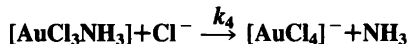
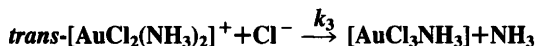
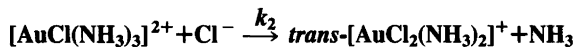
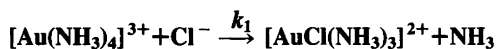


## Amineanionogold(III) Complexes. V. Kinetics of the Consecutive Substitutions of Ammonia by Chloride in Tetraamminegold(III) Ion in Acidic Aqueous Solution

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The replacement of ammonia in tetraamminegold(III) by chloride occurs *via* the following consecutive reactions:



In acidic solution the ligand substitutions take place as direct displacement and no solvent paths were detectable. Second-order rate constants, activation enthalpies and activation entropies at 25.0 °C and unit ionic strengths are:

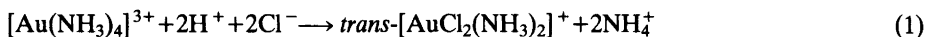
$$k_1 = 0.36 \pm 0.02 \text{ l mol}^{-1} \text{ s}^{-1}, \Delta H_1^\ddagger = 81 \pm 2 \text{ kJ mol}^{-1}, \Delta S_1^\ddagger = 20 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$k_2 = 0.112 \pm 0.002 \text{ l mol}^{-1} \text{ s}^{-1}, \Delta H_2^\ddagger = 78 \pm 1 \text{ kJ mol}^{-1}, \Delta S_2^\ddagger = -1 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$k_3 = (3.7 \pm 0.5) \times 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}, \Delta H_3^\ddagger = 105 \pm 4 \text{ kJ mol}^{-1}, \Delta S_3^\ddagger = 2 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$k_4 = (3.33 \pm 0.02) \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}, \Delta H_4^\ddagger = 97 \pm 2 \text{ kJ mol}^{-1}, \Delta S_4^\ddagger = -7 \pm 4 \text{ kJ mol}^{-1} \text{ K}^{-1}.$$

Two distinct stages with rates differing by five orders of magnitude were observed in the anation of tetraamminegold(III) by bromide.<sup>1,2</sup> The first stage giving the product diamminedibromidogold(III), isolated as the bromide salt and shown by an X-ray single-crystal structure determination to have the *trans*-configuration,<sup>3</sup> consists of two consecutive reactions of comparable rates, whereas in the second and slower stage the two consecutive reactions are well separated. From preparative work,<sup>4</sup> the reaction between tetraamminegold(III) and chloride is known also to occur in two separate stages:



In order to provide a better background for a discussion of the role of reacting- and non-reacting ligands in determining the rate of ligand substitutions in gold(III), we have undertaken an investigation of the kinetics of the anation of tetraamminegold(III) by chloride under conditions similar to those employed previously for the anation by bromide.

## EXPERIMENTAL

**Materials.** Potassium tetrachloridoaurate(III) from H. Drijfhout and Zoon's, Amsterdam, was used as the starting material for the gold compounds  $\text{Rb}[\text{AuCl}_4]$ ,<sup>5</sup>  $[\text{AuCl}_3\text{NH}_3]$ ,<sup>6</sup>  $\text{trans-}[\text{AuCl}_2(\text{NH}_3)_2]\text{Cl} \cdot \frac{1}{3} \text{H}_2\text{O}$ ,<sup>4</sup>  $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ ,<sup>7</sup> and  $[\text{Au}(\text{NH}_3)_4](\text{ClO}_4)_3$ ,<sup>7</sup> which were prepared and purified according to published procedures. Gold was determined spectrophotometrically after conversion to the tetrachloridoaurate(III) ion:  $(\lambda, \epsilon)_{\text{max}} = (313 \text{ nm}, 5360 \pm 10 \text{ l mol}^{-1} \text{ cm}^{-1})$  in 0.10 M hydrochloric acid. Absorption spectra in the UV region for the relevant gold complexes are shown in Fig. 1. Other chemicals were of analytical grade. Stock solutions of hydrochloric acid, perchloric acid, sodium chloride and sodium perchlorate were analyzed using standard methods.

**Spectrophotometric measurements** were performed on a Zeiss DMR 21 spectrophotometer with thermostatted cell-holder and cell compartment.

**Kinetic measurements.** The investigated sequence of reactions of tetraamminegold(III) with chloride was monitored spectrophotometrically. The first reaction step was investigated using the "stopped flow" technique previously described.<sup>1</sup> For the second and slower step, aliquots of the reaction mixture in sealed ampoules were left in a thermostatted waterbath and removed after known intervals, and spectra were subsequently recorded at room temperature.

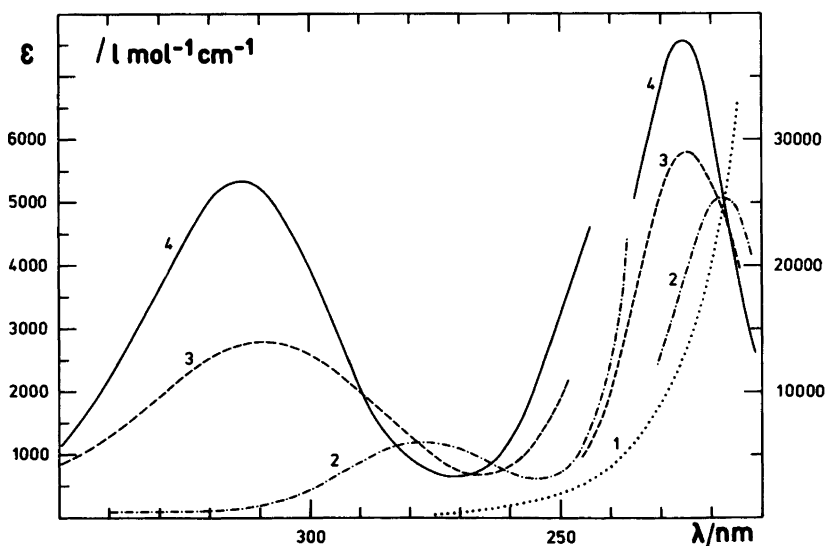


Fig. 1. Absorption spectra of chloroamminegold(III) complexes in aqueous solution at 25 °C. 1:  $[\text{Au}(\text{NH}_3)_4](\text{ClO}_4)_3$  in 1.0 M  $\text{HClO}_4$ ; 2:  $\text{trans-}[\text{AuCl}_2(\text{NH}_3)_2]\text{Cl} \cdot \frac{1}{3} \text{H}_2\text{O}$  in 0.10 M  $\text{HCl} + 0.90 \text{ M HClO}_4$ ; 3:  $[\text{AuCl}_3\text{NH}_3]$  in 0.10 M  $\text{HCl} + 0.90 \text{ M HClO}_4$ ; 4:  $\text{Rb}[\text{AuCl}_4]$  in 0.10 M  $\text{HCl} + 0.90 \text{ M HClO}_4$ .

Table 1. Pseudo first-order rate constants for the consecutive substitution reactions  $[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Cl}^- \xrightarrow{k_1} [\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{NH}_3$  and  $[\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{Cl}^- \xrightarrow{k_2} \text{trans-}[\text{AuCl}_2(\text{NH}_3)_2]^+ + \text{NH}_3$  in acidic aqueous solution.

No.	$t$ /°C	$[\text{Cl}^-]/\text{M}$	pH	$I^a/\text{M}$	$k_1/\text{s}^{-1}$	$k_2/\text{s}^{-1}$	$r(k'_1, k'_2)^b$
1	0.9	0.015	1.83	0.015	$1.71(8) \times 10^{-3}$	$6.1(4) \times 10^{-4}$	-0.925
2	0.9	0.020	1.70	0.020	$2.0(1) \times 10^{-3}$	$7.6(3) \times 10^{-4}$	-0.934
3	0.9	0.025	1.60	0.025	$2.5(3) \times 10^{-3}$	$9.3(8) \times 10^{-4}$	-0.946
4	0.9	0.035	1.46	0.035	$2.7(4) \times 10^{-3}$	$1.3(3) \times 10^{-3}$	-0.958
5	0.9	0.040	1.40	0.040	$2.4(3) \times 10^{-3}$	$1.2(4) \times 10^{-3}$	-0.974
6	0.9	0.060	1.22	0.060	$3.8(4) \times 10^{-3}$	$1.4(1) \times 10^{-3}$	-0.934
7	0.9	0.100	-0.7	5.1	$2.2(2) \times 10^{-3}$	$1.01(5) \times 10^{-3}$	-0.959
8	0.9	0.025	0.00	1.0	$4.6(6) \times 10^{-4}$	$1.6(2) \times 10^{-4}$	-0.924
9	0.9	0.050	0.00	1.0	$7.2(6) \times 10^{-4}$	$3.0(2) \times 10^{-4}$	-0.938
10	0.9	0.075	0.00	1.0	$1.3(2) \times 10^{-3}$	$4.2(4) \times 10^{-4}$	-0.915
11	0.9	0.100	0.00	1.0	$1.9(3) \times 10^{-3}$	$5.2(1) \times 10^{-4}$	-0.879
12	0.9	0.150	0.00	1.0	$3.2(3) \times 10^{-3}$	$8.5(1) \times 10^{-4}$	-0.885
13 <sup>c</sup>	0.9	0.150	0.30	1.0	$2.5(2) \times 10^{-3}$	$8.9(2) \times 10^{-4}$	-0.940
14 <sup>d</sup>	0.9	0.150	0.82	1.0	$2.6(4) \times 10^{-3}$	$7.0(6) \times 10^{-4}$	-0.921
15	0.9	0.20	0.00	1.0	$4.5(5) \times 10^{-3}$	$1.08(4) \times 10^{-3}$	-0.844
16	15.1	0.025	0.00	1.0	$3.0(4) \times 10^{-3}$	$9.1(3) \times 10^{-4}$	-0.917
17	18.0	0.025	0.00	1.0	$4.2(5) \times 10^{-3}$	$1.26(2) \times 10^{-3}$	-0.931
18	25.0	0.025	0.00	1.0	$8.8(8) \times 10^{-3}$	$2.85(5) \times 10^{-3}$	-0.935

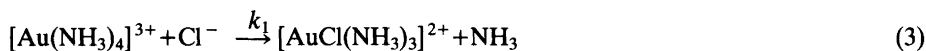
<sup>a</sup> Ionic strength adjusted with perchloric acid, except in experiments Nos. 13 and 14.

<sup>b</sup>  $r(k'_1, k'_2)$  is the correlation coefficient between the two rate constants. <sup>c</sup>  $[\text{Na}^+] = 0.50 \text{ M}$ . <sup>d</sup>  $[\text{Na}^+] = 0.85 \text{ M}$ .

Calculation of rate constants and activation parameters was carried out within the framework of non-linear regression analysis using the numerical procedures described previously.<sup>1</sup>

## RESULTS

In acidic aqueous chloride solution at ambient temperature tetraamminegold(III) nitrate reacts cleanly yielding a product which only slowly undergoes further reaction. This product was identified from its UV-absorption spectrum as *trans*-[AuCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>,<sup>4</sup> cf. eqn. (1), and using the numerical methods discussed previously in detail,<sup>1</sup> the kinetics for the formation of *trans*-[AuCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> from [Au(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup> were found to be consistent with the occurrence of two consecutive reactions of comparable rates when chloride is present in excess:



All experiments were performed with an excess of chloride ion sufficient to ensure pseudo first-order conditions for the reactions of eqns. (3) and (4) ( $c_{\text{Au}} \approx 10^{-3}$  M, see Table 1), and the pseudo first-order rate constants were calculated from spectral changes at the wavelengths 260, 270, 280, and 290 nm by non-linear regression analysis according to the biexponential expression<sup>1</sup>

$$A_\lambda(t) = a_\lambda + b_\lambda e^{-k'_1 t} + c_\lambda e^{-k'_2 t} \quad (5)$$

The result of this numerical analysis of experimental data for different temperatures, chloride-ion concentrations, solution pH and ionic strengths may be found in Table 1, from

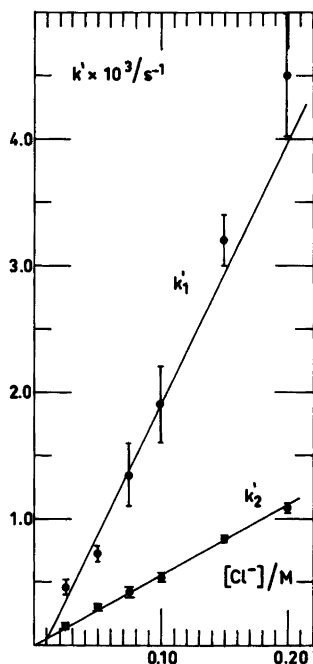


Fig. 2. Pseudo first-order rate constants for the two consecutive reactions  $[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Cl}^- \xrightarrow{k_1} [\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{NH}_3$  and  $[\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{Cl}^- \xrightarrow{k_2} \textit{trans}\text{-}[\text{AuCl}_2(\text{NH}_3)_2]^+ + \text{NH}_3$  as a function of chloride concentration at 0.9 °C and ionic strength 1.0. The bars indicate one standard deviation.

which it may further be seen that the pseudo first-order rate constants for each reaction at a fixed temperature and ionic strength are proportional to the chloride-ion concentration ( $0.025 \leq [\text{Cl}^-] \leq 0.20 \text{ M}$ , see Fig. 2), but show no significant dependence on the hydrogen-ion concentration ( $0.15 \leq [\text{H}^+] \leq 1.0 \text{ M}$ ).

As previously discussed,<sup>1</sup> a so-called "slow-fast" ambiguity arises for consecutive kinetics when the reactions have comparable rates. The assignment made in Table 1 and Fig. 2, viz. that the replacement of the first ammonia ligand in tetraamminegold(III) by chloride is faster than the replacement of the second, has been based on the ionic strength dependence of the rates of the two reactions. In the reaction of eqn. (3) a tripositive ion is reacting with chloride, whereas in the reaction of eqn. (4) a dipositive ion is the substrate. The faster of the two reactions was found to depend more strongly on the ionic strength than the slower, and what is more significant, in the ionic strength region in which Davies' equation is normally considered to be valid,<sup>8</sup> the ionic strength dependence for the fast reaction agrees with that predicted for a tripositive ion reactivity with chloride. The ionic strength dependence for the slow reaction also agrees with that predicted for a dipositive ion, as can be seen from Fig. 3.

*trans*-Dichlorodiamminegold(III) chloride was found to undergo further anation when chloride was present in larger excess yielding tetrachloridoaurate(III), as identified from the UV-absorption spectrum of the final anation-product. This second and slower step in the chloride-anation sequence for tetraamminegold(III) was, like the first and faster step, found to consist of two consecutive reactions of comparable rates [eqns. (6) and (7)].

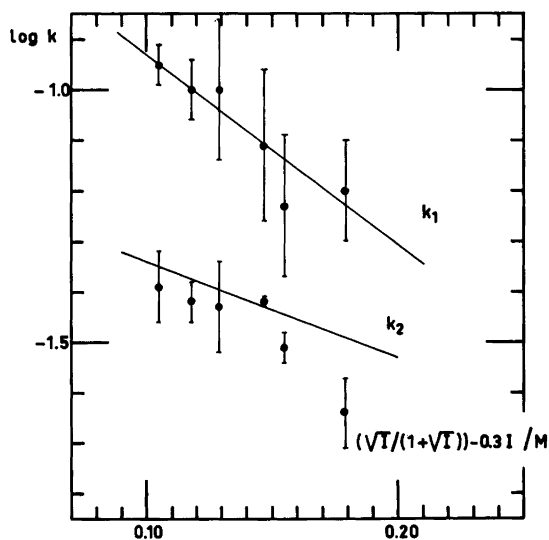


Fig. 3. Second-order rate constants (in  $\text{l mol}^{-1}\text{s}^{-1}$ ) for the two consecutive reactions  $[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Cl}^- \xrightarrow{k_1} [\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{NH}_3$  and  $[\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{Cl}^- \xrightarrow{k_2} \text{trans-}[\text{AuCl}_2(\text{NH}_3)_2]^+ + \text{NH}_3$  at  $0.9^\circ\text{C}$  as a function of ionic strength plotted according to  $\log k = \log k^\circ + 2 \times 0.49 \times z_+ z_- [\sqrt{I}/(1 + \sqrt{I}) - 0.3 \times I]$ .<sup>8</sup> The slope,  $2 \times 0.49 \times z_+ z_-$ , is 3.0 for the fast reaction and 1.9 for the slow reaction, respectively, indicating that chloride is reacting with a tripositive substrate in the fast reaction and with a dipositive substrate in the slow reaction, respectively.

Table 2. Pseudo first-order rate constants for the substitution reaction  $trans-[AuCl_2(NH_3)_2]^+ + Cl^- \xrightarrow{k_3} [AuCl_3NH_3] + NH_3$  in acidic aqueous solution.

No.	<i>t</i> / °C	[Cl <sup>-</sup> ]/M	pH	<i>I</i> <sup>o</sup> /M	<i>k</i> <sub>3</sub> /s <sup>-1</sup>
1	88.0	0.0100	2.00	0.010	2.13(3) × 10 <sup>-4</sup>
2	88.0	0.0500	1.30	0.050	7.2 (2) × 10 <sup>-4</sup>
3	88.0	0.0500	1.00	0.10	6.6 (2) × 10 <sup>-4</sup>
4	88.0	0.0500	0.00	1.00	4.0 (2) × 10 <sup>-4</sup>
5	88.0	0.0500	-0.7	5.00	3.23(8) × 10 <sup>-4</sup>
6	69.0	0.33	0.00	1.00	3.0 (1) × 10 <sup>-4</sup>
7	69.0	0.50	0.00	1.00	5.0 (2) × 10 <sup>-4</sup>
8	69.0	0.67	0.00	1.00	5.9 (3) × 10 <sup>-4</sup>
9 <sup>b</sup>	69.0	0.67	0.48	1.00	5.8 (3) × 10 <sup>-4</sup>
10 <sup>c</sup>	69.0	0.67	0.48	1.00	5.8 (3) × 10 <sup>-4</sup>
11	69.0	1.00	0.00	1.00	9.4 (3) × 10 <sup>-4</sup>
12	65.0	1.00	0.00	1.00	5.8 (2) × 10 <sup>-4</sup>
13	58.0	1.00	0.00	1.00	2.97(8) × 10 <sup>-4</sup>
14	51.0	1.00	0.00	1.00	1.12(4) × 10 <sup>-4</sup>

<sup>a</sup> Ionic strength adjusted with perchloric acid, except in experiments Nos. 9 and 10. <sup>b</sup> [NH<sub>4</sub><sup>+</sup>]=0.67 M. <sup>c</sup> [Na<sup>+</sup>]=0.67 M.



The rate constant for the reaction of eqn. (7) at different temperatures, chloride-ion concentrations, solution pH and ionic strengths was determined in experiments in which the well-characterized<sup>6</sup> compound [AuCl<sub>3</sub>NH<sub>3</sub>] (*c*<sub>Au</sub> ≈ 10<sup>-4</sup> M) was allowed to react with an excess of chloride. Simple first order kinetics were observed in all cases (monitored from spectral changes at 300, 310, 320, and 330 nm), and the pseudo first-order rate constants were found to be proportional to the chloride-ion concentration (0.10 ≤ [Cl<sup>-</sup>] ≤ 1.0 M) but

Table 3. Pseudo first-order rate constants for the substitution reaction  $[AuCl_3NH_3] + Cl^- \xrightarrow{k_4} [AuCl_4]^-$  in acidic aqueous solution.

No.	<i>t</i> / °C	[Cl <sup>-</sup> ]/M	pH	<i>I</i> <sup>o</sup> /M	<i>k</i> <sub>4</sub> /s <sup>-1</sup>
1	88.0	0.0100	2.00	0.010	5.88(7) × 10 <sup>-4</sup>
2	88.0	0.0100	1.30	0.050	5.63(8) × 10 <sup>-4</sup>
3	88.0	0.0100	1.00	0.100	5.51(7) × 10 <sup>-4</sup>
4	88.0	0.0100	0.00	1.00	4.87(5) × 10 <sup>-4</sup>
5	88.0	0.0100	-0.7	5.00	2.87(3) × 10 <sup>-4</sup>
6	69.0	0.10	0.00	1.00	5.53(7) × 10 <sup>-4</sup>
7	65.0	0.10	0.00	1.00	3.87(5) × 10 <sup>-4</sup>
8	57.9	0.10	0.00	1.00	1.85(3) × 10 <sup>-4</sup>
9	37.1	0.10	0.00	1.00	1.58(2) × 10 <sup>-5</sup>
10	37.1	0.40	0.00	1.00	7.3 (1) × 10 <sup>-5</sup>
11	37.1	0.60	0.00	1.00	9.7 (1) × 10 <sup>-5</sup>
12	37.1	0.80	0.00	1.00	1.37(2) × 10 <sup>-4</sup>
13	37.1	1.00	0.00	1.00	1.63(2) × 10 <sup>-4</sup>
14 <sup>b</sup>	37.1	1.00	0.10	1.00	1.60(2) × 10 <sup>-4</sup>
15 <sup>c</sup>	37.1	1.00	0.10	1.00	1.61(2) × 10 <sup>-4</sup>

<sup>a</sup> Ionic strength adjusted with perchloric acid, except in experiments Nos. 14 and 15. <sup>b</sup> [NH<sub>4</sub><sup>+</sup>]=0.20 M. <sup>c</sup> [Na<sup>+</sup>]=0.20 M.

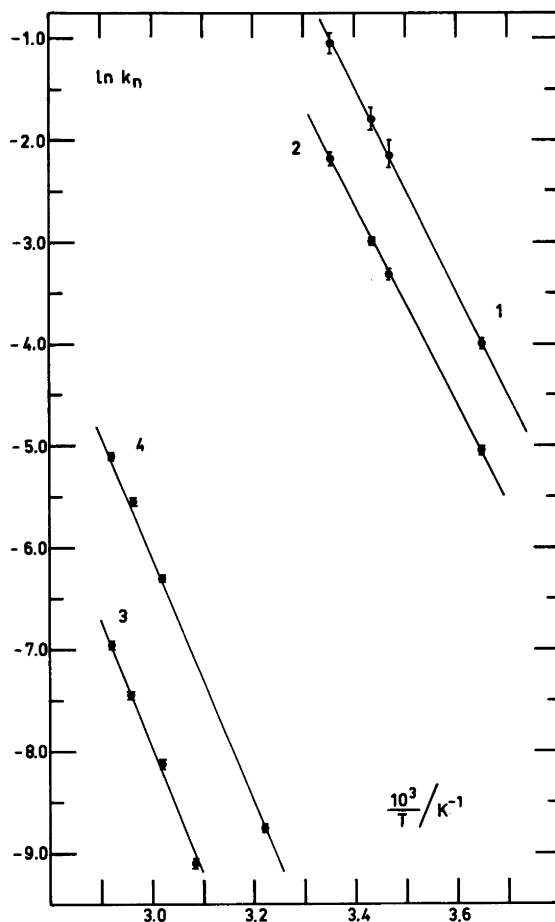


Fig. 4. Arrhenius-type plots for each of the four consecutive replacements of ammonia by chloride in  $[\text{Au}(\text{NH}_3)_4]^{3+}$  in acidic aqueous solution of unit ionic strength:  $k_n$ :  $n=1, 2, 3$ , or  $4$ ; in  $\text{l mol}^{-1}\text{s}^{-1}$ . The bars indicate one standard deviation.

independent of hydrogen-ion concentration and to be unaffected by the presence of ammonium ions, as may be seen from the results of Table 3.

The rate constant for the reaction of eqn. (6) was determined in experiments in which *trans*- $[\text{AuCl}_2(\text{NH}_3)_2]\text{Cl} \cdot \frac{1}{3} \text{H}_2\text{O}$  ( $c_{\text{Au}} \approx 10^{-4} \text{ M}$ ) was allowed to react with excess of chloride ion. Again the pseudo first-order rate constants (calculated from absorbance changes at the  $[\text{AuCl}_3\text{NH}_3]/[\text{AuCl}_4]^-$  isosbestic point 290 nm, cf. Fig. 1) were proportional to the chloride-ion concentration and independent of pH, and they were not affected by the presence of ammonium ions, as may be seen from the results in Table 2. Thus under the experimental conditions employed, the reverse ammoniolysis reactions are unimportant.

The pseudo first-order rate constants of Tables 1, 2 and 3 at different temperatures were converted to second-order rate constants, and Arrhenius-type plots for each of the four reactions showed linearity within estimated errors, see Fig. 4. Using reaction rate theory the activation parameters were evaluated, and may be found in Table 4 together with the second-order rate constants for all four reactions at 25 °C.

Table 4. Rate constants and activation parameters at 25 °C for the reaction of tetraamminegold(III) ions with chloride ions in aqueous 1.0 M HCl, ClO<sub>4</sub>.

Reaction	$k_r/1 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$r(\Delta H^\ddagger, \Delta S^\ddagger)^a$
$[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Cl}^-$ $\xrightarrow{k_1}$	0.36(2)	81(2)	20(4)	-0.9995
$[\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{NH}_3$ $\xrightarrow{k_2}$	0.112(2)	78(1)	-1(3)	-0.9998
$[\text{AuCl}(\text{NH}_3)_3]^{2+} + \text{Cl}^-$ $\xrightarrow{k_3}$	$3.7(5) \times 10^{-6}$	105(4)	2(10)	-0.9998
<i>trans</i> - $[\text{AuCl}_2(\text{NH}_3)_2]^+ + \text{Cl}^-$ $\xrightarrow{k_4}$	$3.33(2) \times 10^{-5}$	97(2)	-7(4)	-0.9998

<sup>a</sup>  $r(\Delta H^\ddagger, \Delta S^\ddagger)$  is the correlation coefficient between the two activation parameters.

Table 5. Rate constants and activation parameters for reaction of tetraamminegold(III) ions with chloride and bromide in acidic aqueous solution of unity ionic strength at 25 °C.

Reaction	Chloride anation <sup>a</sup>				Bromide anation <sup>b</sup>			
	$m^c$	$k_n/1 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H_n^\ddagger/\text{kJ mol}^{-1}$	$\Delta S_n^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$k_n/1 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H_n^\ddagger/\text{kJ mol}^{-1}$	$\Delta S_n^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	
$[\text{Au}(\text{NH}_3)_4]^{3+} + \text{X}^-$ $\xrightarrow{k_1}$	4	0.36	81	20	3.40	73	8	
$[\text{AuX}(\text{NH}_3)_3]^{2+} + \text{NH}_3$ $\xrightarrow{k_2}$	1	0.112	78	-1	6.5	69	2	
$[\text{AuX}(\text{NH}_3)_3]^{2+} + \text{X}^-$ $\xrightarrow{k_3}$	2	$3.7 \times 10^{-6}$	105	2	$9.3 \times 10^{-5}$	88	-26	
<i>trans</i> - $[\text{AuX}_2(\text{NH}_3)_2]^+ + \text{NH}_3$ $\xrightarrow{k_4}$	1	$3.33 \times 10^{-5}$	97	-7	$2.68 \times 10^{-2}$	84	7	

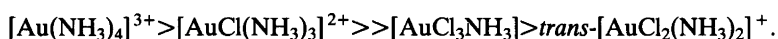
<sup>a</sup> Present work. <sup>b</sup> From Refs. 1 and 2. <sup>c</sup>  $m$  is the number of equivalent leaving ligands.



## DISCUSSION

In the tetraamminegold(III) ion, the rate of substitution of ammonia by chloride is lowered by five orders of magnitude after substitution of the two first ammine ligands. A similar dramatic effect was observed in the bromide anation of the tetraamminegold(III) ion, see Table 5. Common for the anation of tetraamminegold(III) by chloride and bromide is also the absence of significant solvent paths, which are normally observed for this type of reaction in other  $d^8$  low-spin complexes such as those of palladium(II) and platinum(II).<sup>9</sup> This indicates that water is ineffective as an entering ligand in tetraamminegold(III) relative to bromide and even relative to chloride, which is, however, in agreement with the marked softness and high discriminating power of gold(III) complexes.<sup>10</sup>

The magnitude of the rate constants for the consecutive reactions of chloride with tetraamminegold(III) shows that the efficiency of chloride as an entering ligand increases in the order:



This sequence is a result of a combination of *cis*- and *trans*-effects, statistical factors and effects of charge-neutralization in the transition state.

The kinetic *trans*-effect is well-established in platinum(II) chemistry, but the data available for discussing a similar *trans*-effect in gold(III) have been very limited with the notable exception of the relative  $\text{Br}^-/\text{Cl}^-$  *trans*-effect.<sup>3,11-12</sup> The reaction of tetrachloridoaurate(III) with bromide to give tetrabromidoaurate(III) thus proceeds *ca.* 90 % *via* the *trans*-isomer of dibromidodichloridoaurate(III), whereas the reverse reaction takes place mainly *via* the *cis*-isomer, and for either bromide or chloride as the entering ligand in the mixed chlorido/bromido complexes, the rate of substitution was accelerated by a factor of  $14 \pm 3$  by a *trans*-bromide relative to a *trans*-chloride.<sup>11</sup> Similar results were obtained for *trans*-diamminedihalogenidogold(III)<sup>3</sup> and *trans*-dicyanodihalogenidoaurate(III),<sup>12</sup> and in the latter two substrates it was observed that only the activation enthalpies and not the activation entropies depend on the nature of the *trans*-ligand, and that the  $\text{Br}^-/\text{Cl}^-$  *trans*-effect corresponds to *ca.* 5 kJ mol<sup>-1</sup>.<sup>3,12</sup> In order to estimate the relative halogenido/ $\text{NH}_3$  *trans*-effect it is, however, necessary to compare rates for complexes with different charges. In the mixed halogenido/ammine-gold(III) complexes, the halogenido/ $\text{NH}_3$  *trans*-effect is in each case counteracted not only by the statistical factor corresponding to the number of equivalent leaving ligands, but also by the effect of charge neutralization in the transition state. Both of these latter effects are expected to manifest themselves as positive contributions to the entropies of activation.

From a comparison of the rate constants given in Table 4 for the chloride anation of  $[\text{AuCl}_3\text{NH}_3]$  and *trans*- $[\text{AuCl}_2(\text{NH}_3)_2]^+$ , which have one and two equivalent leaving ligands, respectively, it can be estimated that the  $\text{Cl}^-/\text{NH}_3$  *trans*-effect is greater than 5 at 25 °C. Given this lower limit for the  $\text{Cl}^-/\text{NH}_3$  *trans*-effect, it could be expected that  $[\text{AuCl}(\text{NH}_3)_3]^{2+}$  would anate faster than  $[\text{Au}(\text{NH}_3)_4]^{3+}$ . However, for these two latter substrates both the statistical factor (one *versus* four equivalent leaving ligands) and the effect of charge neutralization (a tripositive *versus* a dipositive substrate) are of greater importance, and taken together they render the activation entropy *ca.* 20 J mol<sup>-1</sup>K<sup>-1</sup> more favourable for the anation of  $[\text{Au}(\text{NH}_3)_4]^{3+}$  than for  $[\text{AuCl}(\text{NH}_3)_3]^{2+}$ . At temperatures around 300 K, this entropy effect is so significant that the  $\text{Cl}^-/\text{NH}_3$  *trans*-effect, manifested as a difference of *ca.* 3 kJ mol<sup>-1</sup> in the enthalpy of activation, is completely submerged. It

should also be noted that the entropy effect caused by the charge-neutralization increases with decreasing ionic strength. The replacement of the first ammonia ligand by chloride is thus expected to be accelerated relatively to the replacement of the second as a result of increasing dilution, and as can be seen from Fig. 3, this is in agreement with the experimental findings.

The *trans*-effect has, however, two aspects, *viz.* the *trans*-labilizing and the *trans*-directing, the latter of which is not affected by the charge-neutralization discussed above. The product of the anation reaction of  $[\text{AuCl}(\text{NH}_3)_3]^{2+}$  by chloride has an UV-absorption spectrum identical to that of the well-characterized salt *trans*- $[\text{AuCl}_2(\text{NH}_3)_2]\text{Cl}\cdot 1/3\text{H}_2\text{O}$ ,<sup>3,4</sup> indicating that the product is almost exclusively the *trans*-isomer. *cis*-Diamminedihalogenidogold(III) complexes have not yet been characterized, but a generous estimate of the upper limit for *cis*-product in the reaction of eqn. (4) is 5 %. Anation of *cis*- $[\text{AuCl}_2(\text{NH}_3)_2]^+$  is expected to be much faster than for its *trans*-counterpart, as also indirectly confirmed by a comparison of the rate for the reaction of eqn. (6) with that for the anation of the trimethylenediamine complex *cis*- $[\text{AuCl}_2(\text{tn})]^+$  by chloride



for which a second-order rate constant of  $1.52 \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$  was found in aqueous solution of ionic strength 1.7 at 25 °C.<sup>13</sup>

The difference in rate between the reactions of eqns. (6) and (8) cannot, however, be accounted for solely on the basis of the  $\text{Cl}^-/\text{NH}_3$  *trans*-effect. Saturated amine ligands including ammonia appear to exhibit a significant *cis*-accelerating effect relative to halide ligands as also noted from a comparison of the rate of chloride/bromide interchange reactions in *trans*-diamminedihalogenidogold(III) and tetrahalogenidoaurate(III) complexes.<sup>3</sup> The occurrence of two separate stages, differing in rate by five orders of magnitude, in the anation of  $[\text{Au}(\text{NH}_3)_4]^{3+}$  by either chloride or bromide (*cf.* Table 5) shows likewise that ammonia accelerates *cis*-substitutions relative to halides. The *cis*-effect of ammonia relative to chloride is small in platinum(II) but much greater in palladium(II) complexes,<sup>14</sup> and the available data suggest this *cis*-effect of ammonia to be even more pronounced in gold(III) complexes.

The kinetic parameters for the anation of  $[\text{Au}(\text{NH}_3)_4]^{3+}$  by chloride or bromide are compared in Table 5. Bromide is in all cases more efficient as an entering ligand as a result of a smaller enthalpy of activation (8–17 kJ mol<sup>-1</sup>). The kinetic discrimination of a particular gold(III) complex thus appears to be mainly an enthalpy effect in agreement with findings for thermodynamic discrimination.<sup>15</sup> Available data for ligand substitutions in gold(III) complexes in different solvents indicate that negative entropies of activation are characteristic of ligand substitutions in gold(III) complexes,<sup>3,5,12,16,17</sup> in agreement with the concept of a transition-state in which bond formation is more important than bond breaking. However, it is obvious from the data in Table 5 that charge neutralization during bond formation makes the entropies of activation for the studied anation reactions more positive. The experimental data are admittedly very limited. However, judging from the  $\text{NH}_3/\text{Cl}^-$  and the  $\text{NH}_3/\text{Br}^-$  complexes, the *cis*-effect and effects from charge neutralization in the transition state appear to be more important in determining the rate for gold(III) complexes than for platinum(II) complexes.<sup>14</sup> In that respect gold(III) resembles palladium(II), for which similar results have been found<sup>18,19</sup> in the case of the  $\text{NH}_3/\text{Cl}^-$  complexes.

## REFERENCES

1. Skibsted, L.H. *Acta Chem. Scand. A* 33 (1979) 113.
2. Skibsted, L.H. *Acta Chem. Scand. A* 37 (1983) 613.
3. Kaas, K. and Skibsted, L.H. *Acta Chem. Scand. A* 39 (1985) 1.
4. Mønsted, O. and Skibsted, L.H. *Acta Chem. Scand. A* 38 (1984) 23.
5. Rich, R.L. and Taube, H. *J. Phys. Chem.* 58 (1954) 1.
6. Strähle, J., Gelinek, J. and Kölmel, M. *Z. Anorg. Allg. Chem.* 456 (1979) 241.
7. Skibsted, L.H. and Bjerrum, J. *Acta Chem. Scand. A* 28 (1974) 740.
8. Davies, C.W. *Ion Association*, Butterworths, London 1962, p. 41.
9. Coe, J. In Tobe, M.L., Ed., *M.T.P. International Review of Science, Inorganic Chemistry Series Two*, 9, Butterworths, London 1974, p. 45.
10. Skibsted, L.H. and Bjerrum, J. *J. Indian Chem. Soc.* 54 (1977) 102.
11. Elding, L.I. and Gröning, A.-B. *Acta Chem. Scand. A* 32 (1978) 867.
12. Mason, W.R. *Inorg. Chem.* 9 (1970) 2688.
13. Bandoli, G., Clemente, D.A., Marangoni, G. and Cattalini, L. *J. Chem. Soc. Dalton Trans.* (1973) 886.
14. Poë, A.J. and Vaughan, D.H. *Inorg. Chim. Acta* 1 (1967) 255.
15. Nikolaeva, N.M., Erenburg, A.M. and Antipina, V.A. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* (1972) 126.
16. Cattalini, L. and Tobe, M.L. *Inorg. Chem.* 5 (1966) 1145.
17. Cattalini, L., Orio, A. and Tobe, M.L. *J. Am. Chem. Soc.* 89 (1967) 3130.
18. Reinhardt, R.A. and Sparkes, R.K. *Inorg. Chem.* 6 (1967) 2190.
19. Coe, J.S., Hussain, M.D. and Malik, A.A. *Inorg. Chim. Acta* 2 (1968) 65.

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