

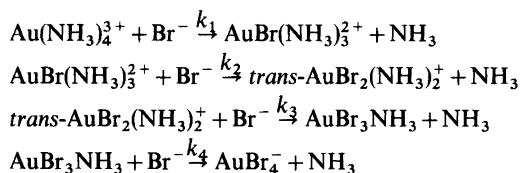
# Amineanionogold(III) Complexes. I. Kinetics of the Consecutive Substitutions of Ammonia by Bromide in Tetraamminegold(III) Ion in Acid Aqueous Solution

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

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



In acid solution the ligand substitutions take place as direct displacements and no solvent paths were detectable. Second-order rate constants and activation enthalpy at 25.0 °C and unit ionic strength are:  $k_1 = 3.40 \pm 0.08 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_1^\ddagger = 73 \pm 3 \text{ kJ mol}^{-1}$ ,  $k_2 = 6.5 \pm 0.4 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_2^\ddagger = 69 \pm 3 \text{ kJ mol}^{-1}$ ,  $k_3 = (9.3 \pm 0.3) \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_3^\ddagger = 88 \pm 3 \text{ kJ mol}^{-1}$ , the fourth reaction being fast as compared to the third.

One intermediate product, the *trans*-diamminedibromidogold(III) ion, was isolated as the bromide salt and as the Magnus-type salt *trans*-diamminedibromidogold(III) tetrabromidoaurate(III).

Ligand substitution reactions of 4-coordinate square planar complexes of Au(III) follow the same general rate law as substitution reactions in the iso-electronic ( $d^8$ , low spin) complexes of Pt(II) and of Pd(II). This rate law is two-termed:  $\text{Rate} = (k_1 + k_2 [\text{Y}])[\text{complex}]$ .

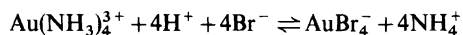
The  $k_1$  route is a solvent path and the  $k_2$  route a direct replacement by the entering ligand, Y. The detailed mechanism of such reactions has been the subject of numerous studies, and large sets of data from systematic studies on Pt(II) and Pd(II) are available and have been extensively reviewed.<sup>1–3</sup>

Studies on substitution reactions of Au(III) complexes have, however, revealed important differences in the reactivity and substitution behaviour of these complexes as compared to those of Pd(II) and Pt(II).<sup>4</sup> Au(III) complexes react faster than those of the latter metal ions (the normal order of reactivity being Au(III) > Pd(II) > Pt(II)), and the reaction rate of Au(III) substrates is much more sensitive to the nature of the entering ligand.<sup>5</sup> Water is relatively ineffective as an entering ligand in Au(III) complexes and consequently the  $k_1$  term in the rate law often vanishes for substitution reactions in aqueous solutions.<sup>6</sup> This observed high discriminating power for the entering ligands (including the ineffectiveness of water) and the generally faster reactions are related to the extreme softness of the Au(III) metal centre.<sup>7,8</sup>

Hydrolysis, ammoniolysis, and anation reactions of  $\text{Pt}(\text{H}_2\text{O})_x(\text{NH}_3)_y\text{Cl}_{4-x-y}$  and of  $\text{Pd}(\text{H}_2\text{O})_x(\text{NH}_3)_y\text{Cl}_{4-x-y}$  have been extensively investigated and used in parameterization of *cis*- and *trans*-effects and charge effect.<sup>9–11</sup> Similar investigations on Au(III) systems have now begun to appear in the literature<sup>6,12,13</sup> and should provide a background for further rationalization of the influence of the

metal centre. For this reason investigations of ligand substitution in amineanionogold(III) complexes were undertaken. This paper reports, as the first part of these studies, the kinetics of the anation of the tetraamminegold(III) ion by bromide ion, including activation parameters for the rate determining steps. The reaction of the tetraamminegold(III) ion with thiosulfate,<sup>14</sup> and the hydrolysis<sup>15</sup> of the former have previously been investigated.

The over-all substitution reaction



has an equilibrium constant<sup>7</sup>  $K_{\text{eq}} \approx 10^{11} \text{ l}^4/\text{mol}^4$ , and in aqueous solutions of sufficient acidity, where hydrolysis and deprotonation<sup>15</sup> are negligible, the tetrabromidoaurate(III) ion is thermodynamically stable. The over-all substitution reaction apparently occurs in two steps, differing greatly in rate. The intermediate product, identified as the *trans*-diamminedibromidogold(III) ion, was isolated as the bromide and as the tetrabromidoaurate(III) salts.

## EXPERIMENTAL

**Materials.** Potassium tetrachloridoaurate(III) from H. Drijfhout and Zoon's, Amsterdam and fine gold (99.99 %) were used as the starting materials for the preparation of the gold compounds. Other chemicals were of analytical grade. Doubly distilled water was employed throughout.

Hydrobromic acid was distilled before dilution. Stock solutions of hydrobromic acid, perchloric acid, ammonium perchlorate, and sodium perchlorate were analyzed using standard methods.

**Instruments.** A Zeiss DMR 21 spectrophotometer with thermostatted cell-holder and cell compartment was used for spectrophotometric measurements.

For spectrophotometric data quoted in the text absorptivities  $\epsilon$  are given in  $\text{l mol}^{-1} \text{ cm}^{-1}$  and wavelengths  $\lambda$  in nm.

**Analysis.** Gold was determined spectrophotometrically after conversion to the tetrabromidoaurate(III) ion:  $(\epsilon, \lambda)_{\text{max}} = (4787, 381)$  in 0.10 M hydrobromic acid.

Analyses for C, N, H, and Au (the latter gravimetric) were made by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

**Preparations.** 1. *Potassium tetrabromidoaurate(III)*.  $\text{K}[\text{AuBr}_4]$  was prepared as described in the literature.<sup>16</sup> Anal.: Au. Absorption spectrum; see Fig. 1.

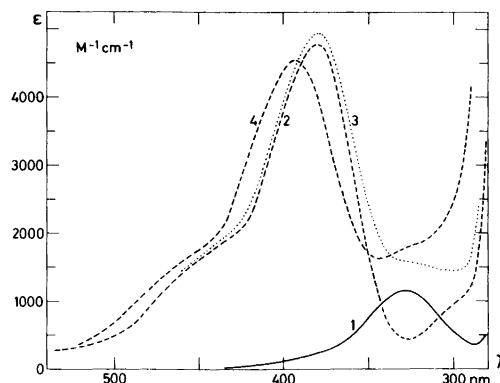


Fig. 1. Absorption spectra: 1. *trans*-diamminedibromidogold(III) bromide in 0.98 M perchloric acid, 0.020 M hydrobromic acid. 2. Potassium tetrabromidoaurate(III) in 0.98 M perchloric acid, 0.020 M hydrobromic acid. 3. *trans*-Diamminedibromidogold(III) tetrabromidoaurate(III) in 0.98 M perchloric acid, 0.020 M hydrobromic acid. 4. *trans*-Diamminedibromidogold(III) tetrabromidoaurate(III) in absolute ethanol. The absorbance of the tetraamminegold(III) ion is negligible at longer wavelengths than  $\sim 280$  nm.

2. *Tetraamminegold(III) nitrate*.  $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$  was synthesized by the previously published method.<sup>15</sup> This compound is stable for years if kept in the dark. On exposure to daylight it slowly turns purple, indicating formation of metallic gold. Anal.: Au.

3. *Tetraamminegold(III) perchlorate*.  $[\text{Au}(\text{NH}_3)_4](\text{ClO}_4)_3$  was also synthesized as described previously<sup>13</sup> and was further purified by reprecipitation from aqueous solution with perchloric acid. This compound rapidly turns purple, and it seems difficult to prepare and to keep it pure. Anal.: Au.

4. *trans*-Diamminedibromidogold(III) bromide. *trans*- $[\text{AuBr}_2(\text{NH}_3)_2]\text{Br}$  was synthesized by the following method: 6.0 g (13.2 mmol) of tetraamminegold(III) nitrate was dissolved in 8 ml of water plus 33 ml of 1.00 M hydrobromic acid at room temperature. This solution was filtered after 3 min and mixed with 15 ml of ice-cold saturated lithium bromide solution. After cooling in ice the precipitate formed was filtered off, washed twice with 5 ml of ice-cold absolute ethanol and once with ether. The product appeared as well-crystallized orange plates. Analysis (Au, N, H, Br) was consistent with the composition  $3[\text{AuBr}_2(\text{NH}_3)_2]\text{Br} \cdot \text{NH}_4\text{Br} \cdot 2\text{H}_2\text{O}$ . Yield 4.7 g (61 %). This product was dissolved in 50 ml of ice-cold 0.10 M perchloric acid and the solution was mixed with 15 ml of ice-cold saturated lithium bromide. The precipitate formed was filtered

off and washed as before. This product consisted of reddish orange, elongated prisms and the analysis (Au, N, H, Br) confirmed the composition  $[\text{AuBr}_2(\text{NH}_3)_2]\text{Br}$ . Yield 3.1 g (50%). The two salts were interconvertible. If the reprecipitation was performed with saturated ammonium bromide the double salt was reformed. The absorption spectra in the UV region were identical.  $(\epsilon, \lambda)_{\text{max}}$  in 0.98 M perchloric acid, 0.020 M hydrobromic acid was:  $[\text{AuBr}_2(\text{NH}_3)_2]\text{Br}$ ,  $\text{NH}_4\text{Br} \cdot 2\text{H}_2\text{O}$ : (1154, 328.5);  $[\text{AuBr}_2(\text{NH}_3)_2]\text{Br}$ : (1159, 328.5); see Fig. 1.

The diamminedibromidogold(III) ion exists as two geometrical isomers. Arguments for assigning the *trans*-configuration to the present complex are presented in the discussion.

5. *trans*-Diamminedibromidogold(III) tetrabromidoaurate(III). The Magnus-type salt *trans*- $[\text{AuBr}_2(\text{NH}_3)_2][\text{AuBr}_4]$  was prepared by mixing a filtered solution of 0.56 g (1.0 mmol) of potassium tetrabromidoaurate(III) in 10 ml  $10^{-2}$  M perchloric acid with a filtered solution of 0.47 g (1.0 mmol) of *trans*-diamminedibromidogold(III) bromide in 17 ml of  $10^{-2}$  M perchloric acid. After cooling on ice the voluminous precipitate formed was filtered off and washed with ice-cold water. The precipitate was dissolved in 5 ml of 96% ethanol on the filter and the solution was mixed with 2 ml of water and placed in a desiccator over water. Large dark reddish brown crystals with metallic lustre consisting of stacked plates were formed on standing overnight. Anal.: Au, N, H, Br. Yield 0.31 g (34%).  $(\epsilon, \lambda)_{\text{max}}$  in 0.98 M perchloric acid, 0.020 M hydrobromic acid: (4948, 380); in absolute ethanol: (4546, 393). The absorption spectrum in aqueous solution is a superimposition of the absorption spectra of the two complex ions; see Fig. 1.

6. Bromodiethylenetriaminegold(III) bromide was prepared by a literature method.<sup>17</sup> Anal.: Au, C, N, H, Br.  $(\epsilon, \lambda)_{\text{max}}$  = (577, 338) in 1.0 M sodium perchlorate at  $\text{pH} \approx 2$ . Absorption spectrum; see Fig. 2.

*Kinetic runs.* The investigated sequence of reactions of the tetraamminegold(III) ion with bromide ion was monitored spectrophotometrically.

The first reaction step was investigated by fixed wavelength experiments. Two solutions (one containing tetraamminegold(III) ion, and one containing bromide ion) were pressed from a thermostatted double syringe into a mixing chamber and into a 1 cm silica flow cell. Using this "stopped flow" technique the reaction could be monitored after a few seconds. Each experiment consisted of separate runs at the four wavelengths 315, 327, 340, and 350 nm — each in duplicate. From the recordings of absorbance *versus* time an appropriate number of data were read off.

The second reaction step was considerably slower. *Prethermostatted* solutions were mixed and

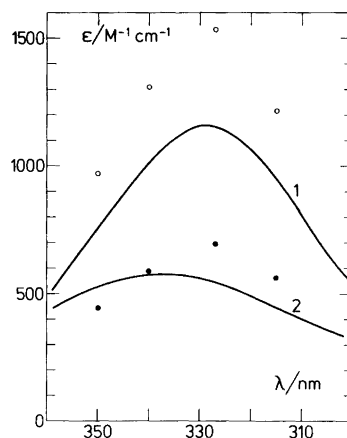


Fig. 2. Absorption spectra in the wavelength region used in monitoring the first reaction step. 1. Spectrum of the product, the *trans*-diamminedibromidogold(III) ion. 2. Spectrum of the bromodiethylenetriaminegold(III) ion. ○, Calculated molar absorptivity of the intermediate product, the triaminebromidogold(III) ion, assuming  $k_2 > k_1$ . ●, Calculated spectrum of the intermediate assuming  $k_1 > k_2$ .

placed in a 1 cm silica cell in the cell compartment and spectra were recorded at known times. In a few experiments running for more than a day, reaction mixtures were left in a thermostatted waterbath; aliquots were removed at known times and spectra recorded at room temperature. The recorded spectra were read off at the six wavelengths 360, 380, 400, 420, 440, and 460 nm. All experiments were run in duplicate.

With a few exceptions tetraamminegold(III) nitrate was used as the starting gold complex in the kinetic experiments (*vide infra*). This salt was preferred to the perchlorate because of its higher purity. No interference from nitrate or significant formation of bromine could be detected at the pH and in the temperature and concentration ranges employed. The rate of the second reaction step was much slower than the first so that the two reaction steps were well separated. The temperature and bromide concentration used in the investigation of the second reaction step ensured virtually complete conversion of tetraamminegold(III) ion into *trans*-diamminedibromidogold(III) ion at the time of recording the first spectrum.

Care was taken to ensure temperature equilibrium in the cell compartment before starting the experiments. The majority of the experiments on the first reaction step were performed at a temperature

close to 0 °C. The thermostat baths were filled with a mixture of ice and water. The equilibrium temperature in the cell was ~0.9 °C.

## CALCULATIONS

Calculations on the kinetic experiments were performed within the framework of non-linear regression analysis using a least-squares criterion for minimization. Measurements at the different wavelengths were included in the same calculation. Thus, the quantity to be minimized was

$$var = \sum_{\lambda} \sum_t \frac{[A_{\lambda,t}(\text{obs}) - A_{\lambda,t}(\text{calc})]^2}{\sigma_A^2}$$

$A_{\lambda,t}$  denotes the absorbance at wavelength  $\lambda$  and at time  $t$  (one kinetic experiment consisted typically of measurement of 200 absorbance values).  $\sigma_A$ , the standard deviation on the absorbance, was tentatively taken as 0.001. The quantity *var* divided by  $f$  (degrees of freedom) has an expectation value close

to unity and *var/f* was used in testing consistency between the experiments and the model used in interpretation of the observed kinetics (goodness of fit).

*First reaction step.* The reaction of the tetraamminegold(III) ion with bromide ion gave a product which only slowly reacted further. This stable intermediate was identified from its UV spectrum as the *trans*-diamminedibromidogold(III) ion:



All experiments were performed with excess of bromide ion in acid solution. This first reaction step showed no simple pseudo first-order kinetics. Plots of  $\ln(A - A_\infty)$  versus time showed systematic deviations from linearity. Analogously, by fitting the data to eqn. (1) the quantity *var/f* was always significantly higher than the expectation value.

$$A_{\lambda}(t) = a_{\lambda} + b_{\lambda}e^{-k't} \quad (1)$$

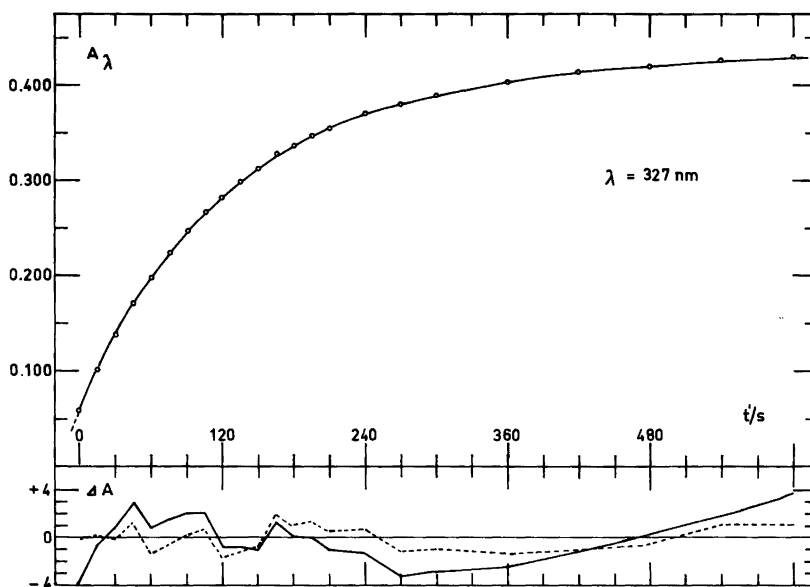


Fig. 3. Absorbance versus time for the first reaction step  $\text{Au}(\text{NH}_3)_4^{3+} + 2\text{Br}^- \rightarrow \text{trans-AuBr}_2(\text{NH}_3)_2^+ + 2\text{NH}_3$ . The example given is experiment No. 5 of Table 1 at  $\lambda = 327$  nm. Experimental points are shown together with the line calculated by means of non-linear regression analysis:  $A_{327}(t) = 0.4356 - 0.2768e^{-0.0062t} - 0.1007e^{-0.0130t}$ . The lower part of the figure shows  $\Delta A = 1000[A_{\lambda,t}(\text{obs}) - A_{\lambda,t}(\text{calc})]$ . Solid line:  $\Delta A$  calculated assuming one rate determining reaction step. Broken line:  $\Delta A$  calculated assuming two consecutive reaction steps.  $t'$  is the time in seconds relative to the first measured absorbance:  $t' = t - 6$ ;  $t$  being relative to mixing time.

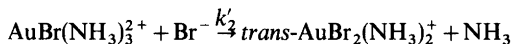
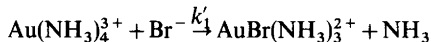
The deviation from this first-order model was always of the same nature; see Fig. 3. Thus, the first reaction step did not consist merely of one rate-determining reaction first-order in complex ion.

The change in absorbance for two consecutive first-order reactions is given by expressions such as eqn. (2).

$$A_{\lambda}(t) = a_{\lambda} + b_{\lambda}e^{-k_b t} + c_{\lambda}e^{-k_c t} \quad (2)$$

By fitting the experimental data to such expressions excellent agreement between experiment and model was obtained. Experiment No. 5 of Table 1 illustrates this. Calculations within the model assuming one first-order reaction gave  $k' = (7.64 \pm 0.03) \times 10^{-3} \text{ s}^{-1}$  with  $\text{var}/f = 3.29$  and  $f = 167$ , whereas the model involving two consecutive first-order reactions led to  $k'_b = (6.2 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$  and  $k'_c = (1.30 \pm 0.13) \times 10^{-2} \text{ s}^{-1}$  with  $\text{var}/f = 1.10$  and  $f = 158$ . In Fig. 3 the absorbance *versus* time at  $\lambda = 327 \text{ nm}$  is shown, together with  $\Delta A = 1000 \cdot [A_{\lambda,t}(\text{obs}) - A_{\lambda,t}(\text{calc})]$  for the two calculations.

It is concluded that the first reaction step consists of two consecutive reactions, each first order in complex and in bromide:



There are two possibilities for identifying  $k'_1$  and  $k'_2$  with  $k'_b$  and  $k'_c$  of eqn. (2):  $k'_1 = k'_b$ ,  $k'_2 = k'_c$  or  $k'_1 = k'_c$ ,  $k'_2 = k'_b$ . This choice is in general difficult, especially when the spectrum of the intermediate product is unknown. A so-called "slow-fast" ambiguity arises, as discussed by Jørgensen and Bjerrum<sup>18</sup> and more recently by others.<sup>19-21</sup> In the actual wavelength range the absorbance increased continuously during the first reaction step (see Fig. 2) and the spectra displayed no isosbestic points at any stage of this reaction step. Relatively slow formation of a strongly absorbing intermediate product or a relatively rapid formation of a more weakly absorbing intermediate account equally well for the continuously increasing absorbance.

From the parameters in eqn. (2) the molar absorptivities can be calculated from eqns. (3)–(6).

$$\epsilon_{\lambda}(\text{Au}(\text{NH}_3)_4^3+) = (a_{\lambda} + b_{\lambda} + c_{\lambda})/c_{\text{Au}} \quad (3)$$

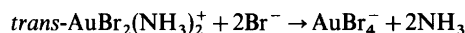
$$\epsilon_{\lambda}(\text{trans-AuBr}_2(\text{NH}_3)_2^+) = a_{\lambda}/c_{\text{Au}} \quad (4)$$

$$\epsilon_{\lambda}(\text{AuBr}(\text{NH}_3)_3^{2+}) = [a_{\lambda} + b_{\lambda}(k'_c - k'_b)/k'_c]/c_{\text{Au}} \quad (5)$$

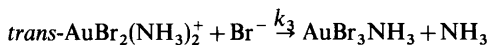
$$\epsilon'_{\lambda}(\text{AuBr}(\text{NH}_3)_3^{2+}) = [a_{\lambda} + c_{\lambda}(k'_b - k'_c)/k'_b]/c_{\text{Au}} \quad (6)$$

If  $k'_b$  denotes the larger rate constant, the assignment  $k'_b = k'_1$  and  $k'_c = k'_2$  corresponds to relatively rapid formation of a weakly absorbing intermediate:  $\epsilon'_{\lambda}(\text{AuBr}(\text{NH}_3)_3^{2+})$ . The reverse assignment  $k'_c = k'_1$  and  $k'_b = k'_2$  corresponds to a slower formation of a more strongly absorbing intermediate:  $\epsilon_{\lambda}(\text{AuBr}(\text{NH}_3)_3^{2+})$ . The two mathematically indistinguishable possibilities can be distinguished if one of the calculated molar absorptivities of the intermediate is physically meaningless or if the ratio  $k'_1/k'_2$  can be varied (*e.g.* by temperature).

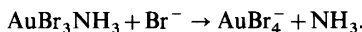
*Second reaction step.* The reaction of *trans*-diamminedibromidogold(III) ion with bromide ion gave a product which was identified by its UV spectrum as the tetrabromidoaurate(III) ion:



All experiments were performed with excess of bromide ion in acid solution. A similar numerical analysis as before revealed excellent agreement between experiment and a model based on one rate-determining reaction step, first order in bromide and in complex. An example will illustrate this: One of the duplicate runs of experiment No. 1 in Table 2, calculated within this model, gave  $k' = (1.923 \pm 0.006) \times 10^{-4} \text{ s}^{-1}$  with  $\text{var}/f = 1.21$  and  $f = 64$ . The absorbance *versus* time at  $\lambda = 380$ , and  $460 \text{ nm}$ , from this experiment is shown in Fig. 4, together with  $\Delta A$  defined as before. The spectra displayed two isosbestic points (see Fig. 1) which persisted during the whole course of the reaction. The rate determining reaction



is thus succeeded by the considerably faster reaction



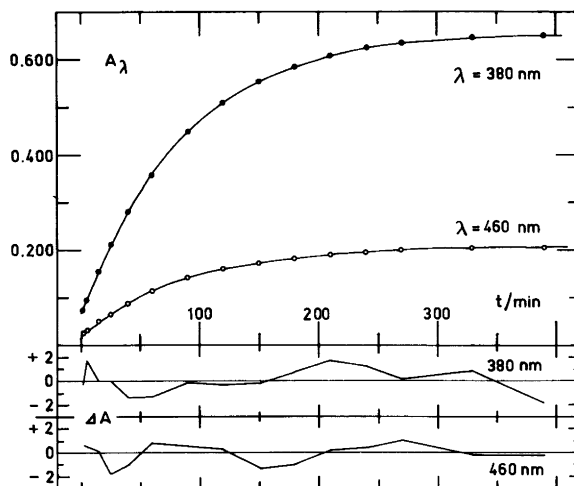


Fig. 4. Absorbance versus time for the second reaction step  $\text{trans-AuBr}_2(\text{NH}_3)_2^+ + 2\text{Br}^- \rightarrow \text{AuBr}_4^- + 2\text{NH}_3$ . The example given is No. 1 of Table 2 at  $\lambda = 380$  and  $460$  nm. Experimental points are shown together with the lines calculated by non-linear regression analysis:  $A_{380}(t) = 0.6604 - 0.5998e^{-0.01154t}$  and  $A_{460}(t) = 0.2073 - 0.1861e^{-0.01154t}$ . The lower part of the figure shows  $\Delta A = 1000[A_{\lambda,t}(\text{obs}) - \Delta A_{\lambda,t}(\text{calc})]$ .

Table 1. Pseudo first-order rate constants for the consecutive substitution reactions  $\text{Au}(\text{NH}_3)_3^{3+} + \text{Br}^- \xrightarrow{k'_1} \text{AuBr}(\text{NH}_3)_2^+ + \text{NH}_3$  and  $\text{AuBr}(\text{NH}_3)_2^+ + \text{Br}^- \xrightarrow{k'_2} \text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$ .  $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$  was used as the starting compound in all experiments,  $C_{\text{Au}} \approx 10^{-4}$  M. The reaction medium was 1.00 M  $\text{H}(\text{Br}, \text{ClO}_4)$  in all experiments except in Nos. 10, 11, and 12.

No.	$t/^\circ\text{C}$	$[\text{Br}^-]/\text{M}$	pH	$k'_1/\text{s}^{-1}$	$k'_2/\text{s}^{-1}$	$r(k'_1, k'_2)^d$
1	0.9	0.00750	0.00	$1.80(11) \times 10^{-3}$	$3.6(4) \times 10^{-3}$	0.950
2	0.9	0.0100	0.00	$2.51(5) \times 10^{-3}$	$5.8(8) \times 10^{-3}$	0.928
3	0.9	0.0150	0.00	$3.96(11) \times 10^{-3}$	$9.4(12) \times 10^{-3}$	0.956
4	0.9	0.0200	0.00	$5.4(2) \times 10^{-3}$	$1.3(2) \times 10^{-2}$	0.964
5	0.9	0.0250	0.00	$6.2(3) \times 10^{-3}$	$1.30(13) \times 10^{-2}$	0.973
6	0.9	0.0300	0.00	$8.2(2) \times 10^{-3}$	$2.2(3) \times 10^{-2}$	0.941
7	0.9	0.0350	0.00	$8.8(7) \times 10^{-3}$	$1.8(3) \times 10^{-2}$	0.978
8	0.9	0.0400	0.00	$9.21(9) \times 10^{-3}$	$1.70(14) \times 10^{-2}$	0.975
9	0.9	0.0450	0.00	$1.19(5) \times 10^{-2}$	$2.6(4) \times 10^{-2}$	0.969
10 <sup>a</sup>	0.9	0.0200	1.30	$4.4(2) \times 10^{-3}$	$1.14(19) \times 10^{-2}$	0.964
11 <sup>b</sup>	0.9	0.0200	1.10	$4.85(8) \times 10^{-3}$	$1.8(3) \times 10^{-2}$	0.913
12 <sup>c</sup>	0.9	0.0200	0.00	$5.19(7) \times 10^{-3}$	$1.61(18) \times 10^{-2}$	0.900
13	15.0	0.00750	0.00	$8.7(3) \times 10^{-3}$	$1.94(13) \times 10^{-2}$	0.953
14	15.0	0.0100	0.00	$1.25(6) \times 10^{-3}$	$2.8(4) \times 10^{-2}$	0.964
15	15.0	0.0150	0.00	$1.77(14) \times 10^{-3}$	$3.3(4) \times 10^{-2}$	0.976
16	15.0	0.0200	0.00	$2.5(3) \times 10^{-3}$	$4.4(8) \times 10^{-2}$	0.984
17	18.0	0.00750	0.00	$1.16(10) \times 10^{-2}$	$2.2(2) \times 10^{-2}$	0.977
18	18.0	0.0100	0.00	$1.78(9) \times 10^{-2}$	$3.7(8) \times 10^{-2}$	0.970
19	18.0	0.0150	0.00	$3.4(2) \times 10^{-2}$	$6.8(12) \times 10^{-2}$	0.971
20	22.0	0.00750	0.00	$1.94(13) \times 10^{-2}$	$4.0(9) \times 10^{-2}$	0.977

<sup>a</sup>  $[\text{Na}^+] = 0.950$  M,  $[\text{H}^+] = 0.050$  M,  $[\text{Br}^-] = 0.0200$  M,  $[\text{ClO}_4^-] = 0.980$  M. <sup>b</sup>  $[\text{NH}_4^+] = 0.200$  M,  $[\text{H}^+] = 0.080$  M,  $[\text{Na}^+] = 0.720$  M,  $[\text{Br}^-] = 0.0200$  M,  $[\text{ClO}_4^-] = 0.980$  M. <sup>c</sup>  $[\text{NO}_3^-] = 0.050$  M,  $[\text{H}^+] = 1.000$  M,  $[\text{Br}^-] = 0.0200$  M,  $[\text{ClO}_4^-] = 0.930$  M. <sup>d</sup>  $r(k'_1, k'_2)$  is the correlation coefficient between the two rate constants.

## RESULTS

The observed pseudo first-order rate constants are presented in Table 1 (first reaction step) and in Table 2 (second reaction step). None of the three rate constants is dependent on the hydrogen ion, ammonium ion, or nitrate ion concentrations in the concentration ranges investigated. Thus, under the conditions employed the reverse reactions are unimportant and nitrate does not interfere.

Fig. 5 shows the pseudo first-order rate constants for the two first reactions as a function of bromide ion concentration at 0.9 °C. The two pseudo first-order rate constants are proportional to the bromide ion concentration and no intercepts (corresponding to a solvent paths) are found. The same is true for the third substitution reaction.

In Table 1 and in Fig. 5 the first reaction has been assigned as being the slower of the two first

reactions. It can be seen that the two observed rate constants are close to each other in magnitude and that they are strongly correlated. This makes the calculation of the intermediate spectrum uncertain. The means of the calculated values of the molar absorptivities at the four wavelengths in question are shown in Fig. 2, together with the absorption spectrum of the bromidodiethylenetriaminegold(III) ion. The latter spectrum has an absorption maximum shifted a full 10 nm toward higher wavelength relative to the maximum for the *trans*-diamminedibromidogold(III) ion, whereas the absorption maximum for the triaminebromidogold(III) ion apparently lies close to that for the *trans*-diamminedibromidogold(III) ion. Neither of the two possibilities for the intermediate spectrum are physically meaningless or unlikely from a chemical viewpoint, as can be seen from a comparison with the spectrum of the bromidodiethylenetriaminegold(III)

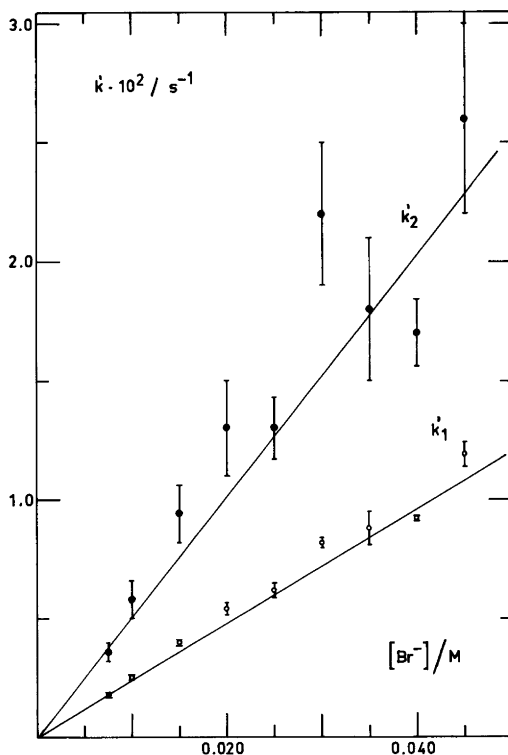


Fig. 5. Pseudo first-order rate constants for the two consecutive reactions  $\text{Au}(\text{NH}_3)_4^{3+} + \text{Br}^- \xrightarrow{k'_1} \text{AuBr}(\text{NH}_3)_3^{2+} + \text{NH}_3$  and  $\text{AuBr}(\text{NH}_3)_3^{2+} + \text{Br}^- \xrightarrow{k'_2} \text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$  as a function of bromide ion concentration at 0.9 °C. The bars indicate one standard deviation. The lines are calculated by means of linear regression analysis.

**Table 2.** Pseudo first-order rate constants for the substitution reaction  $\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{Br}^- \xrightarrow{k_3} \text{AuBr}_3\text{NH}_3 + \text{NH}_3$ . The ionic strength was 1.00 except in experiment No. 11. A 1.00 M  $\text{H}(\text{Br}, \text{ClO}_4)$  medium was used in all experiments with  $\text{pH} = 0.00$ . In experiments Nos. 3 and 4 the medium was 1.00 M  $\text{H}, \text{Na}(\text{Br}, \text{ClO}_4)$  and in No. 5 1.00 M  $\text{H}, \text{Na}, \text{NH}_4(\text{Br}, \text{ClO}_4)$ .  $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$  was used in all experiments except in No. 10 where  $[\text{Au}(\text{NH}_3)_4](\text{ClO}_4)_3$  was used as the starting compound.  $C_{\text{Au}} \approx 10^{-4}$  M.

No.	$t/^\circ\text{C}$	$[\text{Br}^-]/\text{M}$	$\text{pH}$	$k_3'/\text{s}^{-1}$
1	41.5	0.300	0.00	$1.90(2) \times 10^{-4}$
2	41.5	0.500	0.00	$2.94(3) \times 10^{-4}$
3	41.5	0.500	0.30	$2.85(3) \times 10^{-4}$
4	41.5	0.500	1.30	$2.71(2) \times 10^{-4}$
5 <sup>a</sup>	41.5	0.500	1.30	$2.69(2) \times 10^{-4}$
6	38.0	0.0500	0.00	$2.46(9) \times 10^{-5}$
7	38.0	0.200	0.00	$8.60(7) \times 10^{-5}$
8	38.0	0.300	0.00	$1.24(2) \times 10^{-4}$
9	38.0	0.500	0.00	$2.10(2) \times 10^{-4}$
10 <sup>b</sup>	38.0	0.500	0.00	$2.06(2) \times 10^{-4}$
11 <sup>c</sup>	38.0	0.500	0.30	$2.01(2) \times 10^{-4}$
12	35.0	0.300	0.00	$9.37(9) \times 10^{-5}$
13	30.0	0.300	0.00	$5.00(6) \times 10^{-5}$

<sup>a</sup>  $[\text{NH}_4^+] = 0.450$  M. <sup>b</sup> Perchlorate salt used. <sup>c</sup> Ionic strength 0.50 M.

ion or with the spectra of the corresponding series of amminechloridoplatinum(II) complexes.<sup>22</sup> The assignment thus had to be based on the temperature variation of the calculated spectra. The spectrum corresponding to assignment of the first reaction as the slower varies less with temperature than the

**Table 3.** Second-order rate constants for the consecutive substitution reactions  $\text{Au}(\text{NH}_3)_4^{3+} + \text{Br}^- \xrightarrow{k_1}$   $\text{AuBr}(\text{NH}_3)_3^{2+} + \text{NH}_3$  and  $\text{AuBr}(\text{NH}_3)_3^{2+} + \text{Br}^- \xrightarrow{k_2}$   $\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$ .

$t/^\circ\text{C}$	$k_1/\text{l mol}^{-1} \text{s}^{-1}$	$k_2/\text{l mol}^{-1} \text{s}^{-1}$
0.9	0.240(5)	0.51(3)
15.0	1.19(2)	2.48(12)
18.0	1.70(6)	3.07(18)
22.0	2.59(17)	5.3(12)

spectrum corresponding to the reverse assignment. The temperature dependences of the two reactions are, however, close to each other (*vide infra*). Although this somewhat invalidates the use of spectral temperature dependence, the establishment of the first reaction as the slower one also is more consistent with the normal substitution behaviour of square planar complexes.

Second-order rate constants at four temperatures for the two first reactions are given in Table 3. The pseudo first-order rate constants for the third reaction at  $[\text{Br}^-] = 0.300$  M (four temperatures, see Table 2) were converted to second-order rate constants. Arrhenius-type plots for all three reactions showed linearity within estimated errors (Fig. 6), and using reaction rate theory, the activation parameters were evaluated; see Table 4. In this table second-order rate constants corrected to 25.0 °C are presented as well. The activation parameters computed are characterized by very strong correlation and in calculations of rate constants at a certain temperature this correlation must be taken into account.<sup>23</sup>

**Table 4.** Rate constants and activation parameters at 25 °C for the reaction of tetraamminegold(III) ions with bromide ions in acid solution.

Reaction	$k_n/\text{l mol}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	$r(\Delta H^\ddagger, \Delta S^\ddagger)^a$
$\text{Au}(\text{NH}_3)_4^{3+} + \text{Br}^- \xrightarrow{k_1}$ $\text{AuBr}(\text{NH}_3)_3^{2+} + \text{NH}_3$	3.40(8)	73(3)	8(3)	-0.9996
$\text{AuBr}(\text{NH}_3)_3^{2+} + \text{Br}^- \xrightarrow{k_2}$ $\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$	6.5(4)	69(3)	2(10)	-0.9997
$\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{Br}^- \xrightarrow{k_3}$ $\text{AuBr}_3\text{NH}_3 + \text{NH}_3$	$9.3(3) \times 10^{-5}$	88(3)	-26(8)	-0.99990

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



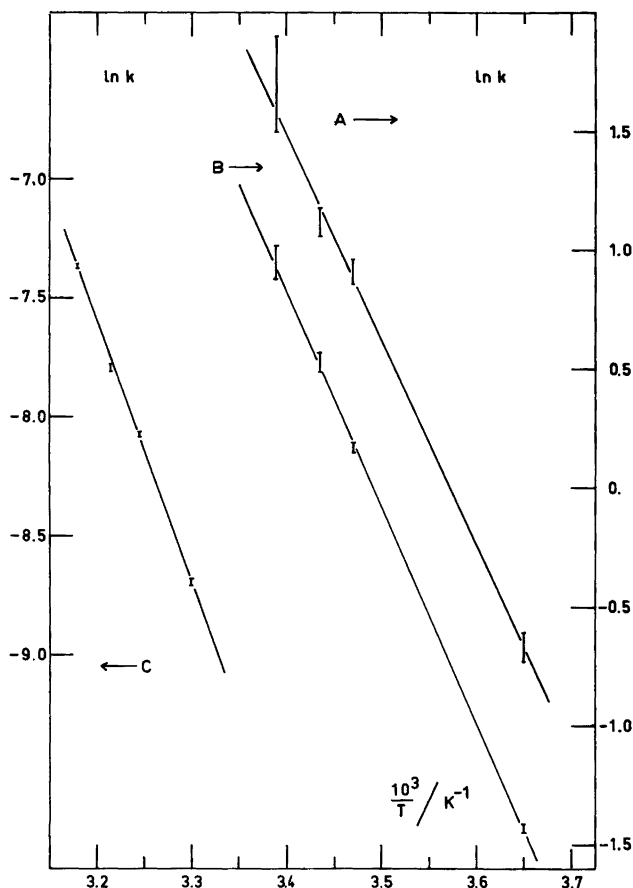


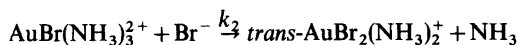
Fig. 6. Arrhenius-type plot. A:  $\text{Au}(\text{NH}_3)_4^{3+} + \text{Br}^- \rightarrow \text{AuBr}(\text{NH}_3)_3^{2+} + \text{NH}_3$ . B:  $\text{AuBr}(\text{NH}_3)_3^{2+} + \text{Br}^- \rightarrow \text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$ . C:  $\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{Br}^- \rightarrow \text{AuBr}_3\text{NH}_3 + \text{NH}_3$ . The bars indicate one standard deviation.

## DISCUSSION

The rate of substitution of ammonia by bromide is lowered by a factor of  $\sim 10^5$  after substitution of the two first ammine ligands in the tetraamminegold(III) ion. A combination of higher activation enthalpy and more negative activation entropy is responsible for this dramatic effect. Similar substitution behaviour, although less pronounced, is seen in the consecutive substitution of ammonia by chloride in the tetraamminepalladium(II) ion.<sup>24</sup> The rate constants for the consecutive reactions show that bromide is more effective as an entering ligand in the present Au(III) substrates in the following order:  $\text{AuBr}(\text{NH}_3)_3^{2+} > \text{Au}(\text{NH}_3)_4^{3+} \gg \text{trans-AuBr}_2(\text{NH}_3)_2^+ < \text{AuBr}_3\text{NH}_3$ . This ordering arises

as a combination of statistical factors, *cis*- and *trans*-effects, and charge effects, these being difficult to separate.

The *trans*-effect, decreasing in the order  $\text{Br}^- > \text{Cl}^- > \text{pyridine} > \text{NH}_3 > \text{H}_2\text{O}$ ,<sup>1</sup> has two aspects, *viz.* the *trans*-directing and the *trans*-labilizing, both of which are kinetic in nature. Both aspects are of importance in the reaction



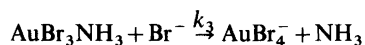
The course of the reaction, the displacement of the *trans*-ligand, is determined by the bromide ligand due to its position in the *trans*-series relative to that of ammonia (*trans*-directing influence). The

Table 5. Rate constants and entropy of activation at 25 °C corrected statistically.<sup>a</sup>

Reaction	<i>m</i>	$k_n m^{-1} / \text{l mol}^{-1} \text{s}^{-1}$	$\Delta S_{\text{corr}}^\ddagger / \text{J mol}^{-1} \text{K}^{-1}$
$\text{Au}(\text{NH}_3)_4^{3+} + \text{Br}^- \xrightarrow{k_1} \text{AuBr}(\text{NH}_3)_3^+ + \text{NH}_3$	4	0.85	-3
$\text{AuBr}(\text{NH}_3)_3^+ + \text{Br}^- \xrightarrow{k_2} \text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{NH}_3$	1	6.5	2
$\text{trans-AuBr}_2(\text{NH}_3)_2^+ + \text{Br}^- \xrightarrow{k_3} \text{AuBr}_3\text{NH}_3 + \text{NH}_3$	2	$4.7 \times 10^{-6}$	-32

<sup>a</sup> *m* is the number of equivalent leaving ligands in the complex.

isolated bromide salt of the product after recrystallization had an UV absorption spectrum identical with that of the reaction mixture. This indicates that the product is almost exclusively *trans*-isomer. Significant formation of the *cis*-isomer would lead to a relatively rapid formation of the tetrabromidoaurate(III) ion. Spectral changes corresponding to formation of this product were not seen under the experimental conditions used in the investigation of the first reaction step. Also, a calculation using *cis*- and *trans*-effects and a tentative charge effect of 5 (see Ref. 9 and references herein) indicate a  $k_2(\text{cis-product}) \approx 0.31 \text{ mol}^{-1} \text{ s}^{-1}$  which agrees with this conclusion. The charge effect and the statistical factor in the two first reactions lower the observed *trans*-labilizing effect. The rate constants and activation entropies corrected statistically (for the number of equivalent leaving ligands) are given in Table 5. The corrected ratio between the two first rate constants,  $\sim 8$ , gives the *trans*-labilizing effect of bromide relative to ammonia. This value, however, is too low and had to be corrected for charge effects. The first reaction is accelerated relative to the second by the partial charge neutralization (in the transition state) of a tripositive ion in the first reaction as compared to a dipositive ion in the second reaction. The reaction



is considerably faster than the preceding reaction, due to the *trans*-labilizing effect of bromide. The charge effect does not counteract the *trans*-labilizing effect to the same degree as in the reaction discussed above.

The great separation in rate of the two first reactions from the two last ones is only partly due to charge effects. Ammonia has a remarkably high

*cis*-effect relative to bromide. The *cis*-effect of ammonia relative to chloride is small in platinum(II) complexes but much greater in palladium(II) complexes.<sup>25</sup> As deduced from the present data this effect of ammonia in *cis*-position is even more pronounced in gold(III) complexes than in palladium(II) complexes.

A more thorough discussion of these effects and of the trends in the activation parameters had to await further experiments and will be postponed until an investigation of the anation of tetraamminegold(III) ion by chloride can be presented.

*trans*-Diamminedibromidogold(III) tetrabromidoaurate(III) is only sparingly soluble in water but readily soluble in ethanol and water-ethanol mixtures. The absorption spectrum in ethanol is red-shifted relative to that in water (Fig. 1) as typical of ionpair formation, indicating an interaction between the complex anion and cation.

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