Displacement of Chelate Ligands from Four-co-ordinate Complexes. Part IV.[1] Reactions of (3-Azapentane-1,5-diamine)- and (3-Methyl-3-azapentane-1,5-diamine)-chlorogold(III) Complexes

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The kinetics of nucleophilic displacement of the chelate ligands 3-azapentane-1,5-diamine(3NH-pd) and 3-methyl-3-azapentane-1,5-diamine (3NMe-pd) from the complexes [AuCl(N–N–N)]Cl$_2$ (N–N–N = 3NH- or 3NMe-pd) have been studied in 5% water–methanol solution at 25 °C. Under the experimental conditions used for the kinetic runs the predominant species in solution are [AuCl$_2$(HN–N–N)]$^{2+}$ and [AuCl$_3$(H$_2$N–N–N)]$^{2+}$ in which the polydentate ligand acts as bi- and uni-dentate. The observed rate equation in both cases is formally analogous to that found in displacement of *NNN'N'*-tetraethylethylenediamine (teen) and *NNN'N'*-tetramethylethylenediamine(tmen) from the complexes [AuCl$_2$(N–N)](ClO$_4$) (N–N = teen or tmen) and is in accord with the mechanism in equation (i). From the kinetic data the values of K_1, K_2, and k_3' have been determined, and the constant for equilibrium (ii) has been measured spectrophotometrically. The complex [AuCl(3NMe-pd)]$^{2+}$ undergoes deprotonation of one of the two co-ordinated primary amine groups and the pK_a values, determined in 0.5 mol dm^{-3} Na[ClO$_4$] and in 0.5 mol dm^{-3} NaCl, are reported.

$$[\mathrm{AuCl_2(HN{-}N{-}N)}]^{2+} \underset{}{\overset{K_1[\mathrm{Cl^-}]}{\rightleftharpoons}} [\mathrm{AuCl_3(HN{-}N{-}N)}]^{+} \overset{K_2[\mathrm{H^+}]}{\rightleftharpoons} [\mathrm{AuCl_3(H_2N{-}N{-}N)}]^{2+} \xrightarrow{k_3'[\mathrm{Cl^-}]} [\mathrm{AuCl_4}]^- + [\mathrm{H_3N{-}N{-}N}]^{3+} \quad \text{(i)}$$

$$[\mathrm{AuCl(N{-}N{-}N)}]^{2+} \overset{K[\mathrm{H^+}][\mathrm{Cl^-}]}{\rightleftharpoons} [\mathrm{AuCl_2(HN{-}N{-}N)}]^{2+} \quad \text{(ii)}$$

THE displacement of bidentate *NNN'N'*-tetraethylethylenediamine (teen) and *NNN'N'*-tetramethylethylenediamine (tmen) from the gold complexes [AuCl$_2$(N–N)]$^+$ (N–N = teen or tmen) has been shown to occur in two consecutive steps each proceeding through the normal associative mechanism.[2] Also the displacement of a tridentate ligand could proceed in an analogous way, but in this case the first ring opening could be favoured by the steric strain of the two condensed five-membered rings, and once the first ' tooth ' is freed its protonation could facilitate the displacement of the adjacent one.

The substitution of 3-azapentane-1,5-diamine (3NH-pd) and *NNN'N'*-tetraethyl-3-azapentane-1,5-diamine (3NH-tepd) by chloride ion from [PdCl(N–N–N)]$^+$ (N–N–N = 3NH-pd or -tepd) has been studied by Poë and Vaughan [3] and found to be a two-stage process. In the first stage an intermediate, in which the polyamine is unidentate and the uncomplexed nitrogen atoms are all protonated, is formed. In the second stage the unidentate ligand is displaced through a complex reaction mechanism which is completely different from that normally observed for displacement of unidentate amines from square-planar substrates.[4] Ring opening and formation of species in which a potentially tridentate amine is only bidentate has been considered for both palladium(II) [5] and gold(III) complexes.[6,7]

Having previously studied the displacement of diamines from gold(III) complexes,[1,2,8] we have extended the investigation to triamines with the hope of evaluating, under favourable conditions, the equilibrium and/or kinetic constants of the various dissociation steps. The complex [AuCl(3NH-pd)]$^{2+}$ is also known to undergo deprotonation of the central NH nitrogen.[9] The acidic properties of the terminal nitrogen atoms could be investigated by reacting the gold complex of 3-methyl-3-azapentane-1,5-diamine (3NMe-pd) with bases.

EXPERIMENTAL

Hydrogen tetrachloroaurate(III) trihydrate was obtained from Johnson, Matthey and Co.; solvents, inorganic salts, and 3-azapentane-1,5-diamine trihydrochloride were all reagent-grade products. 3-Methyl-3-azapentane-1,5-diamine was prepared according to a reported procedure.[10]

Preparation of Complexes.—The salt [AuCl(3NH-pd)]Cl$_2$ was first prepared by Baddley *et al.*,[9] but we used a slightly different procedure. To a solution of HAuCl$_4$·3H$_2$O (1.00 g, 2.5 mmol) in water (2 cm^3), cooled in an ice bath, was added, with stirring, 3NH-pd·3HCl (1.4 g, 6.5 mmol). A yellow complex was first precipitated. To the reaction mixture was then added dropwise Na[OH] (0.46 g, 11.6 mmol) dissolved in water (2 cm^3). The complex which initially precipitated redissolved and after stirring for 2 h at 0 °C a crystalline yellow complex separated from the solution; this was filtered off, washed twice with ethanol, and dried over phosphorus penta-oxide. At this stage the yield was less than 50%; the complete precipitation of the complex was achieved by adding ethanol (5 cm^3) to the mother liquor {Found: C, 11.7; H, 3.3; Cl, 26.3; N, 10.3. [AuCl(3NH-pd)]Cl$_2$ requires C, 11.8; H, 3.2; Cl, 26.2; N, 10.3%}. The complex [AuCl(3NMe-pd)]Cl$_2$ was prepared similarly. {Found: C, 14.0; H, 3.9; Cl, 25.1; N, 9.7. [AuCl(3NMe-pd)]Cl$_2$ requires C, 14.3; H, 3.6; Cl, 25.3; N, 10.0%}.

Kinetics.—Rate data were obtained spectrophotometrically by measuring changes in absorbance with time using an

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[1] Part III, G. Annibale, G. Natile, and L. Cattalini, *J.C.S. Dalton*, 1976, 285.

[2] G. Annibale, G. Natile, and L. Cattalini, *J.C.S. Dalton*, 1975, 188.

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

[4] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley, New York, 1958, p. 388.

[5] J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1969, 2669.

[6] C. F. Weick and F. Basolo, *Inorg. Chem.*, 1966, **5**, 576.

[7] D. L. Fant and C. F. Weick, *Inorg. Chem.*, 1973, **12**, 1864.

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

[9] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poë, *Inorg. Chem.*, 1963, **2**, 921.

[10] F. G. Mann, *J. Chem. Soc.*, 1934, 466.

Optica CF4R double-beam instrument. Separate solutions of complex and reagents were prepared in methanol containing 5% of water, brought to reaction temperature, mixed, and placed in the thermostatted cell of the spectrophotometer. The concentrations of chloride and perchloric acid were determined by standard titrimetric methods; all kinetic runs were in the presence of excess of entering reagents and at constant ionic strength. First-order rate constants were calculated from plots of $\ln(A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least six half-lives respectively. These plots were linear for at least four half-lives. The experimentally determined rate constants, $k_{obs.}/s^{-1}$, are summarized in Tables 1 and 3.

TABLE 1

Values of $k_{obs.}$ for the reaction $[AuCl(3NH\text{-}pd)]^{2+} \longrightarrow [AuCl_4]^-$ at constant $[Cl^-]$ and variable $[H^+]$, $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]), and 25 °C

$10^2[Cl^-]$/ mol dm^{-3}	$10^2[H^+]$/ mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
1.82	18.20	1.31
	27.20	1.84
	36.30	2.28
	45.40	2.68
	54.50	2.99
	63.60	3.44
	72.70	3.68
	81.80	3.96
2.72	9.09	1.48
	18.20	2·67
	27.20	3·54
	36.30	4.43
	45.40	5.06
	54.50	5.69
	63.60	6.00
	72.70	6.45
	77.27	6.81
5.45	3.63	2.30
	5.45	3.37
	7.27	4.19
	9.09	5.08
	18.20	8.80
	27.20	10.90
	36.30	12.70
	45.40	14.00
	54.50	15.50
	63.60	16.70
9.09	3.63	5.56
	5.45	7.87
	7.27	9.96
	9.09	11.80
	18.20	18.40
	27.20	22.20
	36.30	25.30
	45.40	27.80
	54.50	28.30
	63.60	29.80
18.2	3.63	17.50
	5.45	24.10
	7.27	29.00
	9.09	33.20
	18.20	47.50
	27.20	54.40
	36.30	58.70
	63.60	68.20
	72.70	70.90

From the values of $k_{obs.}$ the parameters B_0 and B_1 (Tables 2 and 4) were calculated from least-squares fits and the uncertainties quoted are 95% confidence limits. The constants r, s, and t (see text) were derived from B_0 and B_1 using an unweighted least-squares fit and their uncertainties were derived from those of B_0 and B_1 using the formula for indirect error.

Measurement of the Equilibrium Constant, K, *for the equilibrium:* $[AuCl(3NMe\text{-}pd)]^{2+} \overset{K[H^+][Cl^-]}{\rightleftharpoons} [AuCl_2(3NMe\text{-}Hpd)]^{2+}$.—At a given $[H^+]$ and $[Cl^-]$, all the species involved in equilibria contribute to the total absorbance A_i. Since

$$[AuCl(3NMe\text{-}pd)]^{2+}\ (I) \overset{K[H^+][Cl^-]}{\rightleftharpoons} [AuCl_2(3NMe\text{-}Hpd)]^{2+}\ (II) \overset{K_1[Cl^-]}{\rightleftharpoons} [AuCl_3(3NMe\text{-}Hpd)]^{+}\ (III) \overset{K_2[H^+]}{\rightleftharpoons} [AuCl_3(3NMe\text{-}H_2pd)]^{2+}\ (IV) \text{ and } [AuCl_4]^-$$

the first free end of a polydentate amine has strong basic character [11,12] and the solution was at pH < 3 throughout the experiment, the species $[AuCl_2(3NMe\text{-}pd)]^+$ has not been considered. Using low values of $[Cl^-]$ (<0.3 mol dm^{-3}) and short experimental times, $[AuCl_4^-]$ can also be assumed to be

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 $[Cl^-]$ using the values listed in Table 1. The parameters were obtained from a least-squares fit and quoted uncertainties are 95% confidence limits

$10^2[Cl^-]$/ mol dm^{-3}	$10^{-2}B_0$/s	$10^{-2}B_1$/ mol dm^{-3} s
1.82	10.88 ± 0.74	11.90 ± 0.26
2.72	7.86 ± 0.34	5.42 ± 0.07
5.45	3.86 ± 0.24	1.43 ± 0.02
9.09	2.40 ± 0.08	0.56 ± 0.01
18.20	1.21 ± 0.03	0.16 ± 0.02

TABLE 3

Values of $k_{obs.}$ for the reaction $[AuCl(3NMe\text{-}pd)]^{2+} \longrightarrow [AuCl_4]^-$ at constant $[Cl^-]$ and variable $[H^+]$, $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]), and 25 °C

$10^2[Cl^-]$/ mol dm^{-3}	$10^2[H^+]$/ mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
2.72	18.20	1.24
	36.30	2.08
	63.60	2.92
	84.50	3.33
5.45	9.09	2.50
	18.20	3.98
	36.30	5.94
	63.60	7.40
9.09	9.09	5.00
	18.20	7.47
	36.30	10.60
	63.60	12.40
18.2	9.09	15.30
	18.20	20.50
	36.30	26.30
	63.60	28.50

TABLE 4

Values of the parameters B_0 and B_1 obtained from plots of $1/k_{obs.}$ against $1/[H^+]$ at constant $[Cl^-]$ using the values listed in Table 3. The parameters were obtained from a least-squares fit and quoted uncertainties are 95% confidence limits

$10^2[Cl^-]$/ mol dm^{-3}	$10^{-2}B_0$/s	$10^{-2}B_1$/ mol dm^{-3} s
2.72	15.96 ± 1.19	11.74 ± 0.37
5.45	9.23 ± 1.30	2.81 ± 0.20
9.09	6.08 ± 0.89	1.27 ± 0.14
18.20	2.98 ± 0.34	0.32 ± 0.05

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[11] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.

[12] G. Natile, G. Albertin, E. Bordignon, and A. A. Orio, *J.C.S. Dalton*, 1976, 626.

small. Moreover one experiment made at $[Cl^-] = 0.03$ mol dm^{-3} and various $[H^+]$ ($0.3 < [H^+] < 1.5$ mol dm^{-3}) has shown that equilibrium mixtures of (II)—(IV) of different compositions [ranging from (1) 2, (II) 58, (III) 3.5, and (IV) 36.5% to (I) 0.2, (II) 24, (III) 1.5, and (IV) 74.5%] do not give appreciable changes in absorbance near 280 nm. Therefore, knowing the value of the absorbance at low $[H^+]$ and $[Cl^-]$ ($A_{\min.}$) where (I) is the predominant species and the value of absorbance at high $[H^+]$ and $[Cl^-]$ ($A_{\max.}$) where species (II)—(IV) predominate, by measuring the actual absorbance (A_i) at the same wavelength (284 nm) as a function of $[H^+]$ and $[Cl^-]$, the value of K can be evaluated

$$(A_i - A_{\min.})/(A_{\max.} - A_i) = K[H^+][Cl^-](1 + K_1[Cl^-] + K_1K_2[H^+][Cl^-]) \quad (1)$$

from equation (1) (K_1 and K_2 being known from kinetic data).

Acid–Base Titrations.—The salt $[AuCl(3NMe\text{-}pd)]Cl_2$ behaves as an acid and can be titrated with sodium hydroxide. The titration was made in a beaker thermostatted at 25.0 ± 0.1 °C. A Metrohm Herisau model E500 digital pH meter, in conjunction with a glass electrode, was used to measure the pH. Immediately prior to the titrations the pH meter was standardized with buffer solutions at pH 3.56 (saturated potassium tartrate) and at pH 7.00 (50 cm^3 of 0.1 mol dm^{-3} $K[H_2PO_4]$ and 29.1 cm^3 of 0.1 mol dm^{-3} $Na[OH]$). A microburette (5 cm^3) was used to add the titrant (0.2 mol dm^{-3} $Na[OH]$) to the solution of the complex (*ca.* 5 mmol in 25 cm^3 of water). The volume change during the titration was less than 10%. Complex solutions containing 0.5 mol dm^{-3} NaCl in the first case and 0.5 mol dm^{-3} $Na[ClO_4]$ in the second were used.

RESULTS

Figure 1(*a*) gives the absorbance of a 3.5×10^{-4} mol dm^{-3} solution of $[AuCl(3NMe\text{-}pd)]^{2+}$ in 1.82×10^{-2} mol dm^{-3} LiCl and 10^{-3} mol dm^{-3} $HClO_4$ ($I = 1.7$ mol dm^{-3}, $Li[ClO_4]$). The presence of Cl^- prevents the hydrolysis of the metal–chlorine bond, and the acidic medium is required in order to suppress the protic dissociation of the co-ordinated amine groups. On increasing the $HClO_4$ concentration the absorption maximum at 314 nm first moved to higher wavelengths [until curve (*b*) was obtained] and then moved slightly towards lower wavelengths with further increase in the absorption coefficient [curves (*c*) and (*d*)]. The initial change, (*a*) to (*b*), is associated mainly with shifts in the equilibrium (2). Under the experimental conditions of

$$[AuCl(3NMe\text{-}pd)]^{2+}\ (I) \overset{K[H^+][Cl^-]}{\rightleftharpoons} [AuCl_2(3NMe\text{-}Hpd)]^{2+}\ (II) \quad (2)$$

curve (*b*) ($[HClO_4] = 0.3$ mol dm^{-3}) complex (I) has almost disappeared; (II), however, is not the only other species present since also $[AuCl_3(3NMe\text{-}Hpd)]^+$, (III), and $[AuCl_3(3NMe\text{-}H_2pd)]^{2+}$, (IV), with unidentate ligand, are formed to some extent [approximate composition of the equilibrium mixture in (*b*) is: (I), 4; (II), 68; (III), 2; (IV), 26%]. The spectral changes (*b*) to (*c*) to (*d*) are associated with shifts in the equilibria (3) [approximate composition of the

$$[AuCl_2(3NMe\text{-}Hpd)]^{2+}\ (II) \overset{K_1[Cl^-]}{\rightleftharpoons} [AuCl_3(3NMe\text{-}Hpd)]^+\ (III) \overset{K_2[H^+]}{\rightleftharpoons} [AuCl_3(3NMe\text{-}H_2pd)]^{2+}\ (IV) \quad (3)$$

equilibrium mixtures in (*c*) and (*d*) are: (I) 1, (II) 43, (III) 1.5, (IV) 54.5; and (I) 0.5, (II) 34, (III) 1, (IV) 64.5% respectively]. It is to be noted that under the experimental conditions of curves (*c*) and (*d*) the reaction $[AuCl_3(3NMe\text{-}H_2pd)]^{2+} \longrightarrow [AuCl_4]^-$ takes place causing the spectral changes (1)—(3) shown in Figure 1. Near 280 nm the changes in absorbance are mainly caused by shifts in equilibrium (2) and it is possible, by measuring the absorbance as a function of $[H^+]$ and $[Cl^-]$ (see Experimental section), to evaluate K which is found to be *ca.* 3×10^3 dm^6 mol^{-2}.

Similar behaviour was observed for the $[AuCl(3NH\text{-}pd)]^{2+}$ complex but, because of unfavourable spectral conditions, the constant of equilibrium (4) can only be estimated as $\geqslant 10^4$ dm^6 mol^{-2}.

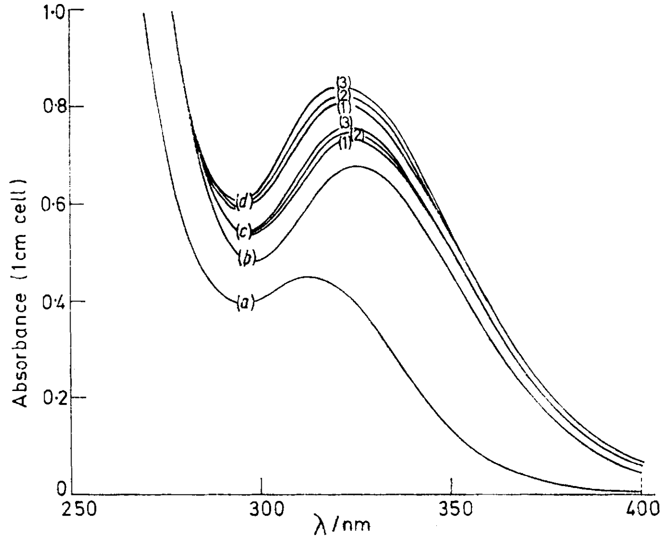

FIGURE 1 Absorption spectrum of 3.5×10^{-4} mol dm^{-3} $[AuCl(3NMe\text{-}pd)]^{2+}$ in 5% v/v water–methanol and $I = 1.7$ mol dm^{-3}, ($Li[ClO_4]$); $[Cl^-] = 1.82 \times 10^{-2}$ mol dm^{-3}; $[H^+] = 10^{-3}$ (*a*) 0.3 (*b*), 1.0 (*c*), and 1.5 mol dm^{-3} (*d*). Spectral changes (1)—(3) of (*c*) and (*d*) are associated with the reaction: $[AuCl_3(3NMe\text{-}H_2pd)]^{2+} + Cl^- + H^+ \longrightarrow [AuCl_4]^- + [3NMe\text{-}H_3pd]^{3+}$

$$[AuCl(3NH\text{-}pd)]^{2+} \overset{K[H^+][Cl^-]}{\rightleftharpoons} [AuCl_2(3NH\text{-}Hpd)]^{2+} \quad (4)$$

In both cases, under the experimental conditions of the kinetic runs, equilibrium (2) can be considered as completely shifted to the right. The spectroscopic course of the displacement reaction is shown in Figure 2 for 3NMe-pd. The presence of a well defined isosbestic point right from the beginning clearly indicates that the reaction occurs in a single step. The wavelength at which the isosbestic point occurs was not the same in different runs since the composition of the equilibrium mixture of (II)—(IV) varies as a function of $[H^+]$ and $[Cl^-]$. The final spectrum showed a peak at 317 nm which corresponds, apart from a small contribution from the ligand, to that of $[AuCl_4]^-$.[13]

Reaction of Displacement of 3NH-pd.—The observed rate constants are given in Table 1. At a given chloride concentration the reaction rate 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 acid concentration. These results are in accord with expression (5), where B_0 and B_1 are respectively the intercept

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[13] 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.

and gradient of the linear plot of $1/k_{\text{obs.}}$ against $1/[\text{H}^+]$ at constant $[\text{Cl}^-]$. Their values, calculated by least-squares fit, are given in Table 2.

$$k_{\text{obs.}} = [\text{H}^+]/(B_0[\text{H}^+] + B_1) \qquad (5)$$

These parameters depend on the concentration of chloride. A plot of $1/B_0$ against $[\text{Cl}^-]$ was linear and passed through the origin (Figure 3). The gradient $[1/r$ in equation (6)] is $(4.47 \pm 0.14) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. Also, B_1 decreased as $[\text{Cl}^-]$ increased but with a more complex dependence than B_0. A plot of $B_1[\text{Cl}^-]$ against $1/[\text{Cl}^-]$

$$B_0 = r/[\text{Cl}^-] \qquad (6)$$

(Figure 4) gave a straight line with intercept $t = 0.89 \pm 0.13$ mol^2 dm^{-6} s and gradient $s = 0.38 \pm 0.01$ mol^3 dm^{-9} s, indicating that the dependence of B_1 on chloride has the form (7).

$$B_1 = (s + t[\text{Cl}^-])/[\text{Cl}^-]^2 \qquad (7)$$

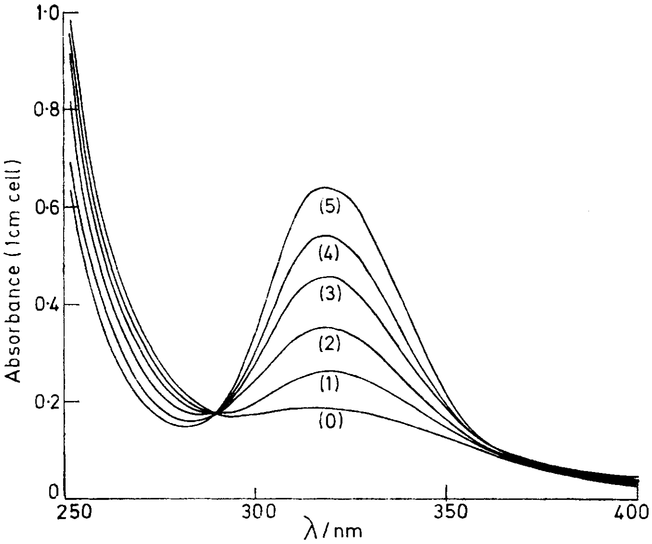

FIGURE 2 Spectroscopic course of the reaction $[\text{AuCl(3NMe-pd)}]^{2+} + 3\text{Cl}^- + 3\text{H}^+ \longrightarrow [\text{AuCl}_4]^- + [\text{3NMe-H}_3\text{pd}]^{3+}$. $[\text{AuCl(3NMe-pd)}^{2+}]_0 = 10^{-4}$, $[\text{H}^+] = 0.363$, $[\text{Cl}^-] = 2.82 \times 10^{-2}$, $I = 1.7$ mol dm^{-3} (Li[ClO$_4$]), 25 °C. Curves (0)—(5) show spectra at zero time and after 15, 36, 70, 120, and 300 min respectively

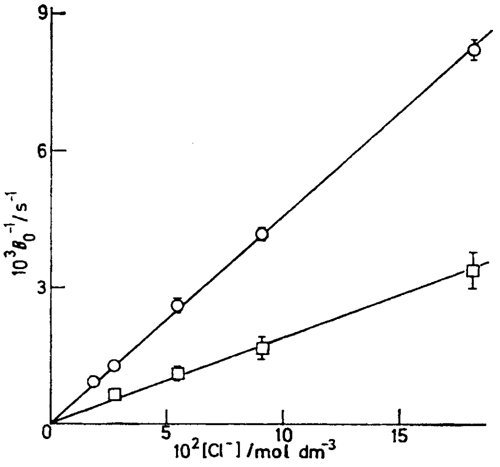

FIGURE 3 Dependence of $1/B_0$ (see text) on $[\text{Cl}^-]$. Circles and squares refer to the reactions $[\text{AuCl(3NH-pd)}]^{2+} + 3\text{Cl}^- + 3\text{H}^+ \longrightarrow [\text{AuCl}_4]^- + [\text{3NH-H}_3\text{pd}]^{3+}$ and $[\text{AuCl(3NMe-pd)}]^{2+} + 3\text{Cl}^- + 3\text{H}^+ \longrightarrow [\text{AuCl}_4]^- + [\text{3NMe-H}_3\text{pd}]^{3+}$ respectively

From equations (5)—(7) we can write expression (8) for the overall dependence of $k_{\text{obs.}}$ on $[\text{H}^+]$ and $[\text{Cl}^-]$.

$$k_{\text{obs.}} = [\text{H}^+][\text{Cl}^-]^2/(r[\text{Cl}^-][\text{H}^+] + s + t[\text{Cl}^-]) \qquad (8)$$

Reaction of Displacement of 3*NMe-pd*.—The observed rate constants are given in Table 3. A plot of the reciprocal of the rate constant against the reciprocal of the hydrogen-ion concentration was also linear and the B_0 and B_1 parameters [equation (5)] obtained by least-squares fit are given in Table 4. The dependence of B_0 on $[\text{Cl}^-]$ was determined by plotting the reciprocal of B_0 against the chloride concentration; a straight line with zero intercept and gradient $1/r$ [equation (6), Figure 3] was obtained; the value of $1/r$ is $(1.77 \pm 0.27) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. The dependence of B_1 on $[\text{Cl}^-]$ is also analogous to that found with the 3NH-pd derivative [equation (7), Figure 4]; values of t and s estimated from the plot of $B_1[\text{Cl}^-]$ against $1/[\text{Cl}^-]$ are 1.56 ± 0.98 mol^2 dm^{-6} s and 0.82 ± 0.31 mol^3 dm^{-9} s respectively.

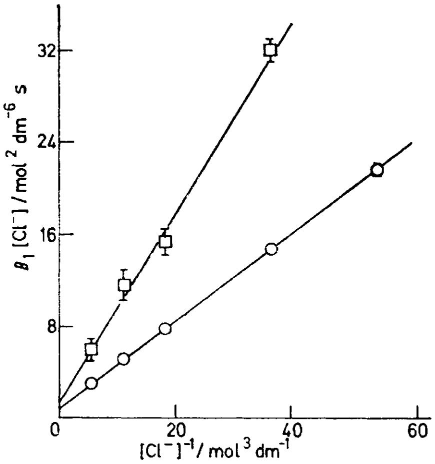

FIGURE 4 Dependence of B_1 $[\text{Cl}^-]$ on $1/[\text{Cl}^-]$. For key see Figure 3

Deprotonation of Co-ordinated 3*NMe-pd*.—The pK_a of equilibrium (9) in 0.5 mol dm^{-3} Na[ClO$_4$] and in 0.5 mol dm^{-3} NaCl was determined.

$$[\text{AuCl(3NMe-pd)}]^{2+} \overset{K_a}{\rightleftharpoons} [\text{AuCl(3NMe-pd—H)}]^+ + \text{H}^+ \qquad (9)$$

A potentiometric titration of $[\text{AuCl(3NMe-pd)}]^{2+}$ with sodium hydroxide gave a distinct end-point after the addition of exactly one equivalent of base per mole of substrate. During the titration the colour of the solution changed from yellow to reddish brown and the pH rose above 7 at the equivalence point. Further addition of base did not cause a sharp increase in pH and no further distinct end-points could be detected. As observed for analogous gold complexes, reduction [7] or the formation of other amido-species probably occurs.[14] The determined pK_a values are 5.7 ± 0.1 in 0.5 mol dm^{-3} Na[ClO$_4$] and 6.8 ± 0.1 in 0.5 mol dm^{-3} NaCl.

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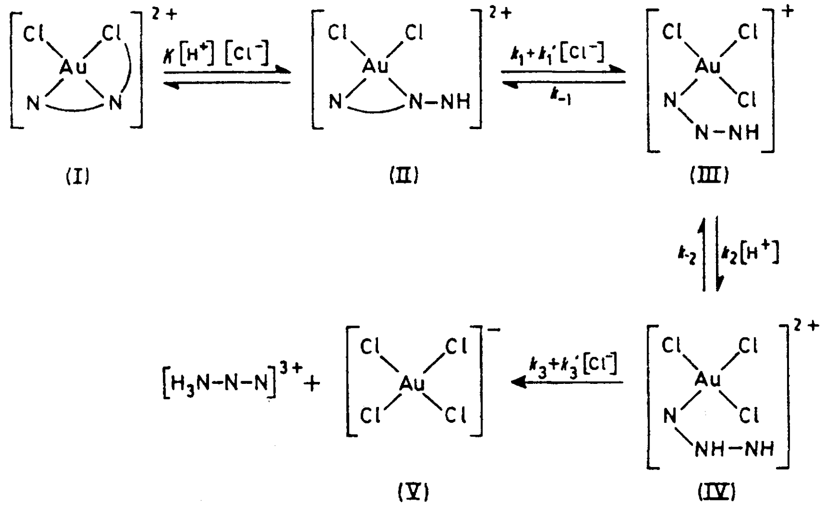
[14] W. H. Baddley and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1087.

DISCUSSION

The experimentally determined rate equation is completely analogous to that found in the displacement of teen and tmen from $[AuCl_2(N{-}N)]^+$ complexes and a similar mechanism can therefore be invoked. The equilibrium (I) $\rightleftharpoons$ (II) is completely shifted to the right under the experimental conditions of the kinetic runs and it therefore does not influence the reaction rate. There is direct spectroscopic evidence that species (II)—(IV) are in equilibrium and, making this assumption, equation (10) may be deduced for the observed rate constant. A direct step (III) $\longrightarrow$ (V) has been ruled out since in this case an additional term independent of $[H^+]$ would appear in the numerator of expression (10), and under these circumstances the observed rate constant would not tend to zero (as observed) as the hydrogen-ion concentration tended to zero. Steps (II) $\longrightarrow$ (III) and (IV) $\longrightarrow$ (V) have been written in the general form for substitution reactions in square-planar complexes, although it will be seen later that k_1 and k_3 are not detectable.

$$k_{\text{obs.}} = \frac{(k_1 + k_1'[\text{Cl}^-])(k_3 + k_3'[\text{Cl}^-])k_2[\text{H}^+]}{k_{-1}k_{-2} + (k_1 + k_1'[\text{Cl}^-])k_{-2} + (k_1 + k_1'[\text{Cl}^-])k_2[\text{H}^+]} \qquad (10)$$



If the steady-state approximation, instead of pre-equilibrium, is made for species (III) and (IV) equation (11) is obtained for the rate constant. In

$$k_{\text{obs.}} = \frac{(k_1 + k_1'[\text{Cl}^-])(k_3 + k_3'[\text{Cl}^-])k_2[\text{H}^+]}{k_{-1}k_{-2} + (k_3 + k_3'[\text{Cl}^-])k_{-1} + (k_3 + k_3'[\text{Cl}^-])k_2[\text{H}^+]} \qquad (11)$$

equations (10) and (11) the dependence of $k_{\text{obs.}}$ on $[H^+]$ and $[Cl^-]$ is formally the same and both expressions are in accord with the experimental rate equation; however, not all the kinetic constants which appear in the denominators of (10) and (11) are the same. Equation (11) was adopted in the interpretation of the kinetic data for the displacement of the bidentate ligands teen and tmen from their $[AuCl_2(N{-}N)]^+$ complexes; in the light of the present results, however, equation (10) would seem to be more appropriate and in the following discussion a direct comparison between the displacement of tridentate (3NH- or 3NMe-pd) and bidentate ligands (teen or tmen) will be made.

From equations (5) and (10) expressions (12) and (13) may be obtained for B_0 and B_1 respectively. The observation that B_0 is inversely proportional to $[Cl^-]$ indicates that k_3 is extremely small and its contribution to

$$B_0 = (k_3 + k_3'[\text{Cl}^-])^{-1} \qquad (12)$$

$$B_1 = \frac{k_{-1}k_{-2} + (k_1 + k_1'[\text{Cl}^-])k_{-2}}{(k_1 + k_1'[\text{Cl}^-])(k_3 + k_3'[\text{Cl}^-])k_2} \qquad (13)$$

the reaction rate is insignificant. Assuming $k_3 = 0$ equation (13) can be rewritten as (14), and a plot of $1/B_1[Cl^-]$ against $[Cl^-]$ should give a curve with intercept (at $[Cl^-] = 0$) $k_1k_3'k_2/(k_{-1}k_{-2} + k_1k_{-2})$ and approaching a limiting value as the chloride concentration increases.

$$\frac{1}{B_1[\text{Cl}^-]} = \frac{(k_1 + k_1'[\text{Cl}^-])k_3'k_2}{k_{-1}k_{-2} + (k_1 + k_1'[\text{Cl}^-])k_{-2}} \qquad (14)$$

Since this intercept appeared to be zero, we can assume that k_1 is also insignificant compared with $k_1'[Cl^-]$. Assuming $k_1 = 0$, equation (14) gives (15) and a plot of $B_1[Cl^-]$ against $1/[Cl^-]$ should be a straight line (as is actually observed) with gradient $s = k_{-1}k_{-2}/k_1'k_2k_3'$ and

$$B_1[\text{Cl}^-] = \frac{k_{-1}k_{-2} + k_1'k_{-2}[\text{Cl}^-]}{k_1'k_2k_3'[\text{Cl}^-]} \qquad (15)$$

intercept $t = k_{-2}/k_2k_3'$. From the values of r, s, and t the kinetic constant $k_3' = 1/r$ and the equilibrium constants $k_1'/k_{-1} = K_1 = t/s$ and $k_2/k_{-2} = K_2 = r/t$ were calculated (Table 5). The analogous constants calculated from the values of r, s, and t for the complexes $[AuCl_2(\text{teen})]^+$ and $[AuCl_2(\text{tmen})]^+$ are also included in Table 5.

The k_3' values of the complexes (Table 5) do not change significantly on going from 3NMe-pd to 3NH-pd and from teen to tmen; however, the constants are about ten times smaller for the tridentate ligands than for the bidentate ones. This difference can be related to the different nature of the donor group which is a primary amine in 3NH-pd and 3NMe-pd and a tertiary amine in teen and tmen. Considering the basicity of the groups displaced in this step [$Et_2(H)\overset{+}{N}\cdot CH_2\cdot CH_2\cdot NEt_2$, $Me_2(H)\overset{+}{N}\cdot CH_2\cdot CH_2\cdot NMe_2$, $H_3\overset{+}{N}\cdot CH_2\cdot CH_2\cdot \overset{+}{N}(H_2)\cdot CH_2\cdot CH_2\cdot NH_2$, and $H_3\overset{+}{N}\cdot CH_2\cdot CH_2\cdot \overset{+}{N}Me(H)\cdot CH_2\cdot CH_2\cdot NH_2$] one finds that log K_b of the first two amines is 6.45 and 5.94 respectively;[15] the corresponding values for the last two amines cannot be measured (the terminal nitrogen atom is more basic than the central one), but should not be much different from that of $H_3\overset{+}{N}\cdot CH_2\cdot CH_2\cdot NH_2$ which is 7.47.[16] In addition to the effect of basicity, the higher steric hindrance of the tertiary amines, when compared to that of primary amines, could also be the cause of their higher reactivity. The values of k_3' can be compared with the rate constant for displacement of nitrogen bases (am) from complexes of the type [$AuCl_3(am)$],[17] and, as expected, they fall in the same range.

TABLE 5

Values of the kinetic constants of equation (10) derived (see text) from results in Tables 2 and 4 and data from ref. 2

Complex	$10^2k_3'$ dm^3 mol^{-1} s^{-1}	(k_1'/k_{-1}) dm^3 mol^{-1}	(k_2/k_{-2}) dm^3 mol^{-1}
$[AuCl(3NH\text{-}pd)]^{2+}$	4.47 ± 0.13	2.4 ± 0.7	25.2 ± 3.7
$[AuCl(3NMe\text{-}pd)]^{2+}$	1.76 ± 0.26	1.9 ± 1.2	36.4 ± 7.7
$[AuCl_2(teen)]^+$	18.8 ± 2.3	3.1 ± 0.8	16.1 ± 4.4
$[AuCl_2(tmen)]^+$	37.0 ± 15	*ca.* 0.5	*ca.* 15.1

The equilibrium constants, $K_1 = k_1'/k_{-1}$, are of the same order of magnitude in the present complexes and their values indicate that the equilibrium between the uni- and bi-dentate forms of the ligand is not greatly shifted in favour of one of the two species. This result would appear to be in contrast with the well known chelate effect;[18] however we are dealing with rather peculiar ligands. The ligands teen and tmen have tertiary amine groups and it has been already shown that on increasing the N-alkyl substitution the rate of reformation of the second bond (k_{-1}) decreases and that of bond rupture (k_1') slightly increases.[15] Apparently, teen does not co-ordinate to Ni^{II} and evidence for the unidentate behaviour of *NN*-diethylethylenediamine towards the same metal ion has been produced. Moreover, in the reaction of tmen with Ni^{II} the ring-closing and ring-opening rates were found to differ only by one order of magnitude. The same steric arguments apply to the complexes of 3NMe-pd and, to some extent, to those of 3NH-pd. In addition, the presence in the latter cases of one adjacent protonated amine group [see intermediate (II) in the reaction scheme], lowering the basicity of the co-ordinated nitrogen, enhances the k_1' value.

The equilibrium constant for protonation of the free end of the polydentate ligand, (III) $\rightleftharpoons$ (IV), is $K_2 = k_2/k_{-2}$. The calculated values of K_2 (Table 5) fall in the same range for all the complexes considered here and are much smaller than those measured for the unco-ordinated ligands (log K_b for $[Hteen]^+$, $[Htmen]^+$, $[3NH\text{-}H_2pd]^{2+}$, and $[3NMe\text{-}H_2pd]^{2+}$ are 6.45, 5.94, 4.6, and 3.1 respectively[15,19]). Among other factors, this could be due to the greater steric hindrance exerted by the metallic residue when compared with that of a proton.

In the reaction scheme we have assumed that in step (II) → (III) the central nitrogen atom, and not the terminal one, is displaced from the metal. In the terminal case we would expect: (*i*) k_3' of the same magnitude in the four complexes; (*ii*) K_1 larger in the teen and tmen complexes than in those of 3NH-pd and 3NMe-pd; and (*iii*) K_2 larger in the 3NH-pd and 3NMe-pd complexes than in those of teen and tmen. All three conclusions are in contrast with the experimental results, which support the assumption that the central nitrogen is displaced first.

So far we have discussed the behaviour of the triamine complexes of Au^{III} in highly acidic chloride solutions. For completeness we must say that in less acidic media deprotonation of the co-ordinated amine occurs. Data concerning the deprotonation of 3NH-pd in $[AuCl(3NH\text{-}pd)]^{2+}$ have been reported by Baddley *et al.*[9]; we have measured the equilibrium constant for deprotonation of 3NMe-pd in the analogous complex. In Table 6 the pK_a values of different co-ordinated amines are compared. It appears that the major differences in these values occur between the different types of acidic nitrogens; in particular on going from primary to secondary nitrogen atoms the pK_a increases by approximately two units. This comparison must be made between data obtained under the same conditions since an anomalous enhancement of pK_a was observed in the presence of co-ordinating ions.[20]

TABLE 6

Acid strengths of some amines co-ordinated to Au^{III}

Complex	pK_a	pK_a([X^-] = 0.5 mol dm^{-3})	Ref.
$[AuCl(3NH\text{-}pd)]^{2+}$	4.0	4.7 (Cl^-)	9
$[AuBr(3NH\text{-}pd)]^{2+}$	4.5	5.2 (Br^-)	9
$[Au(en)_2]^{3+}$	6.3	7.2 (Cl^-)	*a*
$[AuCl(3NMe\text{-}pd)]^{2+}$	5.7	6.8 (Cl^-)	*b*

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