol^{-1}$ $cm^{-1}$) which corresponds, apart for a contribution from the ligand, to that reported[3] for $[AuCl_4]^-$ ($\lambda_{max.}$ 314 nm, ε 4·57 × $10^3$ l $mol^{-1}$ $cm^{-1}$). Therefore the reaction studied is actually displacement of the chelate ligand.

The observed rate constants are given in Table 1. At a given chloride concentration the rate of reaction tended to a limiting value as the acid concentration was increased, and the reciprocal of the rate constant was a linear function of the reciprocal of the hydrogen-ion concentration (Figure 1). These results are in accord with expression (1), where

$$k_{obs} = [H^+]/(B_0[H^+] + B_1) \qquad (1)$$

$B_0$ and $B_1$ are respectively the intercept and gradient of the linear $1/k_{obs}$ against $1/[H^+]$ plot at constant [$Cl^-$]. Their values, calculated by least-squares methods, are given in Table 2. Since the intercepts are small there is a rather large uncertainty in the values of $B_0$. However, the values of $B_1$ have much smaller fractional uncertainties.

TABLE 1

Values of $k_{obs}$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$ at constant [$Cl^-$] and variable [$H^+$], $I$ = 1·7M ($LiClO_4$), and 25 °C

[$Cl^-$] = 1·80 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 7·27 | 0·19 |
| 9·09 | 0·24 |
| 14·50 | 0·36 |
| 27·20 | 0·63 |
| 36·30 | 0·82 |
| 54·50 | 1·08 |
| 63·60 | 1·27 |
| 72·70 | 1·32 |
| 81·80 | 1·40 |

[$Cl^-$] = 3·68 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 3·63 | 0·40 |
| 5·45 | 0·57 |
| 7·27 | 0·73 |
| 9·09 | 0·90 |
| 18·10 | 1·62 |
| 27·20 | 2·14 |
| 36·30 | 2·71 |
| 45·40 | 3·01 |
| 54·50 | 3·42 |
| 63·60 | 3·64 |
| 81·80 | 4·14 |

[$Cl^-$] = 5·35 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 1·82 | 0·39 |
| 2·54 | 0·55 |
| 3·63 | 0·79 |
| 5·45 | 1·11 |
| 7·27 | 1·36 |
| 9·09 | 1·71 |
| 18·10 | 2·91 |
| 27·20 | 3·90 |
| 36·30 | 4·82 |
| 45·40 | 5·13 |
| 54·50 | 5·27 |
| 63·60 | 6·30 |

[$Cl^-$] = 7·36 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 1·82 | 0·71 |
| 2·54 | 0·96 |
| 3·63 | 1·39 |
| 5·45 | 1·92 |
| 7·27 | 2·36 |
| 9·09 | 2·91 |
| 18·10 | 4·79 |
| 27·20 | 6·32 |
| 36·30 | 7·09 |
| 63·60 | 9·61 |

[$Cl^-$] = 9·21 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 1·82 | 1·08 |
| 2·54 | 1·44 |
| 3·63 | 2·05 |
| 5·45 | 2·80 |
| 7·27 | 3·45 |
| 9·09 | 4·41 |
| 18·10 | 6·83 |
| 27·20 | 8·62 |
| 36·30 | 10·00 |

[$Cl^-$] = 2·70 × $10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 2·54 | 7·80 |
| 3·63 | 10·60 |
| 5·45 | 14·10 |
| 7·27 | 17·20 |
| 9·09 | 20·50 |
| 18·10 | 28·20 |
| 27·20 | 33·70 |

TABLE 2

Values of intercepts, $B_0$ (at $1/[H^+] = 0$), and gradients, $B_1$, of straight lines obtained from plots of $1/k_{obs}$ against $1/[H^+]$ at constant [$Cl^-$], and values of intercepts, $B_0'$ (at $1/[Cl^-] = 0$), and gradients, $B_1'$, of straight lines obtained from plots of $[Cl^-]/k_{obs}$ against $1/[Cl^-]$ at constant [$H^+$], using the values from Table 1 (the parameters were obtained from least-squares calculations)

| $10^2[Cl^-]$/M | $10^{-2}B_0$/s | $10^{-2}B_1$/mol $l^{-1}$ s |
|---|---|---|
| 1·80 | 2·78 ± 0·36 | 3·488 ± 0·055 |
| 3·68 | 1·48 ± 0·23 | 0·853 ± 0·020 |
| 5·35 | 0·98 ± 0·18 | 0·437 ± 0·008 |
| 7·36 | 0·72 ± 0·11 | 0·242 ± 0·004 |
| 9·21 | 0·59 ± 0·09 | 0·158 ± 0·003 |
| 27·70 | 0·19 ± 0·02 | 0·027 ± 0·007 |

| $10^2[H^+]$/M | $B_0'$/mol $l^{-1}$ s | $B_1'$/$mol^2$ $l^{-2}$ s |
|---|---|---|
| 2·54 | 20·71 ± 2·83 | 4·04 ± 0·18 |
| 3·63 | 15·81 ± 0·13 | 2·74 ± 0·09 |
| 5·45 | 12·67 ± 0·67 | 1·89 ± 0·04 |
| 7·27 | 11·34 ± 1·09 | 1·44 ± 0·04 |
| 9·09 | 9·20 ± 1·09 | 1·16 ± 0·04 |
| 18·10 | 7·75 ± 0·67 | 0·55 ± 0·04 |
| 27·10 | 6·46 ± 0·27 | 0·39 ± 0·01 |
| 36·30 | 6·17 ± 0·86 | 0·28 ± 0·03 |
| 63·60 | 5·67 ± 0·75 | 0·15 ± 0·03 |

These parameters depend on the concentration of chloride. A plot of $1/B_0$ against [$Cl^-$] was linear and passed through

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* 1M = 1 mol $dm^{-3}$.

[3] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260; A. K. Gongopadhayay and A. Chakravorty, *J. Chem. Phys.*, 1961, **35**, 2206.

TABLE 3

Values of $k_{obs}$ for the reaction $[Au(tmen)Cl_2]^+ \longrightarrow [AuCl_4]^-$ at constant $[Cl^-]$ and variable $[H^+]$, $I = 1{\cdot}7$M ($LiClO_4$), and 25 °C

$[Cl^-] = 3{\cdot}62 \times 10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 5·45 | 0·17 |
| 9·09 | 0·29 |
| 18·10 | 0·56 |
| 54·50 | 1·54 |
| 72·70 | 2·01 |

$[Cl^-] = 5{\cdot}35 \times 10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 2·54 | 0·18 |
| 3·63 | 0·26 |
| 5·45 | 0·39 |
| 9·09 | 0·62 |
| 18·10 | 1·24 |
| 36·30 | 2·36 |
| 54·50 | 3·29 |

$[Cl^-] = 7{\cdot}30 \times 10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 2·54 | 0·32 |
| 3·63 | 0·47 |
| 5·45 | 0·69 |
| 9·09 | 1·12 |
| 18·10 | 2·11 |
| 36·30 | 4·18 |
| 54·50 | 5·53 |
| 63·60 | 6·30 |
| 72·70 | 7·22 |

$[Cl^-] = 9{\cdot}21 \times 10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 1·82 | 0·37 |
| 2·54 | 0·55 |
| 3·63 | 0·74 |
| 5·45 | 1·09 |
| 7·27 | 1·48 |
| 9·09 | 1·82 |
| 18·10 | 3·42 |
| 27·20 | 5·13 |
| 36·30 | 6·44 |
| 45·40 | 7·79 |
| 54·50 | 8·62 |
| 63·60 | 9·71 |
| 72·70 | 10·70 |

$[Cl^-] = 18{\cdot}30 \times 10^{-2}$M

| $10^2[H^+]$/M | $10^3k_{obs}/s^{-1}$ |
|---|---|
| 1·82 | 1·43 |
| 2·54 | 1·93 |
| 3·63 | 2·78 |
| 18·10 | 12·70 |
| 27·20 | 16·60 |
| 36·30 | 20·00 |

TABLE 4

Values of the parameters $B_0$ and $B_1$ obtained either from (*a*) plots of $1/k_{obs}$ against $1/[H^+]$, or (*b*) plots of $[H^+]/k_{obs}$ against $[H^+]$, at constant $[Cl^-]$ using the values from Tables 3 (the parameters were obtained from least-squares calculations)

| $10^2[Cl^-]$/M | | $10^{-1}B_0$/s | $10^{-2}B_1$/mol l$^{-1}$ s |
|---|---|---|---|
| 3·62 | (*a*) | 8·7 ± 2·8 | 3·03 ± 0·03 |
| | (*b*) | 7·2 ± 2·4 | 3·11 ± 0·10 |
| 5·35 | (*a*) | 4·1 ± 4·0 | 1·39 ± 0·02 |
| | (*b*) | 4·7 ± 1·1 | 1·39 ± 0·03 |
| 7·30 | (*a*) | 3·7 ± 2·3 | 0·76 ± 0·01 |
| | (*b*) | 3·5 ± 0·6 | 0·77 ± 0·02 |
| 9·21 | (*a*) | 2·5 ± 2·4 | 0·48 ± 0·01 |
| | (*b*) | 2·7 ± 0·3 | 0·47 ± 0·01 |
| 18·30 | (*a*) | 1·3 ± 1·0 | 0·12 ± 0·01 |
| | (*b*) | 1·5 ± 0·4 | 0·12 ± 0·01 |

**the origin** (Figure 2). The gradient [$1/r$ in equation (2)] was $0{\cdot}188 \pm 0{\cdot}023$ l mol$^{-1}$ s$^{-1}$. The quantity $B_1$ also de-

$$B_0 = r/[Cl^-] \qquad (2)$$

creased as $[Cl^-]$ increased but with a more complicated dependence than $B_0$. A plot of $B_1[Cl^-]$ against $[Cl^-]^{-1}$ (Figure 3) gave a straight line with intercept $t = 0{\cdot}33 \pm 0{\cdot}08$ l$^{-2}$ mol$^2$ s and gradient $s = 0{\cdot}106 \pm 0{\cdot}003$ l$^{-3}$ mol$^3$ s, indicating that the dependence of $B_1$ on chloride takes the form (3).

$$B_1 = (s + t[Cl^-])/[Cl^-]^2 \qquad (3)$$

From equations (1)—(3) we can write expression (4) for the overall dependence of $k_{obs}$ on $[H^+]$ and $[Cl^-]$. It

$$k_{obs} = [H^+][Cl^-]^2/(r[Cl^-][H^+] + s + t[Cl^-]) \qquad (4)$$

follows that, on plotting $[Cl^-]/k_{obs}$ against $1/[Cl^-]$ at constant $[H^+]$, straight lines with intercept $B_0' = r + (t/[H^+])$ and gradient $B_1' = s/[H^+]$ should be obtained (Figure 4). The values of the parameters obtained from the results

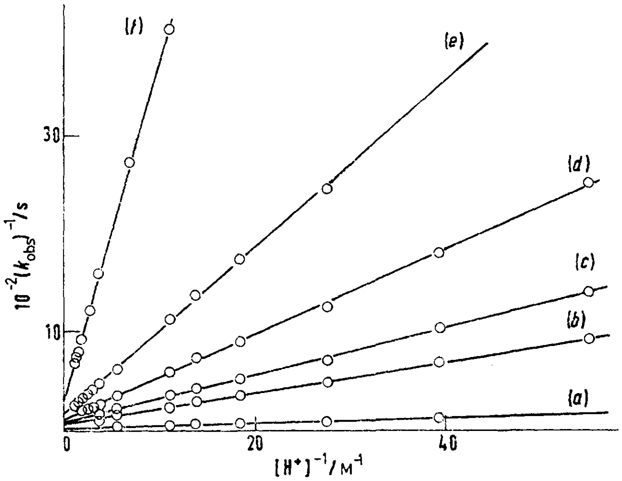


FIGURE 1 Plots of $1/k_{obs}$ against $1/[H^+]$ at constant $[Cl^-]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$: $[Cl^-] = 0{\cdot}277$ (*a*), 0·092 (*b*), 0·074 (*c*), 0·053 (*d*), 0·037 (*e*), and 0·018 (*f*); $I = 1{\cdot}7$M ($LiClO_4$); 25 °C

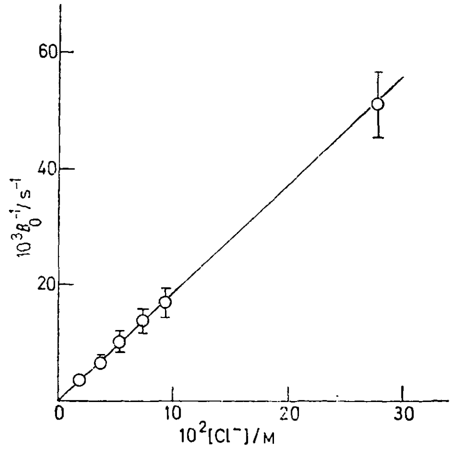


FIGURE 2 Dependence of $1/B_0$ (see text) on $[Cl^-]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$

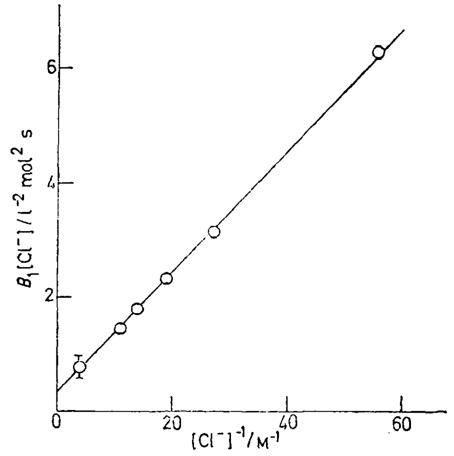


FIGURE 3 Dependence of $B_1[Cl^-]$ on $1/[Cl^-]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$

in Table 1 are summarized in Table 2. Plots of $B_0'$ and $B_1'$ against $1/[H^+]$ gave $1/r = 0{\cdot}191 \pm 0{\cdot}019$ l mol$^{-1}$ s$^{-1}$, $t = 0{\cdot}394 \pm 0{\cdot}054$ l$^{-2}$ mol$^{-2}$ s, and $s = 0{\cdot}102 \pm 0{\cdot}003$ l$^{-3}$ mol$^3$ s (Figures 5 and 6). The agreement of these values with those obtained independently from the previous treatment of the experimental data provides good support to this rate expression.

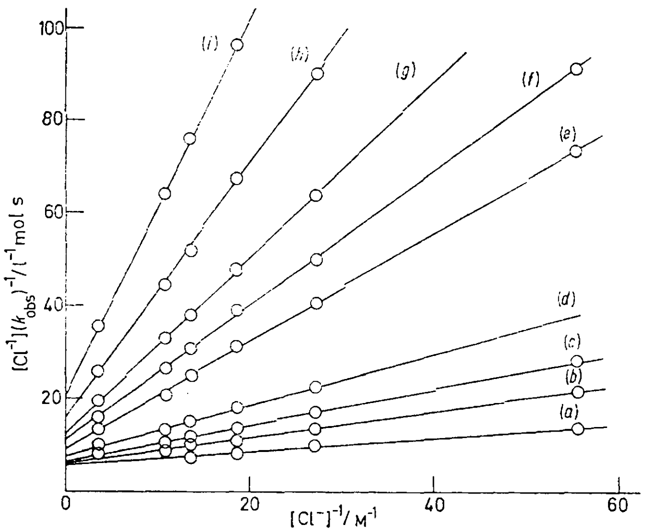


FIGURE 4 Plots of $[Cl^-]/k_{obs}$ against $1/[Cl^-]$ at constant $[H^+]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$: $[H^+] = 0{\cdot}636$ (*a*), 0·363 (*b*), 0·271 (*c*), 0·181 (*d*), 0·091 (*e*), 0·073 (*f*), 0·054 (*g*), 0·036 (*h*), and 0·025 (*i*); $I = 1{\cdot}7$M ($LiClO_4$); 25 °C

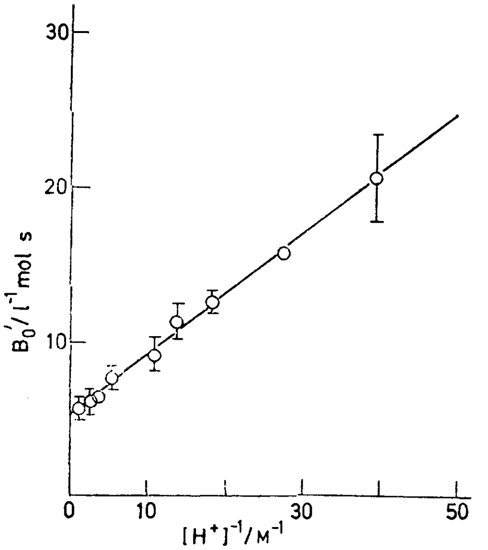


FIGURE 5 Plot of $B_0'$ against $1/[H^+]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$

*Reaction of* $[Au(tmen)Cl_2]ClO_4$.—The spectroscopic course of this reaction was completely analogous to the previous one and the observed rate constants are given in Table 3. In this case, at a given chloride concentration, $k_{obs}$ was nearly a linear function of $[H^+]$ and only at the higher hydrogen-ion concentrations did the straight lines tail off very slightly but significantly. As a consequence, linear plots obtained by plotting the reciprocal of the rate constants against the reciprocal of the hydrogen-ion concentrations had very small intercepts. The $B_0$ and $B_1$ parameters obtained from least-squares calculations are given in Table 4; in this case the uncertainty in the value of $B_0$ was almost as large as the value itself, although there was definitive evidence for its existence. However, a plot of $[H^+]/k_{obs}$ against $[H^+]$ has gradient $B_0$ and intercept $B_1$ and in this case the values of $B_0$ had less uncertainty (see Table 4).

The dependence of $B_0$ on $[Cl^-]$ was determined by plotting the reciprocal of $B_0$ against the chloride concentration; a straight line was obtained with zero intercept and gradient $1/r$; the value of $t$ was $0{\cdot}37 \pm 0{\cdot}15$ l mol$^{-1}$ s$^{-1}$. The dependence of $B_1$ on $[Cl^-]$ was completely analogous to that found in the case of the teen derivative; values of $s$ and $t$ estimated from the plot of $B_1[Cl^-]$ against $[Cl^-]^{-1}$ are respectively $0{\cdot}39 \pm 0{\cdot}01$ l$^{-3}$ mol$^3$ s and $0{\cdot}18 \pm 0{\cdot}08$ l$^{-2}$ mol$^2$ s.

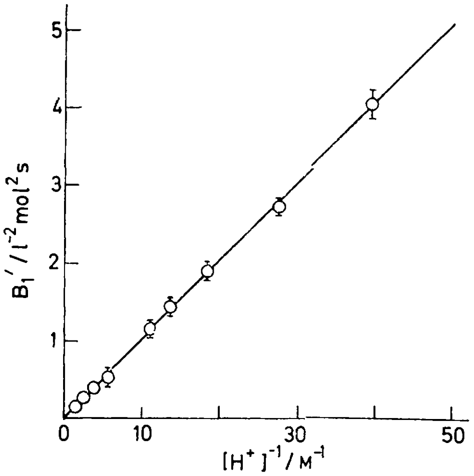
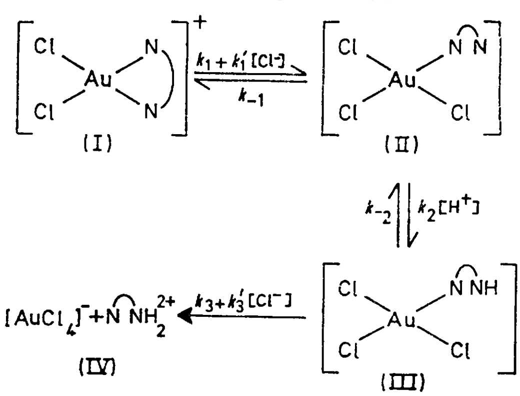


FIGURE 6 Plot of $B_1'$ against $1/[H^+]$ for the reaction $[Au(teen)Cl_2]^+ \longrightarrow [AuCl_4]^-$

DISCUSSION

A reaction mechanism, basically similar to those generally accepted for displacement of chelate groups from square-planar complexes [4,5] and which accounts satisfactorily for the dependence of the observed rate constants on the acid and chloride concentrations, is shown in scheme below from which equation (5) may be deduced



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[4] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

[5] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967, p. 220.

using the stationary-state approximation for the concentrations of the half-bonded species. Some comments

$$k_{\text{obs}} = \frac{(k_1 + k_1'[\text{Cl}^-])(k_3 + k_3'[\text{Cl}^-])k_2[\text{H}^+]}{k_{-1}k_{-2} + k_{-1}(k_3 + k_3'[\text{Cl}^-]) + k_2(k_3 + k_3'[\text{Cl}^-])[\text{H}^+]} \qquad (5)$$

are necessary about this reaction scheme: (*i*) steps (I) ⟶ (II) and (III) ⟶ (IV) have been written in the general form for substitution reactions in square-planar complexes, although it will appear clear later that $k_1$ and $k_3$ are not detectable; (*ii*) it is assumed that displacement of the second nitrogen atom occurs only after protonation at the free site of the unidentate ligand, and the direct step (II) ⟶ (IV) has been excluded on the grounds that the observed rate constants go to zero as the hydrogen-ion concentration decreases; and (*iii*) species (II) and (III) are considered steady-state intermediates, whereas in similar reactions involving displacement of chelated ligands from $\text{Pd}^{\text{II}}$ and $\text{Pt}^{\text{II}}$ complexes other authors have adopted a mechanism involving a preliminary equilibrium between the substrate and half-bonded bidentate ligand.[6-9] The presence from the beginning of two good isosbestic points in the changing spectra of the reaction mixture and the absence of any significant change in $A$ soon after mixing of the reagents is in accord with our assumptions.

Equation (5) is similar to the empirical expression and the parameters $B_0$ and $B_1$ are given by (6) and (7).

$$B_0 = (k_1 + k_1'[\text{Cl}^-])^{-1} \qquad (6)$$

$$B_1 = \frac{k_{-1}k_{-2} + k_{-1}(k_3 + k_3'[\text{Cl}^-])}{(k_1 + k_1'[\text{Cl}^-])(k_3 + k_3'[\text{Cl}^-])k_2} \qquad (7)$$

The observation that $B_0$ is inversely proportional to $[\text{Cl}^-]$ shows that $k_1$ must be extremely small, whereas $k_1'$ is 0·19 l $\text{mol}^{-1}$ $\text{s}^{-1}$ for the $[\text{Au(teen)Cl}_2]^+$ complex and 0·37 l $\text{mol}^{-1}$ $\text{s}^{-1}$ for $[\text{Au(tmen)Cl}_2]^+$. Since $k_1 \simeq 0$, equation (7) can be rewritten as (8) and a plot of

$$\frac{1}{B_1[\text{Cl}^-]} = \frac{k_2k_1'(k_3 + k_3'[\text{Cl}^-])}{k_{-1}k_{-2} + k_{-1}(k_3 + k_3'[\text{Cl}^-])} \qquad (8)$$

$1/B_1[\text{Cl}^-]$ against $[\text{Cl}^-]$ should give a curve with intercept (at $[\text{Cl}^-] = 0$) $k_2k_1'k_3/(k_{-1}k_{-2} + k_{-1}k_3)$ and approaching a limiting value as the chloride concentration is increased (Figure 7); since the intercept appears to be zero we can assume also that $k_3$ is insignificant compared with $k_3'$. Assuming $k_3 = 0$, equation (8) simplifies to (9). According to equation (9) a plot of $B_1[\text{Cl}^-]$ against

$$\frac{1}{B_1[\text{Cl}^-]} = \frac{k_2k_1'k_3'[\text{Cl}^-]}{k_{-1}k_{-2} + k_{-1}k_3'[\text{Cl}^-]} \qquad (9)$$

$1/[\text{Cl}^-]$ should be a straight line, as actually was observed, with gradient $s = k_{-1}k_{-2}/k_2k_1'k_3'$ and intercept $t = k_{-1}/k_2k_1'$. From the known values of $k_1'$ and the values of $s$ and $t$, the ratios $k_{-1} : k_2$ and $k_3' : k_{-2}$ may be calculated (Table 5).

The complexity of equation (5) does not allow evaluation of each constant. Having shown that the $k_1$ and $k_3$ paths make negligible contributions to the reaction rate, it follows that steps (I) ⟶ (II) and (III) ⟶ (IV) in the scheme proceed only by the path that is first order in chloride concentration. This result differs from that obtained in the displacement of 2,2′-bipyridyl from $[\text{Au(bipy)X}_2]^+$ (X = Cl or Br) in which the steady-state intermediates with half-bonded bipy groups undergo displacement of the organic ligand by solvent in preference to anation by $\text{X}^-$.

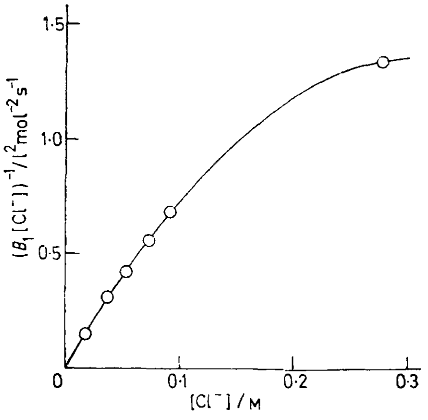

FIGURE 7 Plot of $1/B_1[\text{Cl}^-]$ against $[\text{Cl}^-]$ for the reaction $[\text{Au(teen)Cl}_2]^+ \longrightarrow [\text{AuCl}_4]^-$

TABLE 5

Values of the constants in equation (5) derived (see text) from results in Tables 2 and 4

| Complex | | $k_1'$/ l $\text{mol}^{-1}$ $\text{s}^{-1}$ | $(k_{-1}/k_2)$/ mol $\text{l}^{-1}$ | $(k_3'/k_{-2})$/ l $\text{mol}^{-1}$ |
|---|---|---|---|---|
| $[\text{Au(teen)Cl}_2]^+$ | (*a*) | 0·188 | 0·062 | 3·122 |
| | | ±0·023 | ±0·017 | ±0·778 |
| | (*b*) | 0·191 | 0·075 | 3·862 |
| | | ±0·019 | ±0·013 | ±0·538 |
| $[\text{Au(tmen)Cl}_2]^+$ | | 0·37 | *ca.* 0·066 | *ca.* 0·461 |
| | | ±0·15 | ±0·040 | ±0·205 |

Values derived from (*a*) $B_0$ and $B_1$, (*b*) $B_0'$ and $B_1'$.

It should be recalled at this point that Pearson *et al.*[10] found that, in the reaction $[\text{Pd(pd)}_2] \longrightarrow [\text{Pd(pd)Cl}_2]^-$ (pd = pentane-2,4-dionate), the steady-state intermediates with the half-bonded pd group react with water but not with $\text{Cl}^-$ at any significant rate; Coe *et al.*[6,9] on the other hand found that for replacement of half-bonded protonated en from $[\text{Pd(en)(Hen)Cl}]^{2+}$ and $[\text{Pd(en)(Hen)OH}_2]^{3+}$, $\text{Cl}^-$ is a better entering group than $\text{H}_2\text{O}$, whereas in substitution reactions of *cis*- and *trans*-bis(glycinato)palladium(II) the half-bonded glycinato-groups are replaced by $\text{H}_2\text{O}$ in preference to anation by $\text{Cl}^-$.

Direct comparison of $k_1'$ with the rate constant for displacement of unidentate tertiary amines from square-planar gold(III) complexes could in principle show if some special features are associated with breaking of a chelate ring. To our knowledge the only data avail-

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[6] J. S. Coe, J. R. Lyons, and M. D. Hussain, *J. Chem. Soc.* (*A*), 1970, 90.

[7] A. J. Poe and D. H. Vaughan, *Inorg. Chim. Acta*, 1967, **1**, 255.

[8] A. Giacomelli and A. Indelli, *Inorg. Chem.*, 1972, **11**, 1033.

[9] J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 829.

[10] R. G. Pearson and D. A. Johnson, *J. Amer. Chem. Soc.*, 1964, **86**, 3983.

able in the literature refer to displacement of a heterocyclic nitrogen base from complexes of the type $[AuCl_3(am)]$ [11] and if it is possible to compare the values of $k_1'$ with these data we conclude that in the present case no relevant differences are found between displacement of a unidentate amine and opening of a chelate ring. However, it can be pointed out that heterocyclic amines differ significantly from aliphatic tertiary amines, and that although a lower rate would be expected for a ring-opening process which involves a steric restriction because it is required to open in one specific direction, that is in order to give the half-bonded form, this factor could be compensated by the presence of a positive charge on our reaction substrate.

The relatively small difference (factor of 2) between the values of $k_1'$ for the teen and tmen derivatives could arise from differing steric requirements of the two ligands or the small difference in their basicities.[12] It is not possible from the experimental data to give a value for $k_3'$ which could be usefully compared with $k_1'$. In the displacement of an en group from $[Pd(en)_2]^{2+}$ by HCl in an aqueous medium,[6] values found for rate constants corresponding to $k_1'$ and $k_3'$ in our reaction scheme are respectively $5 \times 10^{-3}$ and $1{\cdot}3 \times 10^{-3}$ l mol$^{-1}$ s$^{-1}$, that is the rate constant corresponding to bimolecular opening of the chelate ring differs by a factor of four from that relative to displacement of the second nitrogen atom.

For the ratio $k_{-1} : k_2$ we obtained the value $0{\cdot}07 : 1$ for both the teen and tmen complexes. These data clearly show that the rate constant for the ring-closing process is *ca.* one tenth of that for protonation of the uncoordinated donor site and since the hydrogen-ion concentrations used in our experiments were of the order of $10^{-1}$M it follows that in the present case the two processes (ring closing and protonation) have comparable rates. Since protonation of amines by $H_3O^+$ is generally a diffusion-controlled process ($k = 10^9$—$10^{10}$ l mol$^{-1}$ s$^{-1}$), this result is very surprising. However, a possible explanation is that in the first intermediate the ' half-bonded ' ligand still retains its original *gauche*-configuration and there might well be residual attraction between the gold atom and the free end of the ligand. It is likely that before protonation can occur the ligand must assume the *trans*-configuration and this interconversion process can be rather slow. Molecular models indicate that the *trans*-conformation of the diamine becomes less favourable as the extent of *N*-alkyl substitution increases due to increased back-side crowding, and this effect appears to be particularly severe for diamines substituted on both nitrogen-donor atoms. We also calculated from the experimental data the values of $k_3'/k_{-2}$ for the two substrates $[Au(teen)Cl_2]^+$ and $[Au(tmen)Cl_2]^+$ and they are 3·5 and *ca.* 0·4 l mol$^{-1}$ respectively, clearly showing that the rate of bimolecular displacement of the second nitrogen atom is comparable with deprotonation of the free end of the bidentate ligand. A high value of $k_3'$ is expected from what is known about the apparent instability of mono complexes involving highly substituted monoamine ligands.[13] The similarities in the values of $k_{-1}$, $k_2$ and $k_3'$, $k_{-2}$ explain why, in reactions involving displacement of these chelating ligands, a simpler kinetic expression is not found.

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[11] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1145.

[12] T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 288 and refs. therein.

[13] D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Amer. Chem. Soc.*, 1971, **93**, 6071.