radii) leads to the presumption of a larger CN for the light elements, thus reinforcing the idea of a CN change in the middle of the series.

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Registry No. $Tb(H_2O)_8^{3+}$, 121096-88-6; $Dy(H_2O)_8^{3+}$, 121096-89-7; $Ho(H_2O)_8^{3+}$, 63213-08-1; $Er(H_2O)_8^{3+}$, 63118-71-8; $Tm(H_2O)_8^{3+}$, 63118-73-0; $Yb(H_2O)_8^{3+}$, 63118-75-2; H_2O, 7732-18-5.

Supplementary Material Available: Listings of sample composition (Table S1), pressure dependence of chemical shifts (Table S2), and pressure dependence of relaxation rates (Table S3) (9 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism for Reaction between Ammine- and Haloamminegold(III) Complexes and Thiocyanate. Competitive Electron Transfer and Substitution

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The reactions in acidic aqueous solution between thiocyanate and each of the gold(III) complexes $Au(NH_3)_4^{3+}$, *trans*-$Au(NH_3)_2Cl_2^+$, and *trans*-$Au(NH_3)_2Br_2^+$ have been studied by use of potentiometric pH measurements and sequential-mixing stopped-flow spectrophotometry. The reactions give a common gold(I) product whereas the rate-controlling steps are different. The reaction between $Au(NH_3)_4^{3+}$ and thiocyanate takes place via rate-controlling substitution of an ammine ligand by thiocyanate with $k = 7.6 \pm 0.1$ M^{-1} s^{-1}, $\Delta^*H^\circ = 61 \pm 1$ kJ mol^{-1}, and $\Delta^*S^\circ = 26 \pm 3$ J mol^{-1} K^{-1} at 25.0 °C, followed by rapid reduction to gold(I) with the overall stoichiometry

$$3Au(NH_3)_4^{3+} + 6SCN^- + 4H^+ + 4H_2O \rightarrow 2Au(SCN)_2^- + Au(SCN)(CN)^- + SO_4^{2-} + 12NH_4^+ \qquad \text{(i)}$$

For *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br), thiocyanate replaces halide in two rapid consecutive and reversible substitution steps without an observable solvent path prior to the slower reduction:

$$\textit{trans}\text{-}Au(NH_3)_2X_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}Au(NH_3)_2XSCN^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{trans}\text{-}Au(NH_3)_2(SCN)_2^+ \qquad \text{(ii)}$$

Second-order rate constants (M^{-1} s^{-1}) at 2.0 °C are as follows: for X = Cl; $k_1 = (9.0 \pm 1.4) \times 10^3$, $k_{-1} = (0.6 \pm 0.2)$, $k_2 = (1.56 \pm 0.21) \times 10^5$, $k_{-2} = (3.4 \pm 0.6) \times 10^2$; for X = Br, $k_1 = (8.9 \pm 0.3) \times 10^4$, $k_{-1} = (1.32 \pm 0.20) \times 10^3$, $k_2 = (1.4 \pm 0.4) \times 10^5$, $k_{-2} = (1.0 \pm 0.7) \times 10^4$. Temperature variation of k_1 gave the following values: for X = Cl; $\Delta^*H^\circ = 33 \pm 7$ kJ mol^{-1}, $\Delta^*S^\circ = -48 \pm 21$ J K^{-1} mol^{-1}; for X = Br, $\Delta^*H^\circ = 30 \pm 11$ kJ mol^{-1}, $\Delta^*S^\circ = -50 \pm 30$ J K^{-1} mol^{-1} at 25.0 °C. Parametrization of the substitution rate constants shows that the nature of the entering ligand is even more important than the trans effect for these complexes, in marked contrast to isoelectronic Pt(II) complexes. The relative stability constants for these short-lived complexes, $K_n = k_n/k_{-n}$, were obtained from the rate constants and are as follows: for X = Cl, $K_1 = (1.5 \pm 0.5) \times 10^4$, $K_2 = (4.6 \pm 0.5) \times 10^2$; for X = Br, $K_1 = 67 \pm 12$, $K_2 = 12 \pm 3$. The ratio K_1/K_2 shows a nonstatistical distribution for the chloro–thiocyanato system, indicating a increased thermodynamic stability for the complex *trans*-$Au(NH_3)_2ClSCN^+$, whereas the bromo–thiocyanato system is approximately statistically distributed. An UV–vis spectrum for the intermediate short-lived complex *trans*-$Au(NH_3)_2BrSCN^+$ was calculated from continuous-flow spectra. Reduction to gold(I) takes place via three parallel paths subsequent to establishment of the rapid substitution equilibria (ii). Each gold(III) complex *trans*-$Au(NH_3)_2X_{2-n}(SCN)_n^+$ is reduced by outer-sphere thiocyanate in second-order reactions. The second-order rate constants, k_{rn} (n = 0, 1, 2), at 25.0 °C are as follows: for X = Cl, $k_{r1} = (2.7 \pm 0.5) \times 10^3$, $k_{r2} = (2.2 \pm 0.4) \times 10^2$; for X = Br, $k_{r0} = 10 \pm 5$, $k_{r1} = (3.0 \pm 0.5) \times 10^2$, $k_{r2} = (2.5 \pm 0.4) \times 10^2$ M^{-1} s^{-1}. Temperature variation of k_{r2} gave $\Delta^*H^\circ = 66 \pm 4$ kJ mol^{-1} and $\Delta^*S^\circ = 21 \pm 12$ J mol^{-1} K^{-1} at 25.0 °C. The mixed chloro– and bromo–thiocyanato complexes are reduced most rapidly, indicating that an asymmetric distribution of electrons along the trans-axis facilitates reduction. It is concluded that reduction takes place by attack of outer-sphere thiocyanate on the sulfur of a coordinated thiocyanate. In keeping herewith, the two complexes *trans*-$Au(NH_3)_2XSCN^+$ (X = Cl, Br), which contain a loosely bound halide ligand in the ground state, also substitute this halide ligand for thiocyanate most rapidly (k_2). A unified mechanism for competitive electron transfer and ligand substitution for the reaction between gold(III) complexes and reducing ligands is suggested.

Introduction

Reactions between gold(III) complexes and efficient nucleophiles such as iodide, thiocyanate, thiosulfate, thiourea, and alkyl sulfides in aqueous solution result in reduction to gold(I).[2-7] As a rule, this type of reaction takes place via rapid ligand substitutions in the gold(III) complexes, followed by an electron-transfer step, which in most cases is slow compared to the initial substitution.[8] For very efficient nucleophiles like iodide attacking complexes with favorable electronic properties, such as $AuBr_4^-$ and possibly also $AuCl_4^-$, reduction might take place directly without any prior substitution.[2,3] For other combinations of nucleophile and substrate, the initial substitution is necessary and rate-controlling for reduction.[8] Examples of this latter type are the reactions between $Au(NH_3)_4^{3+}$ and iodide[3] and possibly also those between $AuCl_4^-$ and anions of carboxylic acids.[9]

For reactions between gold(III) complexes and thiocyanate, there is a subtle balance between the rates of substitution and the rate of electron transfer.[4] The reaction between AuX_4^- (X = Cl, Br) and thiocyanate is complicated with four consecutive substitution steps. Each step gives substitution products, which might participate in the subsequent electron transfer. A complete resolution of the overall kinetics with five parallel electron transfer

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(1) (a) Lund University. (b) The Royal Veterinary and Agricultural University.
(2) Elding, L. I.; Olsson, L.-F. *Inorg. Chem.* **1982**, *21*, 779.
(3) Elding, L. I.; Skibsted, L. H. *Inorg. Chem.* **1986**, *25*, 4084.
(4) Elding, L. I.; Gröning, A.-B.; Gröning, Ö. *J. Chem. Soc., Dalton Trans.* **1981**, 1093.
(5) Nord, G.; Skibsted, L. H.; Halonin, A. S. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 505.
(6) Makotchenko, E. V.; Peschchevitskii, B. I.; Novoselov, R. I. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1978**, *14*, 44; **1981**, *9*, 47, 52, 56.
(7) Annibale, G.; Canovese, L.; Cattalini, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1070.
(8) Skibsted, L. H. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 137.
(9) Maritz, B. S.; van Eldik, R. *Inorg. Chim. Acta* **1976**, *17*, 21; **1976**, *20*, 43; *J. Inorg. Nucl. Chem.* **1976**, *38*, 1545, 1749, 2124; **1977**, *39*, 1935.

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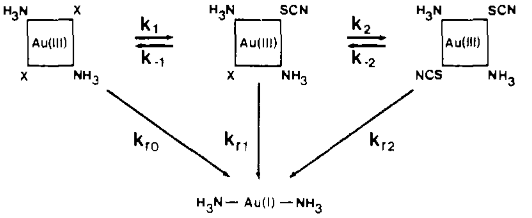

Figure 1. Reaction scheme: X = Cl, Br. The primary product $Au(NH_3)_2^+$ undergoes further, rapid reactions.

reactions becomes very difficult, especially since the rate constants for the reduction of the various mixed halido–thiocyanato–aurate(III) complexes appearing as intermediates may vary several orders of magnitude. Even a low concentration of a particular complex with a large rate constant might therefore give a major contribution to the overall redox rate.[4]

For the substrate complexes *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br), the number of possible reactions is reduced, since the H_3N–Au–NH_3 axis remains unchanged during both initial substitution and subsequent redox steps.[3] This simplification facilitates a more complete resolution of the system described by the scheme in Figure 1 and allows a quantitative evaluation of the parameters that govern both substitution and electron transfer reactions.

Rate constants for substitutions are denoted k_n and k_{-n} (n = 1, 2), and those for reductions, k_{rn} (n = 0, 1, 2). Relative stability constants for the mixed complexes are defined by eq 1 and 2, where

$$K_n = \frac{[Au(NH_3)_2X_{2-n}(SCN)_n^+]}{[Au(NH_3)_2X_{3-n}(SCN)_{n-1}^+]}Q \quad n = 1, 2 \qquad (1)$$

$$K_n = k_n/k_{-n} \quad n = 1, 2 \qquad (2)$$

Q is defined as the ratio between the concentrations of the free ligands according to eq 3. The overall relative stability constants

$$Q = [X^-]/[SCN^-] \qquad (3)$$

β_n are defined by eq 4. The reaction between $Au(NH_3)_4^{3+}$ and

$$\beta_n = \Pi K_n \quad n = 1, 2 \qquad (4)$$

thiocyanate involves a rate-controlling formation of mixed ammine–thiocyanato complexes of gold(III), similar to those that appear as intermediates in the reactions depicted in Figure 1.

Experimental Section

Chemicals and Solutions. The gold compounds *trans*-$[Au(NH_3)_4](NO_3)_3$, *trans*-$[Au(NH_3)_2Cl_2]Cl\cdot{}^1/_3H_2O$, *trans*-$[Au(NH_3)_2Br_2]Br$, and *trans*-$[Au(NH_3)_2Br_2]Br\cdot{}^1/_3NH_4Br\cdot{}^2/_3H_2O$ were synthesized by using $KAuCl_4$ (H. Drijhout & Zoon's) as starting material and purified as described previously.[10-13] Solutions of NaSCN (Mallinckrodt, Analytical Reagent, or Fischer Scientific Corp.) and solutions of gold(III) complexes were freshly prepared before use. The gold(III) solutions contained extra halide (1 mM NaBr or 10 mM NaCl) and $HClO_4$ (10 mM) to suppress formation of aqua and hydroxo complexes. Halide solutions were prepared from stock solutions of NaBr (Merck, Suprapur, or May & Baker) and NaCl (Merck, Suprapur). $HClO_4$ (Merck, p.a.) and $NaClO_4$ (Mallinckrodt, Analytical Reagent, or Merck, p.a.) were kept as 1.00 M stock solutions. All solutions had an ionic strength of 1.00 M adjusted with $NaClO_4$ where nothing else is stated. Water was doubly distilled from quartz or purified by ion exchange and filtration techniques.

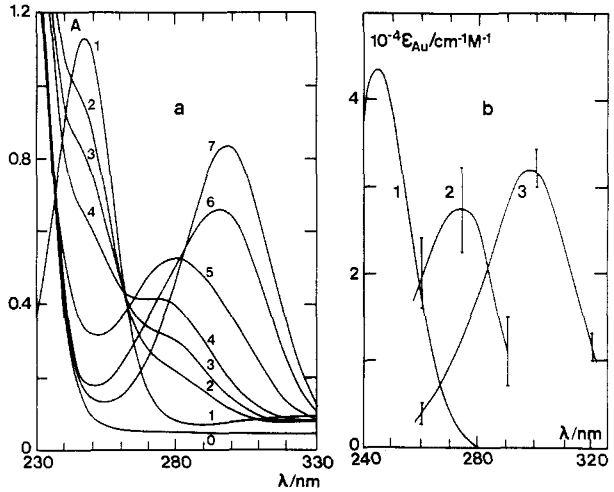

Figure 2. (a) Continuous-flow spectra of solutions containing the short-lived complexes $Au(NH_3)_2Br_{2-n}(SCN)_n^+$ (n = 0, 1, 2) with C_{Au} = 2.5 × 10^{-5} M. Spectrum 0 is that of an equilibrated solution which was used as blank for the resolution of the flow spectra shown in part b. C_{SCN} = 0 M (1), C_{SCN} = 1.0 × 10^{-3} M (2–7), and Q = 200 (2), 100 (3), 50 (4), 10 (5), 2.5 (6), and 0.2 (7). (b) Resolved spectra for *trans*-$Au(NH_3)_2Br_2^+$ (1), *trans*-$Au(NH_3)_2BrSCN^+$ (2), and *trans*-$Au(NH_3)_2(SCN)_2^+$ (3). Spectra 2 and 3 were calculated from spectra 1–6 of part a by use of eq 5.

Table I. Stoichiometries for Reaction between Tetraammine-, *trans*-Dichlorodiammine-, and *trans*-Dibromodiamminegold(III) and Thiocyanate As Established from the Change in Hydrogen Ion Concentration at 25.0 °C

complex	C_{Au}/ mM	$[SCN^-]_0$/ C_{Au}	pH_0	pH_∞	$([H^+]_0 - [H^+]_\infty)$/ C_{Au}
$Au(NH_3)_4^{3+}$	0.521	3.5	2.610	2.736	1.17
	0.429	5.7	2.616	2.713	1.14
	0.430	5.7	2.724	2.863	1.20
	0.437	4.2	2.903	3.216	1.47
	0.482	6.3	2.903	3.219	1.34
	0.414	4.4	3.008	3.382	1.37
	0.427	5.7	3.054	3.506	1.34
	0.391	17.8	3.074	3.483	1.32
	0.410	27.1	3.094	3.474	1.15
	0.433	5.6	3.206	3.996	1.22
	0.435	8.4	3.211	4.128	1.24
	0.390	28.5	3.246	4.243	1.49
trans-Au-	0.473	58.8	2.903	2.811	−0.61
$(NH_3)_2Cl_2^+$	0.935	5.1	3.021	2.806	−0.64
trans-Au-	0.460	4.6	2.903	2.816	−0.61
$(NH_3)_2Br_2^+$	0.820	5.1	3.021	2.817	−0.70

Apparatus. Spectra were recorded by use of a Varian Cary 2200 spectrophotometer. A continuous-flow system with a Hellma flow cell (170-QS) and with a dead time of ca. 0.12 s was used to record spectra of the short-lived complexes formed in the substitution reactions between *trans*-$Au(NH_3)_2X_2^+$ and thiocyanate. The kinetics for the reactions between the mixed-ligand complexes and thiocyanate were monitored by use of a Hi-Tech SFL-43 multimixing stopped-flow module with two consecutive mixing chambers in connection with an UV–visible spectrophotometer unit SU-40A and a MSC-1 data processor unit with program unit ADS-1.

The kinetics for the reaction between $Au(NH_3)_4^{3+}$ and thiocyanate and the overall stoichiometries for the reactions between thiocyanate and the three gold(III) substrate complexes used were determined potentiometrically by using an Ingold 405-M5 combination glass electrode with a 1.0 M NaCl, AgCl reference part.

Spectra. Equal volumes of a solution of *trans*-$Au(NH_3)_2Br_2^+$ and a solution containing NaSCN and NaBr were mixed in the continuous-flow system with a dead time sufficiently long for establishment of the substitution equilibria in the gold(III) system. Not more than 4% of the gold(III) was reduced to gold(I). Flow spectra were recorded at 25 °C by mixing equal volumes of one solution with C_{Au} = 2.50 × 10^{-5} or 5.00 × 10^{-5} M with another solution with C_{SCN} = 2.00 × 10^{-3} M. The spectrum of *trans*-$Au(NH_3)_2(SCN)_2^+$ was estimated from measurements with Q = 0.5, whereas that of *trans*-$Au(NH_3)_2BrSCN^+$ was calculated from the stability constants and the spectra of solutions with Q = 2.5, 10, 50, 100, and 200; cf. Figure 2.

Similar experiments were performed in an attempt to estimate the spectrum of *trans*-$Au(NH_3)_2ClSCN^+$, but the rapid reduction of this complex made an accurate determination impossible.

Overall Stoichiometry. Accurately weighed amounts of the gold compounds were dissolved in 40.00 mL of acidic aqueous sodium perchlorate solution (1.00 M $NaClO_4$ in most cases; $HClO_4$ concentrations determined by titration). The solutions, 3 × 10^{-4} M < C_{Au} < 1.0 × 10^{-3} M

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(10) Skibsted, L. H.; Bjerrum, J. *Acta Chem. Scand., Ser. A* **1974**, *A28*, 740.
(11) Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 113.
(12) Moensted, O.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 23.
(13) Kaas, K.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 1.

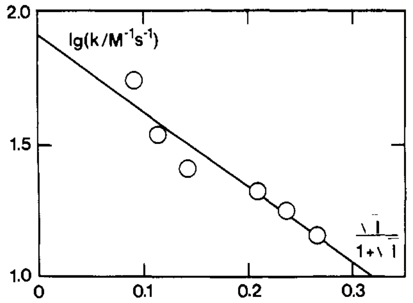

Figure 3. Ionic strength dependence of the second-order rate constant for the reaction between $Au(NH_3)_4^{3+}$ and thiocyanate at 18.0 °C.

Table II. Second-Order Rate Constants for Reaction between Tetraamminegold(III) and Thiocyanate in Acidic Aqueous 1.0 M $NaClO_4$ at 0.4 °C

$[Au(NH_3)_4^{3+}]_0$/ mM	$[SCN^-]_0$/ mM	$[SCN^-]_0/[Au(NH_3)_4^{3+}]_0$	pH_0	$k/M^{-1}\,s^{-1}$
1.09	2.44	2.24	2.575	0.80
0.83	2.44	2.94	2.575	0.89
0.65	2.45	3.77	2.991	0.78
0.56	2.44	4.36	2.991	0.83
0.56	2.46	4.39	2.576	0.74
0.469	2.38	5.07	2.983	0.72
0.432	2.44	5.65	2.991	0.77
0.422	2.46	5.83	2.992	0.83
0.385	2.45	6.36	2.992	0.76
0.337	2.44	7.24	2.991	0.76
0.426	4.79	11.2	2.985	0.67
				av 0.78 ± 0.06

and 2.6 < pH < 3.1, were contained in a thermostated titration vessel at 25.0 °C. When the potential of the combination glass electrode was stable within ±0.1 mV, the reaction was initiated by the addition of a known volume of a 0.100 M NaSCN solution. NaSCN was used in excess, $4 < [SCN^-]/C_{Au} < 30$, and the ionic strength was adjusted by $NaClO_4$ to the same value as in the solution containing gold complex. The reaction was monitored potentiometrically at appropriate intervals of time until a constant reading indicated equilibrium. The definition pH = $-\log [H^+]$ was employed, and solutions of standardized perchloric acid in the actual reaction medium were used as pH standards. These experiments are summarized in Table I.

Reaction between $Au(NH_3)_4^{3+}$ and Thiocyanate. This reaction was monitored by measurements of pH vs time under second-order conditions as a function of both temperature (0.4–25.0 °C) and ionic strength (0.010–0.13 M and at 1.00 M); cf. Table II and Figure 3. Experimental conditions were identical with those used for determination of the stoichiometry.

Reactions between *trans*-$Au(NH_3)_2X_2^+$ and Thiocyanate. The reactions were initiated by mixing equal volumes of *trans*-$Au(NH_3)_2X_2^+$ and a first reagent solution in the first mixing chamber of the stopped-flow instrument. After an appropriate time delay, a second reagent was added in the second mixing chamber and the reaction was monitored spectrophotometrically. Isosbestic points, cf. Figure 2, were used to identify the substitution reactions in the gold(III) system. When possible, the reactions were followed at two different wavelengths, one with increasing and one with decreasing absorbance. Gold concentrations were kept less than 2.5×10^{-5} M to avoid formation of polynuclear complexes, and the reactions were studied under pseudo-first-order conditions with both thiocyanate and halide in excess.

The rate constant k_1 was determined as a function of temperature for both the reactions between *trans*-$Au(NH_3)_2Cl_2^+$ and SCN^- (5.7–35.2 °C) and between *trans*-$Au(NH_3)_2Br_2^+$ and SCN^- (2.0–25.0 °C). With thiocyanate in excess, k_1 is rate-controlling for the formation of *trans*-$Au(NH_3)_2(SCN)_2^+$ since the second substitution step is fast; cf. Figure 1. The formation of the bis(thiocyanato) complex could be followed at 295 and 300 nm, respectively, by mixing of equal volumes of gold substrate and thiocyanate solutions; cf. Table III.

Rate constants k_1 and k_{-1} were determined at 2.0 °C under reversible conditions in the reaction between *trans*-$Au(NH_3)_2Br_2^+$ and thiocyanate. An equilibrium between *trans*-$Au(NH_3)_2(SCN)_2^+$ and *trans*-$Au(NH_3)_2Br(SCN)^+$ determined by the ratio Q_1 was established in the first mixing chamber, and subsequent addition of bromide in the second mixing chamber allowed the establishment of a new equlibrium distribution between *trans*-$Au(NH_3)_2Br(SCN)^+$ and *trans*-$Au(NH_3)_2Br_2^+$ at the ratio Q_2 as shown by the flow scheme in Figure 4a. The reactions were studied at ca. 245 and 270 nm. The latter experiment was performed with two different C_{SCN}, and for each of those, C_{Br} was varied.

Rate constants k_2 and k_{-2} were also determined under reversible conditions by using the same sequential mixing technique as described above in both systems *trans*-$Au(NH_3)_2X_2^+/SCN^-$ (X = Cl, Br). The reactions of the chloro complexes were studied at 265 and 300 nm, both

Table III. First-Order Rate Constants k_1 for Substitution of Halide by Thiocyanate in *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br) as a Function of Concentrations and Temperature

X	t/°C	10^4C_{SCN}/M	Q^c	k_{obsd}/s^{-1}
Br[a]	2.0	2.00	2.5	18.5 ± 1.5
	2.0	6.00	0.83	51 ± 2
	2.0	10.0	0.50	91 ± 2
	12.0	2.00	2.5	30 ± 2
	12.0	4.00	1.3	63 ± 6
	12.0	6.00	0.83	93 ± 8
	25.0	2.00	2.5	47 ± 2
	25.0	3.00	1.7	71 ± 3
	25.0	4.00	1.3	88 ± 10
Cl[b]	5.7	1.00	50	0.99 ± 0.09
	5.7	2.00	50	1.90 ± 0.15
	5.7	3.00	50	3.87 ± 0.15
	5.7	4.00	50	4.96 ± 0.25
	15.5	1.00	50	2.29 ± 0.15
	15.5	2.00	50	4.32 ± 0.06
	15.5	3.00	50	6.31 ± 0.20
	15.5	4.00	50	8.27 ± 0.20
	25.0	1.00	50	3.67 ± 0.10
	25.0	2.00	50	6.78 ± 0.20
	25.0	3.00	50	10.6 ± 0.20
	25.0	4.00	50	13.3 ± 0.5
	35.2	1.00	50	4.75 ± 0.20
	35.2	2.00	50	8.7 ± 0.3
	35.2	3.00	50	15.09 ± 0.20

[a] λ = 300 nm; $C_{Au} = 1.0 \times 10^{-5}$ M. [b] λ = 295 nm; $C_{Au} = 5.0 \times 10^{-6}$ M. [c] Q defined by eq 3 was always sufficiently large to displace the reaction completely to the right (i.e. $k_{-1}[X^-]$ in eq 19 was negligible).

Table IV. Observed First-Order Rate Constants at 2.0 °C for Displacement of the Substitution Equilibria in Figure 1[a]

X	λ/nm	rate consts	10^4C_{SCN}/ M	10^3C_X/ M	Q_1[b]	Q_2[b]	k_{obsd}/s^{-1}
Br	245/277	k_1, k_{-1}	2.50	25.3	1.00	100	55 ± 3
			2.50	50.3	1.00	200	84 ± 6
			2.50	75.3	1.00	300	123 ± 10
	246/265	k_1, k_{-1}	1.25	12.8	2.00	100	25.5 ± 1.5
			1.25	25.3	2.00	200	40 ± 3
			1.25	37.8	2.00	300	58 ± 5
			1.25	50.3	2.00	400	73 ± 5
	265/300	k_2, k_{-2}	1.25	2.00	2.00	16	36 ± 5
			2.50	2.00	1.00	8.0	59 ± 4
			3.75	2.00	0.67	5.3	71 ± 10
			5.00	2.00	0.50	4.0	89 ± 11
	265/300	k_2, k_{-2}	1.00	1.00	2.50	10	32 ± 2
			2.00	2.00	1.25	10	58 ± 4
			3.00	3.00	0.83	10	89 ± 5
Cl	265/300	$k_2\ k_{-2}$	1.50	72.5	16.7	480	47 ± 4
			2.00	72.5	12.5	360	55 ± 2
			2.50	72.5	10.0	290	63 ± 8
			3.00	72.5	8.3	240	72 ± 8
			2.00	42.5	12.5	210	41 ± 4
			2.00	103	12.5	510	65 ± 4
			2.00	133	12.5	660	74 ± 4

[a] $C_{Au} = 1.0 \times 10^{-5}$ M. [b] Q_1 and Q_2 defined by eq 3 denote the start and equilibrium values for the equilibrium displacement according to the flow scheme in Figure 4.

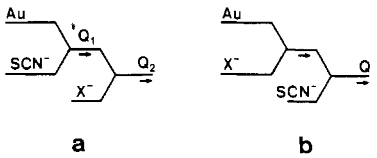

Figure 4. Flow scheme for the sequential-mixing stopped-flow experiments: (a) reversible substitution in the *trans*-$Au(NH_3)_2X_2^+/SCN^-$ system; (b) reduction of *trans*-$Au(NH_3)_2X_2^+$ by SCN^-. X = Cl, Br.

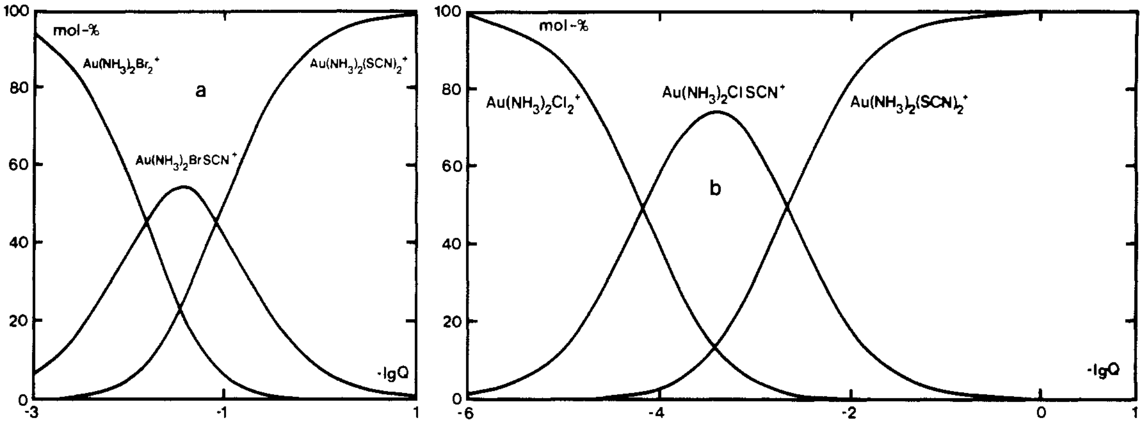

Figure 5. Equilibrium distribution of gold in the short-lived gold(III) complexes formed in the rapid preequilibrium prior to reduction to gold(I). $Q = [X^-]/[SCN^-]$; X = Cl, Br.

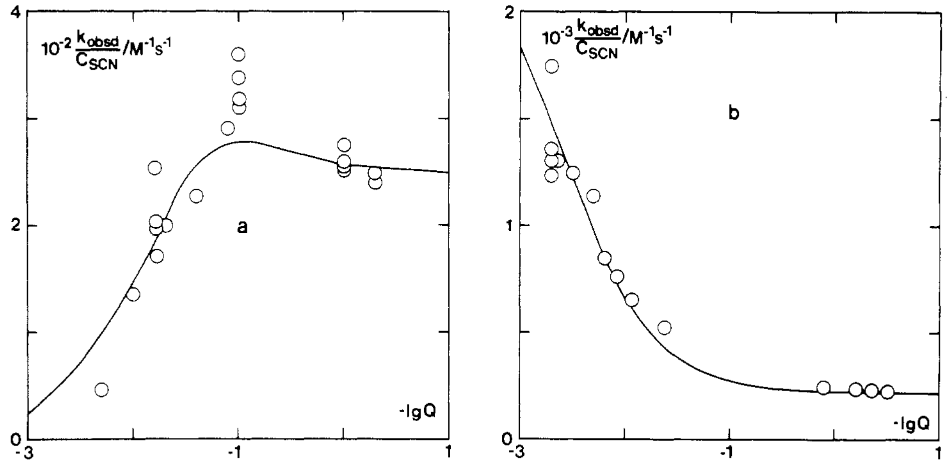

Figure 6. Observed second-order rate constants for reduction divided by the thiocyanate concentration as a function of $-\log Q$: (a) the *trans*-Au(NH$_3$)$_2$Br$_{2-n}$(SCN)$_n$$^+$ system; (b) the *trans*-Au(NH$_3$)$_2$Cl$_{2-n}$(SCN)$_n$$^+$ system. $n = 0, 1, 2$. $Q = [X^-]/[SCN^-]$. X = Cl, Br.

Table V. Temperature Dependence of k_{r2}[a]

	k_{obsd}/s^{-1}			
$10^3C_{SCN}/M$	15.1 °C	25.0 °C	35.0 °C	45.2 °C
1.00	0.13 ± 0.01	0.33 ± 0.01	0.75 ± 0.02	1.81 ± 0.04
2.00	0.25 ± 0.01	0.63 ± 0.01	1.50 ± 0.03	3.44 ± 0.04
3.00	0.36 ± 0.01	0.98 ± 0.01	2.24 ± 0.01	5.37 ± 0.10
4.00	0.47 ± 0.01	1.20 ± 0.02	3.00 ± 0.10	6.50 ± 0.10

[a] X = Br, $Q = 1$, $C_{Au} = 1.5 \times 10^{-6}$ M, $\lambda = 290$ nm.

as a function of C_{SCN} at constant C_{Cl} and vice versa. The bromo complexes were studied at 265 and 300 nm both as a function of C_{SCN} at two different C_{Br} and as a function of C_{SCN} at constant $Q = 10$. Experimental data are contained in Table IV.

The redox kinetics could only be followed for $C_{SCN} > 2.0 \times 10^{-4}$ M. At lower C_{SCN}, subsequent hydrolysis of redox products like (SCN)$_2$ and XSCN seems to become rate-controlling for the redox reaction.[14] After establishment of the rapid substitution equilibrium between the complexes *trans*-Au(NH$_3$)$_2$X$_{2-n}$(SCN)$_n$$^+$ ($n = 0, 1, 2$), the redox reaction could be followed as a subsequent process at 25.0 °C. The rate constant k_{r2} was determined at 295 and 300 nm, cf. Figure 2, by using both complexes *trans*-Au(NH$_3$)$_2$X$_2$$^+$ (X = Br, Cl) as starting materials and for conditions of $Q \leq 1$; cf. Figure 5. The temperature dependence of k_{r2} was determined between 15.1 and 45.2 °C by use of the complex *trans*-Au(NH$_3$)$_2$Br$_2$$^+$; cf. Table V.

The rate of the redox reaction was studied as a function of Q in both systems. The dependence of k_{obsd} on C_{SCN} was determined for $Q = 1$, 10, and 63 (X = Br) and for $Q = 1$ and 500 (X = Cl) as shown by Figure 6. To avoid substitution of the ammine ligands of *trans*-Au(NH$_3$)$_2$X$_2$$^+$ by the excess of X$^-$ in the stock solutions used in those experiments, *trans*-Au(NH$_3$)$_2$X$_2$$^+$ was mixed with X$^-$ in the first mixing chamber and SCN$^-$ was added in the second one to give the constant value of Q for each experiment, as shown by Figure 4b. The wavelength was successively changed from 300 nm toward the UV region to get a maximum change of absorbance for the reaction studied. These experiments are reviewed in Tables VI and VII and Figure 6.

Table VI. Observed Overall First-Order Rate Constants at 25.0 °C for Reduction of the Complexes *trans*-Au(NH$_3$)$_2$Cl$_{2-n}$(SCN)$_n$$^+$ (n = 0, 1, 2) as a Function of Q

$10^5C_{Au}/M$	λ/nm	Q	C_{SCN}/M	k_{obsd}/s^{-1}	$(k_{obsd}/C_{SCN})/M^{-1}\,s^{-1}$
2.5	300	0.31	1.60×10^{-2}	3.56 ± 0.15	222
2.5	300	0.42	1.20×10^{-2}	2.75 ± 0.20	230
2.5	300	0.63	8.00×10^{-3}	1.90 ± 0.08	238
2.5	300	1.25	4.00×10^{-3}	0.99 ± 0.02	246
1.0	300	42	3.00×10^{-3}	1.56 ± 0.02	521
1.0	300	85	3.00×10^{-3}	1.96 ± 0.04	652
1.0	300	118	3.00×10^{-3}	2.31 ± 0.03	768
1.0	300	161	3.00×10^{-3}	2.56 ± 0.04	852
1.0	290	200	1.00×10^{-3}	1.14 ± 0.01	1139
1.0	270	300	1.00×10^{-3}	1.25 ± 0.02	1246
1.0	260	450	1.00×10^{-4}	1.31 ± 0.02	1308
1.0	260	500	3.00×10^{-4}	0.53 ± 0.02	1750
1.0	260	500	6.00×10^{-4}	0.82 ± 0.03	1360
1.0	260	500	9.00×10^{-4}	1.18 ± 0.03	1310
1.0	260	500	1.20×10^{-3}	1.48 ± 0.03	1233

Calculations and Results

Spectra. Prior to calculation of molar absorptivities, the observed absorbances were corrected to zero time by using the reduction rate constants k_{obsd} for the actual Q; cf. Figure 6. Each gold(III) complex contributes to the apparent molar absorptivity ϵ_{Au} according to eq 5, where ϵ_n is the molar absorptivity for the

$$\epsilon_{Au} = \sum_0^2 \alpha_n \epsilon_n \quad n = 0, 1, 2 \tag{5}$$

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(14) Schöneshöfer, M.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 289.

Table VII. Observed Overall First-Order Rate Constants at 25.0 °C for Reduction of the Complexes *trans*-$Au(NH_3)_2Br_{2-n}(SCN)_n^+$ (n = 0, 1, 2) as a Function of Q^a

λ/nm	Q	10^3C_{SCN}/M	k_{obsd}/s^{-1}	$(k_{obsd}/C_{SCN})/M^{-1}\ s^{-1}$
300	0.50	1.00	0.25 ± 0.02	247
300	0.50	2.00	0.48 ± 0.03	240
300	1.00	2.00	0.55 ± 0.01	275
300	1.00	4.00	1.04 ± 0.05	260
300	1.00	6.00	1.54 ± 0.03	256
300	1.00	8.00	2.02 ± 0.08	252
280	10.1	4.00	1.24 ± 0.02	311
280	10.1	3.00	0.95 ± 0.03	318
280	10.1	2.00	0.67 ± 0.01	338
280	10.3	1.00	0.36 ± 0.02	360
280	12.6	2.00	0.58 ± 0.05	291
280	25.1	2.00	0.45 ± 0.04	227
280	50	2.00	0.40 ± 0.04	199
265	63	4.00	0.68 ± 0.03	171
265	63	3.00	0.59 ± 0.02	197
265	63	2.00	0.40 ± 0.01	203
265	63	1.00	0.25 ± 0.01	354
265	100	2.00	0.27 ± 0.06	135
265	200	2.00	0.091 ± 0.003	46

$^a C_{Au} = 5.0 \times 10^{-6}$ M.

Table VIII. Relative Stability Constants, K_n, at 2.0 °C Defined by Eq 1 for the Complexes *trans*-$Au(NH_3)_2X_{2-n}(SCN)_n^+$ (n = 0, 1, 2)

K_n	X = Br	X = Cl
K_1	67 ± 12	$(1.5 \pm 0.5) \times 10^4$
K_2	12 ± 3	$(4.6 \pm 0.5) \times 10^2$

complex *trans*-$Au(NH_3)_2X_{2-n}(SCN)_n^+$ (n = 0, 1, 2) and the molar fraction α_n is determined by eq 6, where $\beta_0 = 1$. At $Q < 1$ the

$$\alpha_n = \beta_n Q^{-n} / \sum_0^2 \beta_i Q^{-i} \qquad n = 0, 1, 2 \tag{6}$$

relative proportion of *trans*-$Au(NH_3)_2Br_2^+$ and *trans*-$Au(NH_3)_2BrSCN^+$ was assumed to be negligible, and the molar absorptivity of the solution is equal to the molar absorptivity of *trans*-$Au(NH_3)_2(SCN)_2^+$. At larger values of Q, all complexes *trans*-$Au(NH_3)_2X_{2-n}(SCN)_n^+$ (n = 0, 1, 2) were assumed to contribute to the total molar absorptivity in the calculation of the molar absorptivity of *trans*-$Au(NH_3)_2BrSCN^+$ from eq 5. The resolved spectra of the individual complexes are displayed in Figure 2b.

Stabilities. The stability constants defined by eq 1 were calculated directly from the second-order rate constants in agreement with eq 2 with exception of K_1 for the substitution reaction of eq 7. This stability constant was calculated from the equilibrium

$$trans\text{-}Au(NH_3)_2Cl_2^+ + SCN^- \rightleftarrows trans\text{-}Au(NH_3)_2ClSCN^+ + Cl^- \tag{7}$$

constant of reaction 8, which is known from a previous equilibrium

$$trans\text{-}Au(NH_3)_2Cl_2^+ + 2Br^- \rightleftarrows trans\text{-}Au(NH_3)_2Br_2^+ + 2Cl^- \tag{8}$$

study,[12] in combination with the equilibrium constants for reactions 9 and 10 calculated from the rate constants determined in the

$$trans\text{-}Au(NH_3)_2Br_2^+ + 2SCN^- \rightleftarrows trans\text{-}Au(NH_3)_2(SCN)_2^+ + 2Br^- \tag{9}$$

$$trans\text{-}Au(NH_3)_2(SCN)_2^+ + Cl^- \rightleftarrows trans\text{-}Au(NH_3)_2ClSCN^+ + SCN^- \tag{10}$$

present study. The obtained stability constants are given in Table VIII. The distribution of gold(III) between the various complexes in the rapid preequilibrium before reduction is shown in Figure 5.

Stoichiometry. Thiocyanate has been shown to be oxidized to cyanide and sulfate by gold(III) in aqueous solution. For solutions with pH > 2.5, the latter of these products is present as SO_4^{2-}, whereas cyanide will be coordinated to gold(I), as the equilibrium for the reaction in eq 11 is displaced to the right, as may be calculated from available thermodynamic data.[8]

$$Au(SCN)_2^- + HCN \rightleftarrows Au(SCN)(CN)^- + SCN^- + H^+ \tag{11}$$

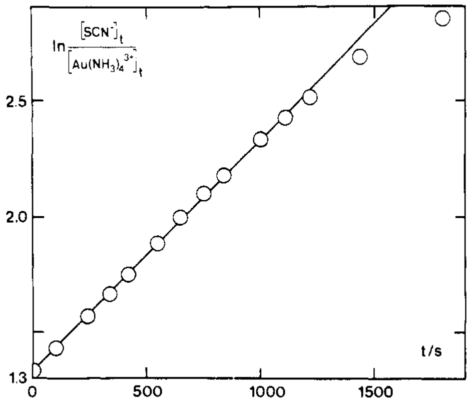

Figure 7. Second-order plot for the reaction between $Au(NH_3)_4^{3+}$ and thiocyanate according to eq 16.

When $Au(NH_3)_4^{3+}$ was allowed to react with thiocyanate in moderately acidic solution, the pH of the solution increased; cf. Table I. The consumption of H^+ was independent of the ratio between $Au(NH_3)_4^{3+}$ and SCN^- when the latter reactant was in excess and corresponded to a consumption of H^+ with the ratio $\Delta[H^+]/C_{Au} = 1.29 \bullet 0.04$; cf. Table I. This ratio is in agreement with the stoichiometry given in eq 12, for which the consumption ratio is expected to be equal to 1.33 at pH ca. 3.

$$3Au(NH_3)_4^{3+} + 6SCN^- + 4H^+ + 4H_2O \rightarrow 2Au(SCN)_2^- + Au(SCN)(CN)^- + SO_4^{2-} + 12NH_4^+ \tag{12}$$

The reactions of the diammine complexes with thiocyanate give rise to a decrease of pH; cf. Table I. At pH ca. 3 the consumption ratio $\Delta[H^+]/C_{Au} = -0.64 \pm 0.02$ is in agreement with the reaction stoichiometry shown in eq 13 (X = Cl, Br).

$$3\,trans\text{-}Au(NH_3)_2X_2^+ + 6SCN^- + 4H_2O \rightarrow 2Au(SCN)_2^- + Au(SCN)(CN)^- + SO_4^{2-} + 6NH_4^+ + 2H^+ \tag{13}$$

Thus, the stoichiometry for the reaction of the ammine- and the haloamminegold(III) complexes is similar to that found previously[15] for the reaction between $AuCl_4^-$ and thiocyanate (eq 14).

$$3AuCl_4^- + 6SCN^- + 4H_2O \rightarrow 2Au(SCN)_2^- + Au(SCN)(CN)^- + SO_4^{2-} + 12Cl^- + 8H^+ \tag{14}$$

Reaction between $Au(NH_3)_4^{3+}$ and Thiocyanate. When thiocyanate was added to a solution of $Au(NH_3)_4^{3+}$, no intermediates of the type $Au(NH_3)_{4-i}(SCN)_i^{3-i}$ (i = 1–4) or hydrolysis products thereof could be detected by use of conventional or stopped-flow spectrophotometry. Potentiometric measurements indicated one slow reaction with a rate law according to eq 15; cf. Table II.

$$-d[Au(NH_3)_4^{3+}]/dt = k_{obsd}[Au(NH_3)_4^{3+}][SCN^-] \tag{15}$$

Integration of eq 15 for second-order conditions yields eq 16 by

$$\ln ([SCN^-]_t/[Au(NH_3)_4^{3+}]_t) = \ln ([SCN^-]_0/[Au(NH_3)_4^{3+}]_0) + ([SCN^-]_0 - 2[Au(NH_3)_4^{3+}]_0)k_{obsd}t \tag{16}$$

use of the stoichiometric coefficients from eq 12. Concentrations of SCN^- and $Au(NH_3)_4^{3+}$ at time t were obtained from eq 17 and 18. Plots of $\ln ([SCN^-]_t/[Au(NH_3)_4^{3+}]_t)$ vs time according to

$$[SCN^-]_t = [SCN^-]_0 - 1.5[H^+]_0 + 1.5[H^+]_t \tag{17}$$

$$[Au(NH_3)_4^{3+}]_t = [Au(NH_3)_4^{3+}]_0 - 0.75[H^+]_0 + 0.75[H^+]_t \tag{18}$$

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[15] Bjerrum, N.; Kirschner, A. *K. Dan. Vidensk. Selsk. Skr., Naturvidensk. Math. Afd.* **1918**, Series 8, Vol. 1.

Table IX. Rate Constants for the Reaction between *trans*-$Au(NH_3)_2X_2^+$ and SCN^- (X = Cl, Br)

$k/M^{-1}\ s^{-1}$	$t/°C$	X = Br	X = Cl
k_1	2.0	$(8.9 \pm 0.3) \times 10^4$	$(9.0 \pm 1.4) \times 10^3$
k_{-1}	2.0	$(1.32 \pm 0.20) \times 10^3$	0.6 ± 0.2
k_2	2.0	$(1.4 \pm 0.4) \times 10^5$	$(1.56 \pm 0.21) \times 10^5$
k_{-2}	2.0	$(1.0 \pm 0.7) \times 10^4$	$(3.4 \pm 0.6) \times 10^2$
k_{r0}	25.0	10 ± 5	not determined
k_{r1}	25.0	$(3.0 \pm 0.5) \times 10^2$	$(2.7 \pm 0.5) \times 10^3$
k_{r2}	25.0	$(2.5 \pm 0.4) \times 10^2$	$(2.2 \pm 0.4) \times 10^2$

eq 16 were linear for more than 80% conversion and gave the second-order rate constant k_{obsd} of eq 15; cf. Table II. A plot according to eq 16 is shown in Figure 7.

Reaction between *trans*-$Au(NH_3)_2X_2^+$ and Thiocyanate. The rate of substitution was found to be linearly dependent on the concentrations of halide and thiocyanate, and no solvent path could be observed. The second-order rate constants for substitution, k_n and k_{-n}, were calculated from the experimental data by linear regression according to eq 19. Substitution of Q according to

$$k_{obsd} = k_n[SCN^-] + k_{-n}[X^-] \qquad (19)$$

eq 3 into eq 19 gives eq 20, which was used to calculate k_{-2} for

$$k_{obsd} = (k_n + Qk_{-n})[SCN^-] \qquad (20)$$

the reaction between *trans*-$Au(NH_3)_2Br_2^+$ and SCN^- from the experimental data obtained at constant Q and with the value of $k_2 = 1.4 \times 10^5\ M^{-1}\ s^{-1}$.

The values of the stability constants for the $Au(NH_3)_2Br_2^+/SCN^-$ system allowed the study of the rate of reduction in a Q interval large enough to cover all three complexes in concentrations, where a determination of each of the individual rate constants k_{rn} (n = 0, 1, 2) could be made. The chloride system could only be studied qualitatively in regions where *trans*-$Au(NH_3)_2ClSCN^+$ and *trans*-$Au(NH_3)_2(SCN)_2^+$ were present in solution; compare Figures 5 and 6. Quantitative measurements at chloride concentrations higher than 1.00 M show a decrease in the reduction rate similar to what has been observed for reactions between dimethyl sulfide and tetrachloroaurate(III) in aqueous methanol.[7]

With thiocyanate in excess and at constant Q, the rate of reduction was linearly dependent on the concentration of thiocyanate, in agreement with both a reduction that is first-order with respect to substrate and thiocyanate and the expression of eq 21 for the observed rate constant for the overall reduction.

$$k_{obsd} = [SCN^-]\sum_0^2 k_{ri}\beta_i Q^{-i} / \sum_0^2 \beta_j Q^{-j} \qquad (21)$$

Introducing α_n, defined by eq 6, the molar fraction of the complex $Au(NH_3)_2X_{2-n}(SCN)_n^+$ in the rapid preequilibrium, into eq 21 gives eq 22. Since α_n is known, the second-order rate constants

$$k_{obsd} = [SCN^-]\sum_0^2 \alpha_n k_{rn} \quad n = 0, 1, 2 \qquad (22)$$

for reduction of each gold(III) complex, k_{rn}, could be calculated from the observed overall reduction rate constants by use of eq 22. The calculated values of the observed second-order rate constants are shown as functions of $-\log Q$ in Figure 6 as solid lines. All rate constants are summarized in Table IX, and the activation parameters are given in Table X.

Discussion

Thermodynamic data for gold(III) complexes in solution are in general scarce. With the exception of the results from potentiometric studies of gold(III) thiocyanato complexes,[16] no stability data seem to be available for the formation of complexes between sulfur-bonding ligands and gold(III) centers.[8] Moreover, monomeric gold(III) thiocyanato complexes are rather short-lived in aqueous solution.[4] Therefore, thermodynamic and spectral data obtained by static methods for these and other sulfur-bonding ligands most likely reflect nonequilibrium situations and must be considered with reservation. The results obtained in the present study is of particular interest since they provide the kinetic data for the deduction of stability constants for a series of mixed-ligand gold(III) thiocyanato complexes and for the correlation between rate of substitution and stability. The combined kinetic and thermodynamic results for the *trans*-dihalodiamminegold(III)/thiocyanato complexes provide a rare example of a series of short-lived gold(III) complexes with half-lives in the millisecond region for which equilibrium constants have been determined and for which, moreover, the rate of reduction of the individual mixed-ligand complexes has been determined. Besides being of intrinsic interest in relation to reaction mechanisms, it also provides part of the information necessary for an understanding of the relative stability of gold(I) and gold(III) complexes in the presence of sulfur-bonding ligands.

Table X. Activation Parameters at 25.0 °C for the Reaction between SCN^- and the Complexes *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br) and $Au(NH_3)_4^{3+}$

complex	rate constant	$\Delta^{*}H°/$ kJ mol^{-1}	$\Delta^{*}S°/$ J K^{-1} mol^{-1}
trans-$Au(NH_3)_2Br_2^+$	k_1	30 ± 11	-50 ± 30
trans-$Au(NH_3)_2Cl_2^+$	k_1	33 ± 7	-48 ± 21
	k_{r2}	66 ± 4	21 ± 12
$Au(NH_3)_4^{3+}$	k_1	61 ± 1	-26 ± 3

Stabilities. A statistical distribution for a series of complexes with a given set of ligands indicates that the free energy of a particular metal–ligand bond is independent of the combination of other ligands bound to the metal center. For a complex system like that described in Figure 1, a deviation in the ratio between K_1 and K_2 from 4 implies that the mixed-ligand complex is either energetically favored ($K_1/K_2 > 4$) or disfavored ($K_1/K_2 < 4$). For the substitution of chloride for bromide in *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br),[13] the ratio is almost independent of temperature and equal to 3.7, close to the statistically expected value. Likewise, the reversible substitution of bromide for thiocyanate in the *trans*-diamminegold(III) complex moiety also deviates only slightly from the expected value with the ratio 5.6.

On the other hand, the substitution of chloride for thiocyanate shows a large deviation with $K_1/K_2 = 33$. The overall stability constant β_2 for the reaction between $Au(NH_3)_2Cl_2^+$ and SCN^- calculated from eq 8 and 9 gives the statistically expected values of $K_1 = 5300$ and $K_2 = 1300$. However, the combination of two statistically distributed complex systems does not necessarily allow such an interpolation, as shown by the experimental constants 15000 and 460, respectively; cf. Table VIII. These values indicate an increased stability for the chloro–thiocyanato complex; cf. Figure 5.

Solid-state structure determinations show that ligands with a strong trans influence in the ground state like SCN^- are not only strongly bound to the metal center, but also weaken the bond to the ligand in trans position, with the result being an asymmetric distribution of electron density along that axis. Further, the total length of the trans axis is shortened compared to what should be expected if the length of the trans axis was determined by the bond lengths of symmetric complexes of the respective ligands.[17] Since the degree of asymmetry is determined by the difference in trans influence between the two ligands trans to each other, the asymmetry is expected to be largest in the case of *trans*-$Au(NH_3)_2ClSCN^+$, which is in agreement with the increased relative stability of this complex.

Kinetics and Mechanism. Rate constants of substitution reactions in square-planar complexes have often been described by empirical relationships of the type given in eq 23,[18,19] where k/m,

$$k/m = (\text{const})CTEL \qquad (23)$$

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(16) Pouradier, J.; Gadet, M.-C. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1467.

(17) Oskarsson, Å. Private communication.

(18) Tucker, M. A.; Colvin, C. B.; Martin, D. S. *Inorg. Chem.* **1964**, *3*, 1373.

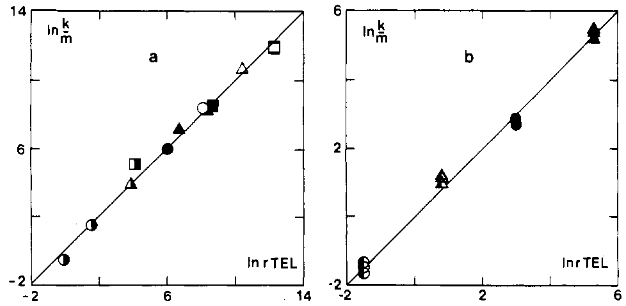


Figure 8. (a) Reversible substitution of Cl$^-$, Br$^-$, and SCN$^-$ in *trans*-Au(NH$_3$)$_2$X$_2$$^+$ (X = Cl, Br, SCN) at 2.0 °C. (b) Reversible substitution of Cl$^-$ and Br$^-$ in AuX$_4$$^-$ (X = Cl, Br) at 25.0 °C. Parametrization was according to eq 24. k/m denotes the observed second-order rate constants divided by the statistical factor. Entering ligands are represented by open symbols (SCN$^-$), half-filled symbols (Cl$^-$) and filled symbols (Br$^-$); trans ligands are represented by squares (SCN$^-$), circles (Cl$^-$), and triangles (Br$^-$).

the statistically corrected rate constant, is proportional to parameters for the effect of cis (C), trans (T), entering (E), and leaving (L) ligands. For the present complexes, the cis effect is constant since the two ammonia ligands are not changed during the reactions, and eq 23 is reduced to eq 24. With $r = 4.46$ M^{-1}

$$k/m = rTEL \tag{24}$$

s^{-1}, which is the statistically corrected rate constant at 2.0 °C for the chosen reference reaction 25, the values given in eq 26 were

$$trans\text{-}Au(NH_3)_2ClBr^+ + Cl^- \rightarrow trans\text{-}Au(NH_3)_2Cl_2^+ + Br^- \tag{25}$$

$$\begin{aligned} T_{Cl^-}:T_{Br^-}:T_{SCN^-} &= 1:10:70 \\ E_{Cl^-}:E_{Br^-}:E_{SCN^-} &= 1:90:700 \\ L_{Cl^-}:L_{Br^-}:L_{SCN^-} &= 1:1:0.2 \end{aligned} \tag{26}$$

found to describe the reversible substitutions of X$^-$ for SCN$^-$ as well as the previously studied[13] substitutions of Cl$^-$ for Br$^-$ in *trans*-Au(NH$_3$)$_2$X$_2$$^+$ (X = Cl, Br). The constant effects of trans, entering, and leaving ligands is characteristic for statistically distributed systems. For nonstatistical systems, the observed rate constant should be larger in the direction toward the mixed complex and/or smaller in the opposite direction compared to the calculated values. This is indeed observed for the stepwise reactions in the *trans*-Au(NH$_3$)$_2$Cl$_2$$^+$/SCN$^-$ system, which fulfill both of the later requirements.

The reversible substitution of Cl$^-$ and Br$^-$ on tetrahaloaurate(III) studied previously[20] was also found to be well described by the parameters of eq 26, with the proportionality factor chosen as the rate constant of reaction 27 at 25.0 °C, which is $r = 0.22$

$$cis\text{-}AuCl_2Br_2^+ + Cl^- \rightarrow AuCl_3Br^+ + Br^- \tag{27}$$

M^{-1} s^{-1}. Thus, *trans*-Au(NH$_3$)$_2$X$_2$$^+$ reacts faster than AuX$_4$$^-$. Changing the two cis ligands and the ionic charge of the complex increases the rate of substitution by a factor of ca. 60 when the difference in temperature is taken into account. It is not possible to separate the effect of cis ligands from that of charge, but the good fit of experimental data to eq 24 shown in Figure 8 indicates that the ratio between the cis effects of chloride and bromide is close to 1. Further, the change of cis ligands from ammine to halide does not affect the statistical behavior of the stability constants.

As can be seen from eq 26, the nature of the entering ligand is *more* important for the rate of reaction than that of the trans ligand. This is in marked contrast to what has been observed for substitution reactions on the isoelectronic Pt(II) complexes[19] (eq 28). This notable difference in substitutional behavior between

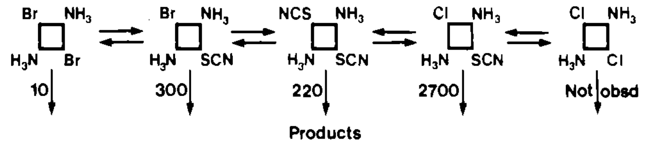


Figure 9. Second-order rate constants k_{obsd}/[SCN$^-$] (M^{-1} s^{-1}) at 25.0 °C for reduction of the complexes *trans*-Au(NH$_3$)$_2$X$_{2-n}$(SCN$^-$)$_n$$^+$ (n = 0, 1, 2) by thiocyanate. The common product is Au(NH$_3$)$_2$$^+$; cf. Figure 1.

$$\begin{aligned} T_{Cl^-}:T_{Br^-}:T_{SCN^-} &= 1:10:300 \\ E_{Cl^-}:E_{Br^-}:E_{SCN^-} &= 1:8:50 \\ L_{Cl^-}:L_{Br^-}:L_{SCN^-} &= 1:1:1 \end{aligned} \tag{28}$$

Pt(II) and Au(III) complexes confirms the earlier indications[8,20] of a very high discrimination power for entering ligands for the softer Au(III) center and explains the very large spectrum of reaction rates exhibited.

The experimental rate law of eq 15 for the Au(NH$_3$)$_4$$^{3+}$–SCN$^-$ reaction indicates a rate-controlling reaction between Au(NH$_3$)$_4$$^{3+}$ and SCN$^-$. The ionic strength dependence is also compatible with a reaction between +3 and −1 charged ions in the rate-controlling step; cf. Figure 3. Two reaction mechanisms are feasible.

The first is a direct reduction of Au(NH$_3$)$_4$$^{3+}$ by attack of SCN$^-$ directly on a coordinated NH$_3$ or the metal center and concomitant elimination of an oxidation product such as SCN$^+$ or NCSNH$_3$$^+$ resulting from a two-electron transfer to the metal center. The structure of the transition state for such a reaction mechanism is not obvious, and this mechanism will not be considered further.

The second is a rate-controlling initial ligand substitution reaction at Au(NH$_3$)$_4$$^{3+}$

$$Au(NH_3)_4^{3+} + SCN^- \rightarrow Au(NH_3)_3SCN^{2+} + NH_3 \tag{29}$$

followed either by rapid trans substitution

$$Au(NH_3)_3SCN^{2+} + SCN^- \rightarrow trans\text{-}Au(NH_3)_2(SCN)_2^+ + NH_3 \tag{30}$$

and a rapid reductive elimination

$$trans\text{-}Au(NH_3)_2(SCN)_2^+ + SCN^- \rightarrow SCN^- + Au(NH_3)_2^+ + (SCN)_2 \tag{31}$$

or followed by direct rapid reductive elimination

$$trans\text{-}Au(NH_3)_3(SCN)^{2+} + SCN^- \rightarrow Au(NH_3)_2^+ + (SCN)_2 + NH_3 \tag{32}$$

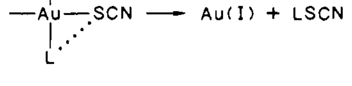
For both of these two reaction sequences (either (29), (30), and (31) or (29) and (32)) the gold(I) product Au(NH$_3$)$_2$$^+$ is rapidly converted to a mixture of Au(SCN)$_2$$^-$ and Au(SCN)(CN)$^-$, the cyanide being formed by hydrolysis of (SCN)$_2$ in a reaction sequence that is also rapid compared to the rate-determining reaction of eq 29.[14]

As expected for square-planar substitution reactions, the activation entropies are all negative; cf. Table X. Notably, $\Delta^{\ddagger}S°$ for the reactions

$$Au(NH_3)_4^{3+} + Y^- \rightarrow Au(NH_3)_3Y^{2+} + NH_3 \tag{32a}$$

where Y = Cl, Br, I, and SCN decreases, being 20, 8, −1, and −26 J K^{-1} mol^{-1}, respectively,[3,11,21] reflecting a decrease in solvation for the entering ligands.

The rate of reduction is linearly dependent on the concentration of excess thiocyanate at constant Q, and the reaction is therefore likely to proceed via an intermolecular attack by an outer-sphere SCN$^-$ on the gold(III) complexes, as has also been concluded from a previous study.[4] This makes an intramolecular mechanism of the type shown by eq 33 very unlikely. Moreover, the nature of



$$\underset{L}{-Au-}SCN \longrightarrow Au(I) + LSCN$$

(33)

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[19] Elding, L. I.; Gröning, A.-B. *Chem. Scr.* **1977**, *11*, 8.

[20] Elding, L. I.; Gröning, A.-B. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 867.

[21] Ventegodt, J.; Øby, B.; Skibsted, L. H. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 453.

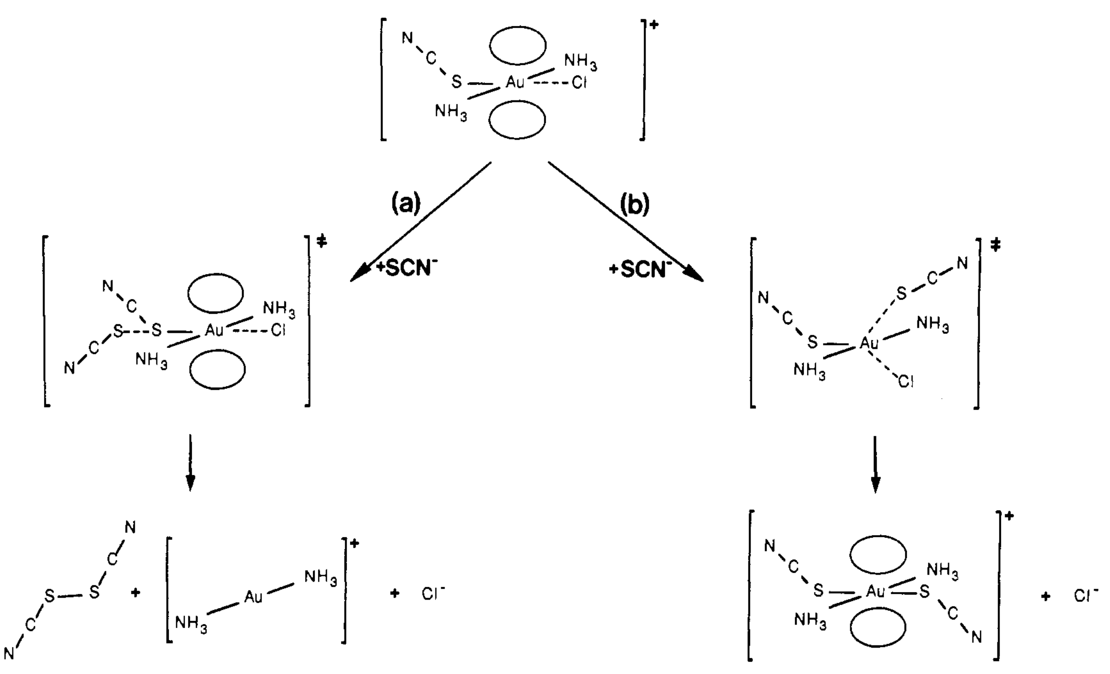

Figure 10. Proposed intimate mechanisms for the competitive reductive elimination (a) and substitution (b) processes. On both sides of the coordination plane of gold(III) there is a high electron density due to the filled d_{z^2}, d_{xz}, and d_{yz} orbitals, indicated by the shaded areas.

the primary product for such a mechanism in the present case with L = NH_3 is less obvious. On the other hand, the linear dependence does not distinguish between an axial attack on the metal ion of the complex and an attack on one of the ligands (see discussion below).

The rate of reduction of the present diamminedihalogold(III) complexes by SCN^- follows a common pattern with a maximum rate of reduction for the mixed halothiocyanato complexes; cf. Figure 9. For complexes with S-bonded ligands, the site of attack on the complex by a reducing ligand has been suggested to be either a halide trans to the S-bonded ligand,[7] or the S-bonded ligand itself[5] with additional direct interaction with the metal center. A comparison of the reduction rate constants for the present complexes seems to provide more detailed information on the intimate mechanism for the process of electron transfer to the gold(III) center.

(i) Bromide is a better bridging ligand than chloride in cases where the halide is known to act as the bridging ligand for electron transfer.[22] For the complexes *trans*-$Au(NH_3)_2XSCN^+$ (X = Cl, Br); however, the chloro complex is reduced more rapidly than the bromo complex. Further, the rate constant for reduction of *trans*-$Au(NH_3)_2Br_2^+$ is the lowest among those determined.

(ii) The reduction requires a two-electron transfer, and it is likely that the electrons are supplied from a region with high electron density close to the metal center. For the complexes *trans*-$Au(NH_3)_2XSCN^+$ (X = Cl, Br), such a region is expected to be found between the sulfur and the metal center since thiocyanate is known to have a much larger trans influence than chloride and a somewhat better trans influence than bromide, which is also verified by the present study. The halide ligands, particularly chloride in *trans*-$Au(NH_3)_2ClSCN^+$, are more loosely bound to the metal center and have a less efficient orbital overlap, which should make electron transfer to the gold(III) center from this direction more difficult.

(iii) Assuming a common mechanism for the reduction of the complexes *trans*-$Au(NH_3)_2ClSCN^+$, *trans*-$Au(NH_3)_2BrSCN^+$, and *trans*-$Au(NH_3)_2(SCN)_2^+$ gives a sequence of reduction rates, which decrease with increasing stability, in agreement with the expected reduction potentials for the respective complexes.

Observations i–iii strongly favor a mechanism with a thiocyanate attack on a coordinated thiocyanate, when such is available, and subsequent reductive elimination. However, since at least *trans*-$Au(NH_3)_2Br_2^+$ is reduced directly by SCN^- without initial substitution, an alternative mechanism involving either attack on the metal center or the halide must also be operating.

We then arrive at the intimate mechanism for electron transfer and substitution depicted in Figure 10. The Au–S bond trans to a halide is already polarized, prior to attack by a thiocyanate ion, more in the case of trans chloride than bromide. The filled d_{z^2}, d_{xz}, and d_{yz} orbitals of the metal force the attacking thiocyanate to approach from a direction close to the coordination plane where a direct S–S interation may take place and a $d^8 \rightarrow d^{10}$ electron transfer to the empty $d_{x^2-y^2}$ orbital can occur. Additional interaction between the filled orbitals of the metal center and empty d orbitals of the entering sulfur is probably not extensive, since that implies an electron transfer in the opposite direction.

In accord with this picture, the highest substitution rates of halide for thiocyanate are observed for the two mixed-ligand complexes. This might in part be due to the ground-state trans influence of thiocyanate, which weakens the bond to the leaving halide ligand, leading to the parallel substitution path (b) in Figure 10.

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Registry No. $Au(NH_3)_4^{3+}$, 43739-93-1; *trans*-$Au(NH_3)_2Cl_2^+$, 90491-17-1; *trans*-$Au(NH_3)_2Br_2^+$, 70148-53-7; SCN^-, 302-04-5.

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(22) For instance: Elding, L. I.; Gustafson, L. *Inorg. Chim. Acta* **1977**, *24*, 239.