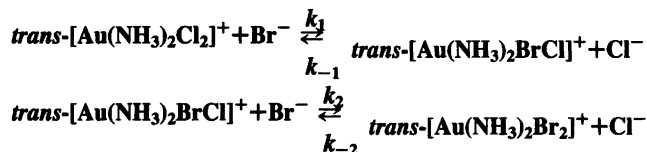


## Amineanionogold(III) Complexes. IV. The Crystal Structure and Bromide Chloride Interchange Kinetics of *trans*-Diamminedibromidogold(III) Bromide

KAREN KAAS and L.H. SKIBSTED

Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark

The crystal and molecular structure of *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]Br has been determined by X-ray diffraction methods. The crystals are monoclinic, space group *C2/m*, with *Z*=2, and with unit cell dimensions *a*=8.916(2), *b*=6.1134(14), *c*=6.6285(14) Å, and *β*=98.002(17)°. The structure was solved and refined from diffractometer data. The *R*-factor decreased from 0.059 to 0.034 when a secondary isotropic extinction correction was applied. The complex ion is planar as it lies in a crystallographic mirror plane and has *C<sub>2h</sub>* symmetry. In acid aqueous solution the reversible ligand substitution



takes place as direct displacements and no solvent paths were detectable. Second-order rate constants and activation enthalpies at 25.0 °C and unit ionic strength are:  $k_1=2150(30) \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_1^\ddagger=28.0(1.2) \text{ kJ mol}^{-1}$ ,  $k_{-1}=17.6(4) \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_{-1}^\ddagger=40.1(1.7) \text{ kJ mol}^{-1}$ ,  $k_2=9800(300) \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $\Delta H_2^\ddagger=22(2) \text{ kJ mol}^{-1}$ ,  $k_{-2}=328(7) \text{ l mol s}^{-1}$ ,  $\Delta H_{-2}^\ddagger=35(2) \text{ kJ mol}^{-1}$ . These substitutions are faster than the corresponding substitutions in tetrahalogenidoaurate(III) complexes but slower than those in *trans*-dicyanidodihalogenidoaurate(III).

Anation of tetraamminegold(III) by chloride or bromide in acidic aqueous solution in which deprotonation and hydrolysis are suppressed<sup>1</sup> takes place in two kinetically separated steps,<sup>2,3</sup> and diamminedichloridogold(III) and diamminedibromidogold(III) have been isolated as the chloride and the bromide salt, respectively.<sup>2,3</sup> On the basis of kinetic arguments both of these intermediates have tentatively been assigned the *trans*-configuration. In order to provide a better background for a correlation between structure, stability, and reactivity of gold(III) complexes, we have undertaken a determination of the crystal structure of diamminedibromidogold(III) bromide and a determination of the activation parameters for the reversible exchange of bromide with chloride in this complex dissolved in acidic aqueous solution. We report here the results of this combination of an X-ray single-crystal structure determination and a stopped-flow spectrophotometric investigation.

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## EXPERIMENTAL

**Materials.** *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·1/3H<sub>2</sub>O<sup>4</sup> and *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]Br<sup>2</sup> were both prepared and purified as previously described. Other chemicals were of analytical grade. Hydrobromic acid was distilled before dilution. Stock solutions of hydrobromic acid, hydrochloric acid, perchloric acid, and sodium perchlorate were analyzed using standard methods.

*Spectrophotometric measurements* were performed on a Zeiss DMR 21 spectrophotometer.

*Kinetic measurements.* The kinetic investigation was made in aqueous solution of unit ionic strength in the temperature range 19–41 °C. The reactions were followed using a Durrum-Gibson stopped-flow spectrophotometer (The Royal Danish School of Pharmacy) with teflon-coated pistons and modified to contain a Zeiss M4 Q III monochromator. Equal volumes of a gold(III) complex containing solution and a solution with the appropriate chloride/bromide ratio, both of unit ionic strength, were mixed and the transmission was recorded as a function of time at a fixed wavelength on a Tektronix RM 564 storage oscilloscope and transferred to a Nicolet 170 data collecting system. Solutions of *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> or *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> were freshly prepared by dissolution of weighed amounts of the chloride or the bromide salt, respectively, in the actual medium. *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>-stock solutions contained excess chloride (0.05 < [Cl<sup>-</sup>] < 1.0 M) to suppress hydrolysis. For *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup>, hydrolysis is less significant and the presence of the bromide counter ion ensures that less than 1 % of the complex is hydrolyzed.<sup>3</sup>

*Calculation of rate constants and activation parameters* was made within the framework of non-linear regression analysis, using the numerical procedures previously described.<sup>2</sup>

*Crystal structure determination.* The crystal used for X-ray investigation was selected from a 100 mg sample of *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]Br reprecipitated from 2 ml of ice-cold 0.1 M HClO<sub>4</sub> by the slow addition of 0.3 ml of an ice-cold saturated aqueous LiBr solution, and washed with absolute ethanol and subsequently with ether. The compound forms reddish-orange prismatic needles, and the selected crystal had developed forms {001} and {00 $\bar{1}$ } with the distance 0.20 mm, {110} and { $\bar{1}\bar{1}0$ } with 0.11 mm and {110} and {110} with 0.09 mm.

X-ray diffraction photographs showed that the crystals are monoclinic, and the systematic absences (*hkl*, *h+k* odd) characterized the space group as *C2*, *Cm* or *C2/m*. The data collection was performed on a Picker FACS-1 diffractometer at the H.C. Ørsted Institute, using graphite-monochromated MoK $\alpha$  radiation. The intensities were measured at room temperature (22 °C), operating the diffractometer in a  $\theta, 2\theta$  scan mode at a rate of 2° min<sup>-1</sup> in  $2\theta$ . The scan range was from  $2\theta - (1.0 + 0.231 \tan \theta)$  to  $2\theta + (1.2 + 0.462 \tan \theta)$ , and the background counts were made for 20 s at each end of the scan range. The experimental stability was monitored by measuring 3 standard reflexions after every 50 reflexions. Intensities for all 1068 reflexions in a quarter of a sphere in reciprocal space in the range  $2.4 \leq 2\theta < 75^\circ$  were measured. The data were corrected for Lorentz, polarization and absorption effects ( $\mu/\rho$  values from International Tables for X-ray Crystallography,<sup>5</sup> grid 12×12×16). The data appeared to be severely affected by isotropic secondary extinctions, and two of the standard reflexions showed a 8–10 % decay, whereas the third increased about 5 % in intensity. The latter phenomenon was probably due to a decrease in extinction (the corrections made during refinement amounted to about a factor of 2 for the standard reflexions). No attempt was made to correct for decay. The intensities for 51 pairs of reflexions with *h*=0 related by crystal symmetry were measured but were not averaged. 948 reflexions had intensities with  $I/\sigma(I) \geq 2.5$ , they were classified as observed and used in the structure analysis.

*Determination and refinement of the structure.* The structure was solved and refined by conventional Patterson and Fourier methods. The refinement was performed by the method of full matrix least squares, minimizing  $\sum w(|F_o| - |F_c|)^2$ , and assuming the space group to be *C2/m*. Anisotropic thermal parameters were refined for gold and bromine, whereas an isotropic thermal parameter was refined for nitrogen. The refinement terminated at *R*=0.059, 88 reflexions which had  $||F_o| - |F_c|| > 5$  being omitted at this stage. It was not possible to find a reasonable weighting scheme until a secondary isotropic extinction correction was applied to the calculated structure factors. During the following cycles of

**Table 1.** Final fractional coordinates with estimated standard deviations for *trans*-diamminedibromidogold(III) bromide. The other half of the molecule (atoms designated by a prime in Fig. 1) is generated by  $x'=x$ , and  $z'=-z$ .

Atom	x	y	z
Au	0	0	0
Br <sup>-</sup>	0.5	0	0.5
Br	0.22445(9)	0	-0.16953(12)
N	0.1252(9)	0	0.2821(11)

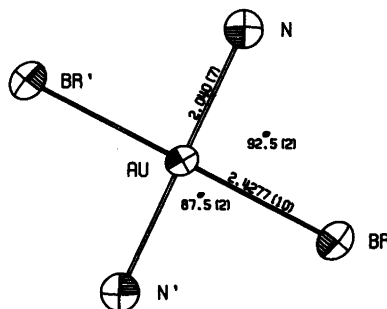
**Table 2.** Thermal parameters for *trans*-diamminedibromidogold(III) bromide in  $\text{\AA}^2 \times 10^2$ . T.F.=exp.  $\{-2\pi^2(U_{11}a^{*2}h^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+U_{22}b^{*2}k^2+2U_{23}b^*c^*kl+U_{33}c^{*2}l^2)\}$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Au	2.238(19)	2.104(19)	1.848(18)	0	0.530(10)	0
Br <sup>-</sup>	2.43(5)	3.19(5)	3.67(5)	0	0.45(4)	0
Br	2.85(4)	2.98(4)	2.94(3)	0	1.08(3)	0
N	2.95(12)					

refinement the extinction coefficient reached a value of  $5.61(15) \cdot 10^{-4}$ . The weights used follow the expression  $w^{-1}=3+\sigma^2|F|-0.06|F|+0.001|F|^2-2 \sin\theta/\lambda$ . In the last cycle of the least-squares refinement the maximum shift was 0.24 and the unit weighted- and weighted residuals,  $R$  and  $R_w$  were 0.034 and 0.040, respectively. Due to the considerable anomalous dispersion and extinction corrections, the difference electron-density maps showed considerable noise, and neither these maps nor Fourier maps calculated with the final  $(|F_o|-|F_c|)$  as coefficients showed any peaks which could be interpreted as the hydrogen atoms. The final atomic parameters are listed in Tables 1 and 2. The following computer programmes were used: The Vanderbilt system for diffractometer operations,<sup>6</sup> a data reduction programme of local origin, the X-ray system<sup>7</sup> for the crystal structure analysis, and ORTEP II<sup>8</sup> for the illustrations. The atomic scattering factors for neutral atoms and the anomalous dispersion corrections added to the scattering factor of Au and Br were taken from International Tables for X-ray Crystallography.<sup>5</sup> Listings of observed and calculated structure amplitudes may be obtained from the authors.

## CRYSTAL DATA

*trans*-Diamminedibromidogold(III) bromide  $[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br}$ ,  $M=470.78$ . Space group  $C2/m$  monoclinic (No. 12).  $a=8.916(2)$   $\text{\AA}$ ,  $b=6.1134(14)$   $\text{\AA}$ ,  $c=6.6285(14)$   $\text{\AA}$ ,  $\beta=98.002(17)^\circ$ ,  $V=357.79$   $\text{\AA}^3$ ,  $Z=2$ ,  $D_m>3.3$   $\text{g cm}^{-3}$ ,  $D_x=4.37$   $\text{g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha)=388.2$   $\text{cm}^{-1}$ .



**Fig. 1.** ORTEP drawing of the *trans*- $[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$  cation, the thermal ellipsoid encloses 50 % probability. The ion has crystallographic  $2/m$  symmetry. The hydrogen atoms could not be located.

Table 3. Interatomic distances and angles in  $trans-[Au(NH_3)_2Br_2]^+$  and related complexes.

Complex	$[AuBr_4]^-$	$[Au(NH_3)_4]^{3+}$	$trans-[Au(NH_3)_2Br_2]^+$	$trans-[Pt(NH_3)_2Br_2]$
Compound Reference	$Rb_2Au_2Br_6$ 9	$[Au(NH_3)_4](NO_3)_3$ 10	$trans-[Au(NH_3)_2Br_2]$ Present study	$trans-[Pt(NH_3)_2Br_2]$ 11
Metal-Br (Å)	2.438(4)	2.02(1)	2.4277(10)	2.45(1)
Metal-N (Å)	89.26(9)	88.6(6)	2.040(7)	2.08(1)
Angle <sup>a</sup> (°)			87.5(2)	89.5(5)

<sup>a</sup> The smallest ligand-metal-ligand angles. All the mentioned complexes are planar.

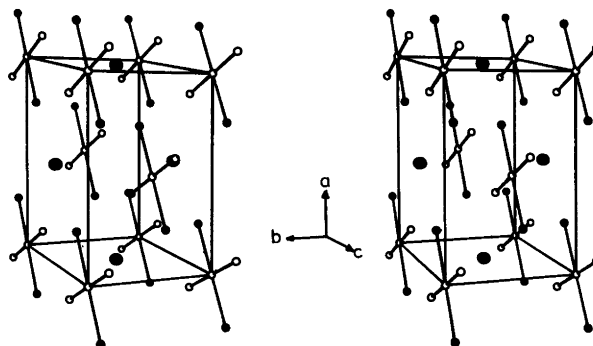


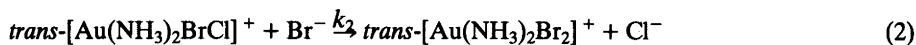
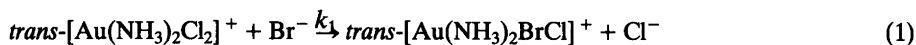
Fig. 2. Stereoscopic illustration of the contents of the unit cell. Thermal ellipsoids enclosing 50 % probability are shown for the bromide ion.

*Description and discussion of the structure.* The structure consists of *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> cations and Br<sup>-</sup> anions held together by electrostatic forces. The complex ion with atomic labelling is shown in Fig. 1 together with the interatomic distances and angles. The cation is planar as it lies in a crystallographic mirror plane and has 2/m (C<sub>2h</sub>) symmetry. Refinement in space group C2 might have resulted in an out-of-plane deviation for Au, but the thermal parameters (Table 2) show very little anisotropy. However, with the above-mentioned large corrections for absorption, anomalous dispersion, and extinction, a deviation from planarity was not likely to be significant. The Au-Br and Au-N distances do not differ significantly from the values found in tetrabromidoaurate(III)<sup>9</sup> and tetraamminegold(III),<sup>10</sup> respectively, and are only marginally shorter than in the analogous platinum(II) complex *trans*-[Pt(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>11</sup> (Table 3). The ligand-metal-ligand angles in *trans*-[Au-(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> deviate from 90° by 2.5(2)°, probably due to the packing of the complex ions in the crystal, where the interionic Br-N distances are relatively short.

*Packing.* It can be seen from the stereo pair in Fig. 2 that all complex ions lie in planes perpendicular to the *b*-axis with *y*=0 and  $\frac{1}{2}$ . Both Au and Br<sup>-</sup> occupy special positions with 2/m symmetry. The shortest distances between Br and N in different complex ions are 3.461(4) Å and 3.619(7) Å, which are only slightly larger than the distances of 3.103(8) Å and 3.238(8) Å found between Br and N within the complex ions. The shortest Br-Br distance is 3.7838(9) Å. The bromide ions are placed in holes with the shortest Br<sup>-</sup>-Br distance of 3.5118(11) Å and the shortest Br<sup>-</sup>-N distance of 3.451(8) Å and 3.623(4) Å.

## KINETIC RESULTS

The reaction of *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> with excess bromide in 1.00 M H(Br, Cl, ClO<sub>4</sub>) gave rapidly and quantitatively the product *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> as evidenced by the UV-absorption spectrum. The reaction occurs in two steps,



but simple pseudo first-order kinetics were observed irrespective of whether the reaction was monitored at 307 nm (a *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>BrCl]<sup>+</sup>/*trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> isosbestic

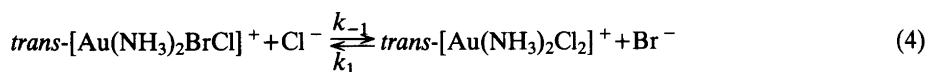
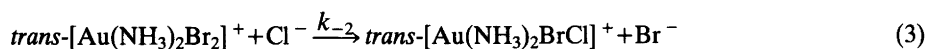
**Table 4.** Pseudo first-order rate constants for the substitution reaction  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Cl}^-$  obtained from stopped-flow spectrophotometric measurements. The reaction medium was 1.00 M  $\text{H}(\text{Br}, \text{Cl}, \text{ClO}_4)$  in all experiments except No. 4. Monitoring wavelength was 307 nm except in experiment No. 5 for which the mean of the values calculated at 307, 328, and 281 nm is reported.  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl} \cdot 1/3\text{H}_2\text{O}$  was used as starting compound and  $C_{\text{Au}} \approx 3 \cdot 10^{-4}$  M.

No.	$t/\text{ }^\circ\text{C}$	$[\text{Br}^-]/\text{M}$	$[\text{Cl}^-]/\text{M}$	$k_1'/\text{s}^{-1}$ <sup>a</sup>
1	19.2	0.0250	0.0250	43.0(1.9)
2	25.0	0.0125	0.0250	26.5(5)
3	25.0	0.0250	0.0250	53(2)
4 <sup>b</sup>	25.0	0.0250	0.0250	54(1)
5	25.0	0.0500	0.0250	100(2)
6	25.0	0.0500	0.500	108(3)
7	25.0	0.100	0.0250	211(4)
8	29.8	0.0250	0.0250	64.1(1.6)
9	35.8	0.0250	0.0250	83(2)

<sup>a</sup> Mean values of at least two experiments. <sup>b</sup>  $[\text{Na}^+] = 0.95$  M.

point<sup>4</sup>) or at other wavelengths. This observation indicates that reaction (2) is fast compared to reaction (1). As the rate of reaction (1) was found to be close to the limit for the stopped-flow technique, the kinetics of the even faster reaction (2) were not investigated further. The pseudo first-order rate constant for reaction (1) was found to be independent of hydrogen ion concentration ( $0.05 \leq [\text{H}^+] \leq 1.0$  M) and of chloride ion concentration ( $0.025 \leq [\text{Cl}^-] \leq 0.50$  M), but proportional to the bromide ion concentration ( $0.0125 \leq [\text{Br}^-] \leq 0.10$ ), as can be seen from Table 4. These observations indicate that the chloride–bromide interchange in reaction (1) is a direct displacement without a significant solvent path. Solvent paths have been found for the analogous reactions of the corresponding platinum(II) and palladium(II) complexes.<sup>12</sup>

Reaction of  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$  with excess chloride gave analogous results. However, for the stepwise reactions,



simple pseudo first-order kinetics were found only when the reaction was monitored at a wavelength corresponding to a  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+/\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$  isobestic point, such as 291 nm.<sup>4</sup> At 291 nm the increase in absorbance is solely due to reaction (3), and the pseudo first-order rate constants reported in Table 5 were consequently assigned to reaction (3). These constants are proportional to the chloride ion concentration, again indicating the absence of a solvent path. At other monitoring wavelengths the absorbance changes associated with reaction (3) were followed by much slower changes. This indicates that reaction (4) is slow as compared to reaction (3). However, a direct experimental determination of  $k_{-1}$  was hampered by the magnitude of the equilibrium constant  $3.65 \times 10^3$  for the exchange of the two chlorides with bromide in  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+$  at 25 °C<sup>4</sup> and thus it was not attempted.

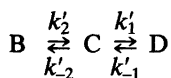
Table 5. Pseudo first-order rate constants for the substitution reaction  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Cl}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Br}^-$  obtained from stopped-flow spectrophotometric measurements. The reaction medium was 1.00 M  $\text{H}(\text{Br}, \text{Cl}, \text{ClO}_4)$  in all experiments. Monitoring wavelength was 291 nm except in experiment No. 3 for which the mean of the values calculated at 291, 328 and 340 nm is reported.<sup>a</sup>  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br}$  was used as starting compound and  $C_{\text{Au}} \approx 3 \cdot 10^{-4}$  M.

No.	$t/^\circ\text{C}$	$[\text{Cl}^-]/\text{M}$	$k'_{-2}/\text{s}^{-1b}$
1	19.2	0.300	74(2)
2	25.0	0.200	63(2)
3	25.0	0.300	98(2)
4	25.0	0.400	121(9)
5	25.0	0.500	154(4)
6	29.8	0.300	124(2)
7	40.5	0.300	232(16)

<sup>a</sup> At 328 and 340 nm, calculated for the initial fast absorbance change, cf. Fig. 3. <sup>b</sup> Mean value of at least two experiments.

The second-order rate constants and the activation parameters at 25.0 °C for reactions (1) and (3) were calculated using reaction rate theory from the rate constants of Tables 4 and 5. Combination of these kinetic parameters with  $\Delta H^\circ$  and  $\Delta S^\circ$  for the stepwise chloride-bromide interchange known from previous equilibrium studies<sup>4</sup> allowed the calculation of the kinetic parameters for reactions (2) and (4). Table 6 thus contains a full thermodynamic and kinetic characterization of the chloride-bromide interchange reactions of *trans*-diamminedihalogenidogold(III) in aqueous solution of unit ionic strength.

The consistency between the results from the thermodynamic studies and the kinetic studies was proven by experiment No. 3 of Table 5, in which  $\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$  was allowed to react with chloride. In this experiment the 328 nm absorbance was followed to constancy (shown in Fig. 3). Under these conditions reaction (3) is succeeded by the two opposing reactions (4) and (1). For the general first-order kinetic scheme



the absorbance as a function of time is described by<sup>13</sup>

$$A_\lambda(t) = a + b \cdot e^{-\gamma_1 t} + c \cdot e^{-\gamma_2 t}$$

when  $[\text{B}] = [\text{C}] = 0$  at  $t = 0$ . The coefficients  $\gamma_1$  and  $\gamma_2$  are related to the four rate constants by

$$\left. \begin{matrix} \gamma_1 \\ \gamma_2 \end{matrix} \right\} = \frac{1}{2} \left[ (k'_1 + k'_2 + k'_{-1} + k'_{-2}) \pm \sqrt{(k'_1 + k'_2 + k'_{-1} + k'_{-2})^2 - 4(k'_1 k'_2 + k'_1 k'_{-2} + k'_{-1} k'_{-2})} \right]$$

From the experimental values of  $A_{328}(t)$  (cf. Fig. 3) the two coefficients were calculated by non-linear regression analysis:  $\gamma_1 = 113 \pm 5 \text{ s}^{-1}$  and  $\gamma_2 = 8.1 \pm 0.4 \text{ s}^{-1}$ , which are in agreement with  $\gamma_1 = 108 \pm 5 \text{ s}^{-1}$  and  $\gamma_2 = 6.9 \pm 0.7 \text{ s}^{-1}$  calculated directly from the four rate constants at the actual bromide- and chloride ion concentrations.

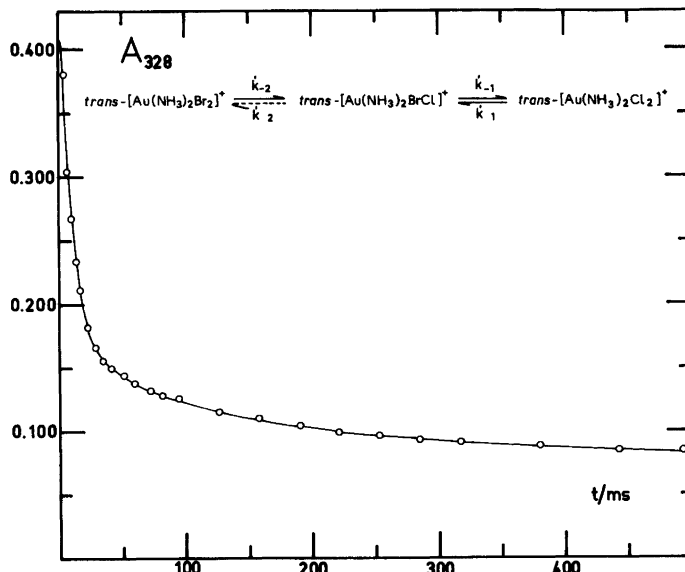


Fig. 3. 328 nm absorbance as a function of time in the stopped-flow experiment No. 3 of Table 5.  $\text{trans-[Au(NH}_3)_2\text{Br}_2]^+$  was reacted with  $\text{Cl}^-$  at  $25.0^\circ\text{C}$  giving the product complex distribution:  $\alpha_{\text{trans-[Au(NH}_3)_2\text{Br}_2]^+} = 0.03$ ,  $\alpha_{\text{trans-[Au(NH}_3)_2\text{BrCl}]^+} = 0.28$ ,  $\alpha_{\text{trans-[Au(NH}_3)_2\text{Cl}_2]^+} = 0.69$  as calculated from the equilibrium constants of Ref. 4. Experimental points are shown and the curve calculated according to  $A_{328}(t) = a + b \cdot e^{-\lambda_1 t} + c \cdot e^{-\lambda_2 t}$  by non-linear regression analysis;<sup>2</sup> see Results.

## DISCUSSION

The assignment of the *trans*-configuration to the square planar complex salts  $[\text{Au(NH}_3)_2\text{Br}_2]\text{Br}$  and  $[\text{Au(NH}_3)_2\text{Cl}_2]\text{Cl} \cdot 1/3\text{H}_2\text{O}$  obtained as intermediates in the anation reaction of  $[\text{Au(NH}_3)_4]^{3+}$  with hydrobromic and hydrochloric acid, respectively, has been based upon kinetic arguments assuming the kinetic *trans*-effect of coordinated halide to be greater than that of coordinated ammonia.<sup>2,4,14</sup> The present X-ray single crystal determination confirmed the *trans*-configuration for the  $[\text{Au(NH}_3)_2\text{Br}_2]^+$  intermediate and, since the two diamminedihalogenido complexes are interconvertible,<sup>4</sup> also for the  $[\text{Au(NH}_3)_2\text{Cl}_2]^+$  intermediate. In particular, the confirmation of the *trans*-configuration for these diammine complexes also verifies the halide/ammonia *trans*-effect order in gold(III) square planar complexes.

The rate constants for the consecutive replacement of chloride in  $\text{trans-[Au(NH}_3)_2\text{Cl}_2]^+$  by bromide and of bromide in  $\text{trans-[Au(NH}_3)_2\text{Br}_2]^+$  by chloride at  $25^\circ\text{C}$ , normalized to take account of the number of equivalent leaving ligands (Table 7), indicate that a *trans*-bromide accelerates the halide substitution by factors of  $9.1 \pm 0.3$  [reactions (1) and (2)] and  $9.3 \pm 0.3$  [reactions (3) and (4)], respectively, relative to a *trans*-chloride. The kinetic Br/Cl *trans*-effect is thus the same as for both *trans*-dichloridodihalogenido- and *trans*-dibromidodihalogenidoaurate(III) complexes for which a value of  $14 \pm 3$  was found under identical experimental conditions<sup>15</sup> and it is only marginally larger than the value of 5.8 found for the substitution of bromide with chloride in  $\text{trans-[Au(CN)}_2\text{Br}_2]^-$ .<sup>16</sup>



Table 6. Thermodynamic and kinetic parameters for the reversible stepwise replacement of chloride with bromide in *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (*n*=1) and *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>BrCl]<sup>+</sup> (*n*=2) in aqueous 1.00 M (H,Na)(Br,Cl,ClO<sub>4</sub>) at 25.0 °C.<sup>a</sup>

<i>n</i>	<i>K<sub>n</sub></i>	$\Delta H_n^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_n^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	<i>k<sub>n</sub></i> (l mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H_n^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S_n^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	<i>k<sub>-n</sub></i> (l mol <sup>-1</sup> s <sup>-1</sup> )	$\Delta H_{-n}^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S_{-n}^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
1	122(2)	-12.1(1.2)	-1(4)	2150(30)	28.0(1.2)	-87(4)	17.6(4) <sup>b</sup>	40.1(1.7) <sup>b</sup>	-86(4) <sup>b</sup>
2	29.9(5)	-13.5(6)	-17(2)	9800(300) <sup>b</sup>	22(2) <sup>b</sup>	-95(8) <sup>b</sup>	328(7) <sup>b</sup>	35(2)	-78(8)

<sup>a</sup> Reactions defined in eqns. (1)–(4); see Results. Thermodynamic results from Ref. 4. <sup>b</sup> Calculated from equilibrium data and rate parameters for reverse reaction.

Table 7. Normalized rate constants<sup>a</sup> l mol<sup>-1</sup> s<sup>-1</sup> for chloride-bromide interchange reactions in *trans*-gold(III) complexes at 25 °C in aqueous perchlorate solution at 25 °C.

	$X_2=(NH_3)_2$ , ( <i>z</i> =+) <sup>b</sup> Ionic strength 1.0 <i>m</i> k·m <sup>-1</sup>	$X_2=Cl_2$ , ( <i>z</i> =-) <sup>c</sup> Ionic strength 1.0 <i>m</i> k·m <sup>-1</sup>	$X_2=Br_2$ , ( <i>z</i> =-) <sup>d</sup> Ionic strength 1.0 <i>m</i> k·m <sup>-1</sup>	$X_2=(CN)_2$ , ( <i>z</i> =-) <sup>e</sup> Ionic strength 0.51 <i>m</i> k·m <sup>-1</sup>
<i>trans</i> -[AuX <sub>2</sub> Cl <sub>2</sub> ] <sup>z</sup> +Br <sup>-</sup> → <i>trans</i> -[AuX <sub>2</sub> BrCl] <sup>z</sup> +Cl <sup>-</sup>		2 1075(15) 4 15.8(6)	2 0.015(1) 2 14.8(8)	0.014(1)
<i>trans</i> -[AuX <sub>2</sub> BrCl] <sup>z</sup> +Cl <sup>-</sup> → <i>trans</i> -[AuX <sub>2</sub> Cl <sub>2</sub> ] <sup>z</sup> +Br <sup>-</sup>	1 17.6(4)	1 0.26(3) 0.015(2)	1 (0.19) <sup>f</sup>	1 143 8.1
<i>trans</i> -[AuX <sub>2</sub> Br <sub>2</sub> ] <sup>z</sup> +Cl <sup>-</sup> → <i>trans</i> -[AuX <sub>2</sub> BrCl] <sup>z</sup> +Br <sup>-</sup>	2 164(4)	2 (3.5) <sup>f</sup>	4 2.7(6) 0.016(4)	2 835 5.1
<i>trans</i> -[AuX <sub>2</sub> BrCl] <sup>z</sup> +Br <sup>-</sup> → <i>trans</i> -[AuX <sub>2</sub> Br <sub>2</sub> ] <sup>z</sup> +Cl <sup>-</sup>	1 9800(300)	1 240(20) 0.024(4)	1 185(13) 0.019(1)	

<sup>a</sup> *m* is the number of equivalent leaving ligands in the complex. <sup>b</sup> *trans*-Diamminedihalogenogold(III) complexes – present study. <sup>c</sup> *trans*-Dichloridodihalogenoaurate(III); from Ref. 15. <sup>d</sup> *trans*-Dibromidodihalogenoaurate(III) – from Ref. 15. <sup>e</sup> *trans*-Dicyanidodihalogenoaurate(III); from Ref. 16. <sup>f</sup> Ratio between rate constants for reactions in *trans*-dibromidodihalogenoaurate(III) and *trans*-dichloridodihalogenoaurate-(III) and *trans*-diamminedihalogenogold(III). <sup>g</sup> Ratio between rate constants for reactions in *trans*-dibromidodihalogenoaurate(III) and *trans*-diamminedihalogenogold(III). <sup>h</sup> Ratio between rate constants for reactions in dicyanidodihalogenoaurate(III) and *trans*-diamminedihalogenogold(III). <sup>i</sup> Indirectly calculated; see Ref. 15.

While the *trans*-effect in these different gold(III) substrates appears to be independent of charge and of the nature of the *cis*-ligands, this is not the case for the absolute rates of substitution. A comparison of the rate constants for reactions (1) to (4) with the rate constants for the equivalent reaction steps in the overall substitution process<sup>15</sup>



shows that the reactions of *trans*-diamminedihalogenidogold(III) are faster without exception. The statistically corrected rate constants for substitution in the anionic *trans*-dichlorodihalogenidoaurate(III) and *trans*-dibromidodihalogenidoaurate(III) are, as can be seen in Table 7, only *ca.* 1/60th of the normalized rate constants for substitution in *trans*-diamminedihalogenidogold(III). A corresponding difference in bond length is not found, as can be seen in Table 3 for Au-Br in  $[\text{AuBr}_4]^-$  compared to *trans*- $[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+$ . This is in accordance with the suggestion<sup>12,15</sup> that bond-making rather than bond-breaking is the more important in the transition state for ligand substitution in gold(III) complexes. Certainly, the charge neutralization during bond formation in reactions (1) to (4) is expected to accelerate these reactions relative to halide exchange in the anionic tetrahalogenidoaurate(III) complexes. However, the rate constants for substitution of bromide with chloride in *trans*-dicyanodibromidoaurate(III) (Table 7) show these reactions to be significantly *faster*<sup>16</sup> than reactions (3) and (4), in spite of the transition state charge neutralization in the latter reactions. Cyanide is a  $\pi$ -acceptor and as such it is capable of delocalizing electronic charge away from the metal. The resulting increase in effective positive charge on the metal center is expected to facilitate bond formation for the entering ligand, since the vacant  $p_z$  metal orbital is involved in both bond formation and in the  $\pi$ -structure of square planar complexes.<sup>17</sup> This accounts at least partly for the remarkably high kinetic *cis*-effect of cyanide relative to both ammonia and to the  $\pi$ -donating ligands chloride and bromide. However, it should be noted that a similar *cis*-effect was not found<sup>18</sup> for the replacement of heterocyclic amines by anions in the neutral complexes  $[\text{AuCl}_3(\text{amin})]$  and *trans*- $[\text{Au}(\text{CN})_2\text{Cl}(\text{amin})]$  dissolved in methanol. This suggests that charge effects are important only in the more polar reaction media. In keeping herewith is the observation of a significant levelling effect on the rates of substitution of chloride in  $[\text{Au}(\text{dien-H})\text{Cl}]^+$  (dien-H=deprotonated 1,4,7-triazaheptane) by other anions when comparing methanol with water as reaction medium.<sup>19</sup>

Models involving transition states of increased coordination number have been successful in accounting for the experimental observations on ligand substitution for gold(III) complexes and for  $d^8$  low-spin square planar complexes in general.<sup>12</sup> A transition state with a net increase in bonding is expected to have a negative entropy of activation, and negative values were indeed found for reactions (1) to (4), as can be seen in Table 6. Solvation of bromide is weaker than of chloride, as indicated by the entropies of these ions dissolved in water:  $S_{\text{Br}^-}^\circ - S_{\text{Cl}^-}^\circ = 26.1 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>20</sup> Consequently, bonding of a bromide in a transition state is expected to result in a more negative entropy of activation than bonding of a chloride, since the net decrease in solvation is smaller during the bromide bonding. The statistically corrected entropies of activation (Table 8) are *ca.*  $10 \text{ J mol}^{-1} \text{ K}^{-1}$  more negative for the reactions in which bromide replaces chloride than for the reverse reactions. A similar effect is seen for the substitution of ammonia in *trans*-diamminedihalogenidogold(III) complexes for which ammonia/bromide exchange has an entropy of activation  $28 \text{ J mol}^{-1}$

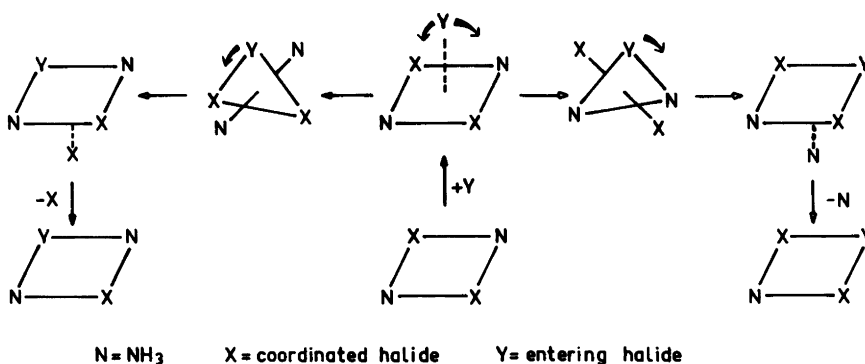
Table 8. Statistically corrected rate constants, enthalpies of activation, and statistically corrected entropies of activation for ligand substitution reactions in *trans*-diamminedihalogenidogold(III) complexes in 1.0 M aqueous perchlorate solution at 25 °C.<sup>a</sup>

Reaction	$m$	$k \text{ m}^{-1}$ ( $\text{l mol}^{-1} \text{ s}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	Ref.
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Cl}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Br}^-$	2	164(4)	35(2)	-84(8)	Present work
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Cl}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^-$	1	17.6(4)	40.1(1.7)	-86(4)	Present work
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Br}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Cl}^-$	2	1075(15)	28.0(1.2)	-93(4)	Present work
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{BrCl}]^+ + \text{Br}^- \rightarrow \text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Cl}^-$	1	9800(300)	22(2)	-95(8)	Present work
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Cl}_2]^+ + \text{Cl}^- \rightarrow [\text{AuNH}_3\text{Cl}_3] + \text{NH}_3$	2	$1.9(3) \times 10^{-6}$	105(4)	-4(10)	3
$\text{trans-}[\text{Au}(\text{NH}_3)_2\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{AuNH}_3\text{Br}_3] + \text{NH}_3$	2	$4.7(2) \times 10^{-5}$	88(3)	-32(8)	2

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

## Halide substitution

## Ammine substitution



$K^{-1}$  more negative than ammonia/chloride exchange. These observations provide strong evidence for a transition state in which bond formation is important.

The enthalpies of activation are smaller for the reactions where bromide replaces chloride than for the reverse reactions. However, in contrast to the entropies, the enthalpies also depend on the nature of the *trans*-ligand, and the Br/Cl *trans*-effect discussed above thus corresponds to ca. 5 kJ mol<sup>-1</sup>. The substitution of an ammonia with a halide is a very slow process compared to the halide exchange reactions in the same substrate. As can be seen from the data in Table 8, this difference is caused solely by larger enthalpies of activation for the processes in which an Au-N bond is cleaved. In fact, the larger enthalpies are counteracted by more favourable entropies of activation. This marked enthalpy effect indicates that bond breaking occurs to a significant degree in the transition state. The great difference in the rate constants for the anation of the closely related substrates [AuNH<sub>3</sub>Cl<sub>3</sub>] (3.3·10<sup>-5</sup> l mol<sup>-1</sup> s<sup>-1</sup>)<sup>3</sup> and [AuH<sub>2</sub>OCl<sub>3</sub>] (2.3·10<sup>3</sup> l mol<sup>-1</sup> s<sup>-1</sup>)<sup>21</sup> by chloride in aqueous solution at 25 °C likewise shows that the leaving ligand has a distinctive influence on the reaction rate, and that bond breaking is important in the transition state.

These observations on the effects of both the entering and the leaving ligand on the rates of ligand substitution in ammineanionogold(III) complexes together support the picture of an associative mechanism in which bond formation and bond breaking are concerted processes.<sup>22</sup> The pentacoordinated intermediates suggested for square planar substitution processes,<sup>12</sup> and depicted in the scheme for the halide interchange and ammonia halide exchange reactions, thus correspond to transition states in the substitution processes, rather than to reaction intermediates. The complex ion in *trans*-[Au(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>]Br has angles distorted away from 90 ° as seen in Fig. 1, but this distortion is, as already stated, most likely due to the packing in the crystal and is not likely to be found in solution. The transition state with a halide-halide axis and leading to ammine substitution has a much larger energy than the transition state with a nitrogen-nitrogen axis and leading to halide exchange (Table 8). Certainly, the X-ray structure describes the ground state and provides no direct information about the transition state, but it is noteworthy that the complex ion is *not* distorted from planarity, *i.e.* "on the way" to any of the two trigonal bipyramidal transition states of Scheme 1. Such a distortion was found in trichlorido(triphenylphosphine)gold(III) in which the *trans*-Cl-Au-P angle deviates 10.1° from linearity.<sup>23</sup> In this highly distorted complex the *trans*-chloride is substituted orders of magnitude faster than in the planar tetrachlor-

idoaurate(III). A more moderate tetragonal distortion was observed in the amido complex  $[\text{Au}(\text{dien-H})\text{Cl}]\text{ClO}_4$ ,<sup>24</sup> but this distortion is not accompanied by any significant rate acceleration for chloride/bromide exchange when compared to the almost planar  $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ ,<sup>24,25</sup> as seen from the rate constant at 25 °C and ionic strength 0.2 for the two processes:  $162 \pm 14$  and  $164 \pm 6 \text{ l mol}^{-1} \text{ s}^{-1}$ , respectively. These reactions are slow compared to reaction (1), confirming not only that chloride has a stronger *trans*-effect than an amine, but also, which is somewhat surprising, stronger than an amide ligand.

Both ammine and halide substitution reactions are, according to the model depicted in the scheme, initiated by the bonding of a halide as a fifth ligand.<sup>12</sup> The nature of such intermediates has been somewhat controversial.<sup>15,25–27</sup> The closest Au–Br<sup>–</sup> and the closest interionic Au–Br distances are 4.51 and 3.98 Å, respectively, and are much longer than the Au–Br bonds (2.43 Å, see Tables 1 and 3). The square pyramidal pentacoordinate intermediate common for the two reaction sequences of the scheme is on the basis of the crystallographic Au–Br distances not very likely to be found as a stable species in solution. It should rather be considered as a common stage along the reaction coordinates.

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