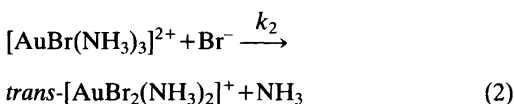
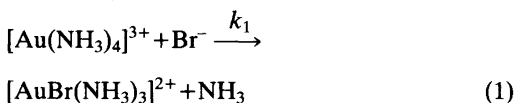


Amineanionogold(III) Complexes. III. Kinetics of the Substitution of Ammonia by Bromide in Amminetribromidogold(III) in Acid Aqueous Solution

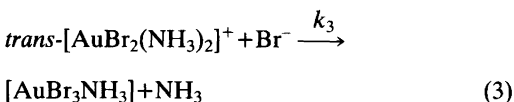
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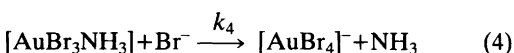
Two distinct stages with rates differing by five orders of magnitude are observed in the reaction sequence in which the four ammonia ligands in the square planar tetraamminegold(III) ion are replaced by bromide.¹ The first stage giving *trans*-diamminedibromidogold(III) as product consists of two consecutive reactions of comparable rates,



The second and slower stage appears as a simple pseudo first-order reaction when bromide is in excess, and the replacement of one ammonia in *trans*- $[\text{AuBr}_2(\text{NH}_3)_2]^+$ has been identified as the experimentally observed slow reaction of the overall process in acid solution,



The last ammonia is replaced by bromide,



at a rate which is fast compared to the rate of reaction (3).

The rate constants and activation parameters for the first three reactions in the reaction sequence (1)–(4) in 1.0 M H(Br,ClO₄) have

been determined previously, but since reaction (4) is preceded by a much slower reaction, the kinetic parameters for this reaction were not accessible from kinetic experiments in which solutions of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ or *trans*- $[\text{AuBr}_2(\text{NH}_3)_2]\text{Br}$ were allowed to react with bromide.¹

Strähle *et al.*² have recently prepared $[\text{AuCl}_3\text{NH}_3]$ by thermal decomposition of $\text{NH}_4[\text{AuCl}_4]$. Since halide exchange reactions at Au(III) centers are fast compared to reactions (1)–(4),^{3–5} $[\text{AuCl}_3\text{NH}_3]$ can be used as a precursor for $[\text{AuBr}_3\text{NH}_3]$, thus allowing a direct study of reaction (4) and thereby a completion of the work started in Ref. 1. The results from such kinetic studies are reported here together with a discussion based on activation parameters of the factors which control the rate of replacement of ammonia by bromide at Au(III) centers.

The rate of replacement of ammonia by bromide in $[\text{AuBr}_3\text{NH}_3]$ was monitored spectrophotometrically. All kinetic experiments were performed with excess of bromide ion in acidic solution, and simple pseudo first-order kinetics were observed in all experiments. The observed pseudo first-order rate constants, which are given in Table 1 together with the experimental conditions, are more than a factor 10³ greater than those expected for Cl[−]/Br[−] exchange reactions,^{3,5} and any interference from halide exchange reactions on reaction (4) could therefore be excluded. From experiments 2–4, 8, and 9 of Table 1 it is seen that the first-order constants are directly proportional to $[\text{Br}^-]$, indicating that the substitution reaction takes place as a direct displacement without any significant contribution from a solvent path.^{1,3,5} Experiments 4–7 indicate, in accordance with the results previously obtained for reactions (1)–(3), that both NH₄⁺ and H⁺ in the concentration range studied have only minor effects on the reaction rate. From the dependence of the pseudo first-order rate constants on $[\text{Br}^-]$ and from the temperature dependence (experiments 1,3,10, and 11), the second-order rate constant and the activation parameters for reaction (4) at 25 °C were estimated. These values are compared in Table 2 with those previously obtained for reactions (1)–(3).

Effects due to the charge of the nucleophile in combination with the charge of the substrate as well as separate effects due to *cis*- and *trans*-ligands have been used in parameterization of the reactivity of *d*⁸ low-spin square planar complexes. The influence of these different factors is normally discussed on the basis of rate constants for consecutive ligand substitution reactions in series of complexes such as $[\text{Pt}(\text{H}_2\text{O})_x(\text{NH}_3)_y\text{Cl}_{4-x-y}]$, and $[\text{AuBr}_x\text{Cl}_{4-x}]$ ^{3,6,7} obtained at one

Table 1. Pseudo first-order rate constants for the substitution reaction $\text{AuBr}_3\text{NH}_3 + \text{Br}^- \xrightarrow{k_4} \text{AuBr}_4^- + \text{NH}_3$ in acidic aqueous solution. A 1.00 M $\text{H}(\text{Br}, \text{ClO}_4)$ medium was used in all experiments except Nos. 5, 6, and 7.

No.	$t/^\circ\text{C}$	$[\text{Br}^-]/\text{M}$	pH	k_4'/s^{-1}
1	19.5	0.0150	0.00	$2.18(3) \times 10^{-4}$
2	25.0	0.0100	0.00	$2.52(14) \times 10^{-4}$
3	25.0	0.0150	0.00	$3.76(15) \times 10^{-4}$
4	25.0	0.0200	0.00	$5.01(7) \times 10^{-4}$
5 ^a	25.0	0.0200	0.52	$5.09(9) \times 10^{-4}$
6 ^b	25.0	0.0200	0.52	$4.02(3) \times 10^{-4}$
7 ^c	25.0	0.0200	1.10	$3.98(5) \times 10^{-4}$
8	25.0	0.0300	0.00	$7.54(10) \times 10^{-4}$
9	25.0	0.0400	0.00	$1.04(1) \times 10^{-3}$
10	29.6	0.0150	0.00	$6.89(13) \times 10^{-4}$
11	34.4	0.0150	0.00	$1.19(5) \times 10^{-3}$

^a $[\text{NH}_4^+] = 0.70 \text{ M}$, $[\text{H}^+] = 0.30 \text{ M}$, $[\text{Br}^-] = 0.0200 \text{ M}$, $[\text{ClO}_4^-] = 0.98 \text{ M}$. ^b $[\text{Na}^+] = 0.70 \text{ M}$, $[\text{H}^+] = 0.30 \text{ M}$, $[\text{Br}^-] = 0.0200 \text{ M}$, $[\text{ClO}_4^-] = 0.98 \text{ M}$. ^c $[\text{Na}^+] = 0.92 \text{ M}$, $[\text{H}^+] = 0.080 \text{ M}$, $[\text{Br}^-] = 0.0200 \text{ M}$, $[\text{ClO}_4^-] = 0.98 \text{ M}$.

Table 2. Rate constants and activation parameters for the reaction of tetraamminegold(III) ions with bromide in aqueous 1.0 M $\text{H}(\text{Br}, \text{ClO}_4)$ at 25 °C.

Reaction	$k_n/\text{l mol}^{-1}\text{s}^{-1}$	$\Delta H_n^\ddagger/\text{kJ mol}^{-1}$	$\Delta S_n^\ddagger/\text{J mol}^{-1}\text{K}^{-1}$	Ref.
$[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Br}^- \xrightarrow{k_1} [\text{AuBr}(\text{NH}_3)_3]^{2+} + \text{NH}_3$	3.40(8)	73(3)	8(3)	1
$[\text{AuBr}(\text{NH}_3)_3]^{2+} + \text{Br}^- \xrightarrow{k_2} \text{trans}-[\text{AuBr}_2(\text{NH}_3)_2]^+ + \text{NH}_3$	6.5(4)	69(3)	2(10)	1
$\text{trans}-[\text{AuBr}_2(\text{NH}_3)_2]^+ + \text{Br}^- \xrightarrow{k_3} [\text{AuBr}_3\text{NH}_3] + \text{NH}_3$	$9.3(3) \times 10^{-5}$	88(3)	-26(8)	1
$[\text{AuBr}_3\text{NH}_3] + \text{Br}^- \xrightarrow{k_4} [\text{AuBr}_4]^- + \text{NH}_3$	$2.68(9) \times 10^{-2}$	84(4)	7(9)	Present work ^a

^a The correlation coefficient between the two activation parameters is -0.9998.

fixed temperature. However, the data of Table 2 provide an opportunity for a discussion of these factors in relation to the activation parameters for a series of Au(III) substrates.

The difference between the rates of bromide substitution of the two first and the subsequent and more robust ammine ligands is primarily a consequence of a higher enthalpy of activation. However, for the third ammine ligand it is also a consequence of a more negative entropy of activation. It is noteworthy that the enthalpies of activation for the substitution of the two first ammine ligands are identical within the experimental uncertainties, and that the enthalpies

of activation for substitution of the last two ammine ligands are likewise equal. Thus, the remarkably high *cis*-effect of ammonia relative to bromide in Au(III) complexes, which has been shown to be purely kinetic in nature,⁴ is mainly an enthalpy effect. The labilizing effect of two *cis*-ammonia relative to two *cis*-bromide ligands thus corresponds to $\approx 15 \text{ kJ/mol}$, *viz.* the difference between $\Delta H_4^\ddagger (\approx \Delta H_3^\ddagger)$ and $\Delta H_2^\ddagger (\approx \Delta H_1^\ddagger)$.

The rate constants and the entropies of activation given in Table 3 have been corrected statistically for the number of equivalent leaving ligands. The *trans*-labilizing effect of bromide relative to ammonia is 575 calculated from the

Table 3. Statistically corrected rate constants and entropies of activation for the successive substitution of ammonia with bromide in tetraamminegold(III) ions in aqueous 1.0 M H(Br,ClO₄) at 25 °C.^a

Reaction	<i>m</i>	<i>k_n</i> <i>m</i> ⁻¹ /l mol ⁻¹ s ⁻¹	Δ <i>S</i> _{n,corr} [‡] /J mol ⁻¹ K ⁻¹
$[\text{Au}(\text{NH}_3)_4]^{3+} + \text{Br}^- \xrightarrow{k_1} [\text{AuBr}(\text{NH}_3)_3]^{2+} + \text{NH}_3$	4	0.85	-3
$[\text{AuBr}(\text{NH}_3)_3]^{2+} + \text{Br}^- \xrightarrow{k_2} \text{trans}-[\text{AuBr}_2(\text{NH}_3)_2]^+ + \text{NH}_3$	1	6.5	2
$\text{trans}-[\text{AuBr}_2(\text{NH}_3)_2]^+ + \text{Br}^- \xrightarrow{k_3} [\text{AuBr}_3\text{NH}_3] + \text{NH}_3$	2	4.7 × 10 ^{-5^b}	-32
$[\text{AuBr}_3\text{NH}_3] + \text{Br}^- \xrightarrow{k_4} [\text{AuBr}_4]^- + \text{NH}_3$	1	2.7 × 10 ⁻²	7

^a *m* is the number of equivalent leaving ligands in the complex. ^b Incorrectly given as 4.7 × 10⁻⁶ in Ref. 1.

corrected rate constants for reactions (3) and (4). This difference in rate is mainly an entropy effect, since $\Delta H_4^\ddagger - \Delta H_3^\ddagger = -4 \pm 5$ kJ/mol whereas $-298(\Delta S_{4,\text{corr}}^\ddagger - \Delta S_{3,\text{corr}}^\ddagger) = -12 \pm 4$ kJ/mol. However, the *trans*-effect of bromide relative to ammonia is only 8 when calculated from the results for the two first substitution reactions. The expected acceleration of the second substitution reaction relative to the first due to an entropy effect is hardly observed, since $-298(\Delta S_{2,\text{corr}}^\ddagger - \Delta S_{1,\text{corr}}^\ddagger) = -2 \pm 3$ kJ/mol. Charge neutralization during bond formation generally makes a positive contribution to the entropy of activation for substitution reactions with associative activation. The data of Table 3 do indeed show this effect to be significant for the present series of Au(III) substrates. It is remarkable that the partial charge neutralization in the transition state of the tripositive $[\text{Au}(\text{NH}_3)_4]^{3+}$ accelerates the substitution of the first ammine to essentially the same extent as the presence of a *trans*-bromide ligand accelerates the substitution of the second ammine ligand. However, it should be noted that the *trans*-directing influence of bromide relative to ammonia is not affected, since only *trans*- $[\text{AuBr}_2(\text{NH}_3)_2]^+$ was observed as a product of reaction (2).¹

In conclusion, the present results suggest that the high *cis*-effect of ammonia relative to bromide is an enthalpy effect whereas the more modest *trans*-effect of bromide relative to ammonia is an entropy effect. Bond formation in the transition state has been shown to be more important in Au(III) complexes than in other square planar complexes.⁵ Charge neutralization appears to play a significant role during this bond

formation step.

In the mixed chlorido-bromido complexes $[\text{AuBr}_x\text{Cl}_{4-x}]^-$, bromide is about 65 times better than chloride as an entering ligand and the Br⁻/Cl⁻ *trans*-effect is ~14.³ If these trends are assumed to be valid also for mixed ammine-halogenido complexes, then the prediction can be made that in the anation of $[\text{Au}(\text{NH}_3)_4]^{3+}$ with chloride, the relative rates of the two first ammonia/chloride exchange reactions should be reversed compared to the analogous ammonia/bromide exchange reactions. This would be a unique substitution behaviour for a square planar complex, and it would be an important verification of the significance of charge neutralization during bond formation in the transition state of ligand substitutions in cationic Au(III) complexes. An investigation of the reaction of $[\text{Au}(\text{NH}_3)_4]^{3+}$ with chloride is now in progress.⁹

Experimental. $[\text{AuCl}_3\text{NH}_3]$ synthesized by the method of Strähle *et al.*² was dissolved in the various reaction media prepared from analytical grade chemicals and analyzed using standard methods. Prethermostatted solutions with $c_{\text{Au}} \approx 10^{-4}$ M were placed in a 1 cm quartz cell in the thermostatted cell-holder of a Zeiss DMR 21 spectrophotometer and UV-spectra were recorded at known times. All experiments were run in duplicate.

Calculations. The recorded spectra were read off at the four wavelengths 360, 380, 400, and 420 nm and the calculations were done by non-linear regression analysis, as described previously.¹ Under the present conditions the reaction showed pseudo first-order kinetics (goodness-of-fit test). An Arrhenius-type plot showed linearity within the estimated uncertainty and the activation parameters were evaluated using reaction rate theory.

* The *trans*-configuration of this product has now been confirmed by an X-ray single-crystal structure determination of the bromide salt.⁸

Acknowledgements. The author is grateful to Jacob Ventegodt for assistance in the experimental work and to Dr. Martin Hancock for linguistic help.

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Received July 18, 1983.