

Competitive Substitution and Electron Transfer in Reactions between Haloamminegold(III) and Halocynoaurate(III) Complexes and Thiocyanate

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Kinetics for reactions between thiocyanate and *trans*-Au(CN)₂Cl₂⁻, *trans*-Au(CN)₂Br₂⁻, and *trans*-Au(NH₃)₂Cl₂⁺ in an acidic, 1.00 M perchlorate aqueous medium have been studied by use of conventional and diode-array UV/vis spectroscopy and high-pressure and sequential-mixing stopped-flow spectrophotometry. Initial, rapid formation of mixed halide–thiocyanate complexes of gold(III) is followed by slower reduction to Au(CN)₂⁻ and Au(NH₃)₂⁺, respectively. This is an intermolecular process, involving attack on the complex by outer-sphere thiocyanate. Second-order rate constants at 25.0 °C for reduction of *trans*-Au(CN)₂XSCN⁻ are $(6.9 \pm 1.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for X = Cl and $(3.1 \pm 0.7) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for X = Br. For reduction of *trans*-Au(CN)₂(SCN)₂⁻ the second-order rate constant at 25.0 °C is $(3.1 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and the activation parameters are $\Delta H^\ddagger = (55 \pm 3) \times 10^2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = (-17.8 \pm 0.8) \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta V^\ddagger = (-4.6 \pm 0.5) \text{ cm}^3 \text{ mol}^{-1}$. The activation volume for substitution of one chloride on *trans*-Au(NH₃)₂Cl₂⁺ is $(-4.5 \pm 0.5) \text{ cm}^3 \text{ mol}^{-1}$, and that for reduction of *trans*-Au(NH₃)₂(SCN)₂⁺ $(4.6 \pm 0.9) \text{ cm}^3 \text{ mol}^{-1}$. The presence of π -back-bonding cyanide ligands stabilizes the transition states for both substitution and reductive elimination reactions compared to ammine. In particular, complexes *trans*-Au(CN)₂XSCN⁻ with an unsymmetric electron distribution along the X–Au–SCN axis are reduced rapidly. The observed entropies and volumes of activation reflect large differences in the transition states for the reductive elimination and substitution processes, respectively, the former being more loosely bound, more sensitive to solvational changes, and probably not involving any large changes in the inner coordination sphere. A transition state with an S–S interaction between attacking and coordinated thiocyanate is suggested for the reduction. The stability constants for formation of the very short-lived complex *trans*-Au(CN)₂(SCN)₂⁻ from *trans*-Au(CN)₂X(SCN)⁻ (X = Cl, Br) by replacement of halide by thiocyanate prior to reduction can be calculated from the redox kinetics data to be $K_{\text{Cl},2} = (3.8 \pm 0.8) \times 10^4$ and $K_{\text{Br},2} = (1.1 \pm 0.4) \times 10^2$.

Introduction

Reactions between gold(III) complexes and good nucleophiles often result in reduction to gold(I).¹ The two-electron redox reaction may take place either as a direct bimolecular process between the gold(III) complex and the reductant^{2–4} or through initial replacement of ligands in the inner coordination sphere by the reducing agent followed by reduction.^{3,5–10} The rate of substitution may in some cases be similar to that of electron transfer, giving rise to a competition between substitution equilibria and redox reactions. In the case of gold(III) complexes, such a situation has been documented only for reactions involving thiocyanate and thioethers as nucleophiles.^{11–14} The competition between substitution and redox reactions offers

a unique possibility for evaluation of relationships between structure, stability, and reactivity at metal centers undergoing substitution and reductive elimination reactions in parallel processes with one and the same nucleophile. The transition states for these two reactions, both resulting from an attack by the nucleophile on the complex, must have different properties. An analysis of entropies and volumes of activation that reflect geometrical changes in the activation process may assist in elucidating these mechanistic differences.

The reaction between thiocyanate and *trans*-Au(NH₃)₂X₂⁺ (X = Cl, Br) has been studied in detail.¹⁴ Here, rapid pre-equilibria between short-lived, mixed halide–thiocyanate complexes of gold(III) precede the slower reduction. The distribution between the gold(III) complexes in the pre-equilibrium is determined by the ratio between the concentrations of free halide and thiocyanate, $Q = [X^-]/[\text{SCN}^-]$. A change of this ratio gives rise to a variation of the observed overall reduction rate constant. Resolution of the observed rate constants into those for parallel reduction of each of the complexes *trans*-Au(NH₃)₂X_{2–n}(SCN)_n⁺ ($n = 0, 1, 2$) shows that the second-order rate constants for reduction vary largely depending on the composition and electronic structure of the complexes.¹⁴ In particular, the presence of an asymmetric charge distribution along the X–Au–SCN axis results in rapid electron transfer. A large difference in ground-state *trans*-influence between X⁻ and SCN⁻ thus seems to facilitate reduction. The aim of the present work was to further test the generality of these observations by

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- (1) Skibsted, L. H. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 137–184.
- (2) Elding, L. I.; Olsson, L. F. *Inorg. Chem.* **1982**, *21*, 779–784.
- (3) Elding, L. I.; Skibsted, L. H. *Inorg. Chem.* **1986**, *25*, 4084–4087.
- (4) Berglund, J.; Elding, L. I. *Inorg. Chem.* **1995**, *34*, 513–519.
- (5) De Filippo, D.; Devillanova, F.; Preti, C. *Inorg. Chim. Acta* **1971**, *5*, 103–108.
- (6) Schulman, V. M.; Saveleva, Z. A.; Novoselov, R. I. *Russ. J. Inorg. Chem.* **1973**, *18*, 376–379.
- (7) Nord, G.; Skibsted, L. H.; Halonin, A. S. *Acta Chem. Scand.* **1975**, *A29*, 505–512.
- (8) Natile, G.; Bordignon, E.; Cattalini, L. *Inorg. Chem.* **1976**, *15*, 246–248.
- (9) Hall, A. J.; Satchell, D. P. N. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1278–1284.
- (10) Makotchenko, E. V.; Peschevitskii, B. I.; Novoselov, R. I. *Izv. Sib. Otd. Akad. Nauk. SSR, Ser. Khim. Nauk.* **1981**, 56–61.
- (11) Hall, A. J.; Satchell, D. P. N. *J. Chem. Soc., Dalton Trans.* **1977**, 1403–1409.
- (12) Annibale, G.; Canovese, L.; Cattalini, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1017–1021.

(13) Elding, L. I.; Gröning, A.-B.; Gröning, Ö. *J. Chem. Soc., Dalton Trans.* **1981**, 1093–1100.

(14) Elmroth, S.; Skibsted, L. H.; Elding, L. I. *Inorg. Chem.* **1989**, *28*, 2703–2710.

use of the softer metal center in the complex $\text{trans-Au}(\text{CN})_2\text{X}_2^-$ ($\text{X} = \text{Cl}, \text{Br}$).

Experimental Section

Chemicals and Solutions. $\text{KAu}(\text{CN})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{KAu}(\text{CN})_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$ were prepared according to the literature.¹⁵ The bromide complex was synthesized by oxidation of an aqueous solution of $\text{KAu}(\text{CN})_2$ (Degussa) with liquid bromine (Merck, p.a.). The chloride complex was synthesized by oxidation of $\text{KAu}(\text{CN})_2\text{Br}_2$ in water with chlorine (prepared from HCl and KMnO_4) followed by flux with N_2 to remove BrCl . Solid compounds were obtained by evaporation of the water at room temperature. Their UV/vis spectra agreed satisfactorily with those reported.¹⁶ Yields were 65–80% for $\text{KAu}(\text{CN})_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$ and 92–98% for $\text{KAu}(\text{CN})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ as determined gravimetrically. $[\text{Au}(\text{NH}_3)_2\text{Cl}_2]\text{Cl} \cdot 1/3\text{H}_2\text{O}$ and $[\text{Au}(\text{NH}_3)_2\text{Br}_2]\text{Br} \cdot 1/3\text{NH}_4\text{Br}$ were synthesized as described previously.^{17,18} Solutions of gold(III) complexes were used within 5 days from preparation. They contained added halide (10 mM NaCl and 1 mM NaBr , respectively) and HClO_4 (10 mM) to suppress formation of aqua and hydroxo complexes. Stock solutions of NaSCN (Mallinckrodt, analytical reagent) were prepared from the solid salt directly before use. NaCl (Merck, Suprapur), NaBr (Merck, Suprapur, or May & Baker), HClO_4 (Merck, p.a.) and NaClO_4 (Merck, p.a.) were kept as 1.00 M stock solutions. Ionic strength was 1.00 M adjusted with NaClO_4 . Water was doubly distilled from quartz.

Apparatus. Spectra were recorded by use of a Varian Cary 2200 spectrophotometer. Formation of short-lived gold(III) complexes in the reaction between $\text{trans-Au}(\text{CN})_2\text{X}_2^-$ and SCN^- was monitored by use of a continuous-flow system with a dead time of ca. 0.1 s comprised of a 1:1 mixing chamber and a Hellma flow cell (170-QS) connected to a HP 8452 diode-array spectrophotometer equipped with HP 89510 A UV/vis software. The kinetics were followed by use of a Hi-Tech SFL-43 sequential-mixing stopped-flow system in connection with an SU-40A UV/vis spectrophotometer unit. Activation volumes were determined by use of an HPSF-56 Hi-Tech high-pressure stopped-flow spectrophotometer equipped with a digital pressure indicator.¹⁹

Flow Spectra. Equal volumes of a solution of $\text{trans-Au}(\text{CN})_2\text{X}_2^-$ and a solution containing excesses of both NaSCN and NaX were mixed in the continuous-flow system to obtain a reaction mixture with constant concentration ratio $Q = C_{\text{X}}/C_{\text{SCN}} \cong [\text{X}^-]/[\text{SCN}^-]$ (all experiments performed with ligands in large excess compared to gold complexes). The spectra of the steady-state mixtures were recorded at 24.0 ± 0.4 °C every 3 s until successive spectra became identical, usually after 2–3 scans. A reaction mixture of a previous run, equilibrated for 10–20 min, was used as the reference. For reactions between $\text{trans-Au}(\text{CN})_2\text{Cl}_2^-$ and SCN^- the total concentrations after mixing were $C_{\text{Au}} = 1.55 \times 10^{-5}$ M and $C_{\text{SCN}} = 6.0 \times 10^{-4}$ M, resulting in Q values of 11.6, 32.6, 65.2, 167, 267, 433, and 850. The corresponding values for the reaction between $\text{trans-Au}(\text{CN})_2\text{Br}_2^-$ and SCN^- were $C_{\text{Au}} = 1.76 \times 10^{-5}$ M, $C_{\text{SCN}} = 2.55 \times 10^{-4}$ M, and $Q = 11.6, 22, 35.6, 52, 102, 152, 242, 502, \text{ and } 802$. Difference spectra are given in Figure 1.

Sequential-Mixing Stopped-Flow Kinetics. Reactions between $\text{trans-Au}(\text{CN})_2\text{X}_2^-$ and thiocyanate were initiated by mixing a solution of the gold complex directly in the first mixing chamber of the stopped-flow instrument with ionic medium for measurements with $Q \leq 1$ and with solutions containing halide (1.00 mM to 1.00 M) for measurements with $Q > 1$. Thiocyanate was added in the second mixing chamber, and the reaction was monitored under pseudo-first-order conditions with thiocyanate in excess (0.377–10 mM), in the temperature interval 2.0–40.0 °C. Total concentrations of gold varied between 3.0×10^{-6} M and 2.0×10^{-5} M. The experiments are summarized in Table 1, in Supporting Information Tables S1 and S2, and in Figure 2. Addition of gold(I) as $\text{Au}(\text{CN})_2^-$ (3.7×10^{-5} and 3.7×10^{-4} M) had no influence on the kinetics; cf. data in Table 1.

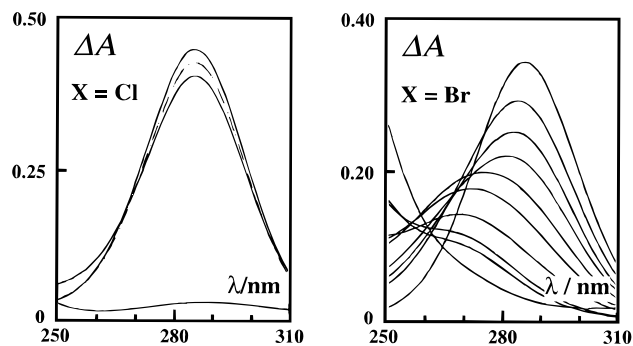


Figure 1. Continuous-flow difference spectra of the short-lived complexes $\text{trans-Au}(\text{CN})_2\text{X}_{2-n}(\text{SCN})_n^-$: $\text{X} = \text{Cl}$, from top to bottom, $Q = 33, 267, 850, \infty$ (no thiocyanate added); $\text{X} = \text{Br}$, from top to bottom at 290 nm, $Q = 11.6, 22, 35.6, 52, 102, 242, 502, 802, \infty$ (no thiocyanate added). ΔA denotes relative absorbances, recorded with an equilibrated mixture of reaction products (aged for 10–20 min) as the reference.

Table 1. Observed Pseudo-First-Order Rate Constants for Reduction of $\text{trans-Au}(\text{CN})_2(\text{SCN})_2^-$ as a Function of Temperature

$10^5 C_{\text{Au}}/\text{M}$	$t/^\circ\text{C}$	$10^3 C_{\text{SCN}}/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$
Reaction with $\text{trans-Au}(\text{CN})_2\text{Br}_2^-$ ^a			
2.00	2.0	0.377	0.0155 ± 0.0011
2.00	2.0	2.32	0.105 ± 0.008
2.00	2.0	4.68	0.216 ± 0.006
2.00	2.0	7.01	0.307 ± 0.009
2.00	2.0	9.67	0.390 ± 0.009
1.97	13.0	2.49	0.32 ± 0.05
1.97	13.0	4.98	0.48 ± 0.05
1.97	13.0	7.45	0.77 ± 0.06
1.97	13.0	9.95	1.13 ± 0.06
1.97	25.0	2.49	0.76 ± 0.04
1.97	25.0	4.98	1.49 ± 0.04
1.97	25.0	7.45	2.21 ± 0.07
1.97	25.0	9.93	2.98 ± 0.09
1.97	25.0	9.95	3.07 ± 0.10
0.883 ^b	25.0	10.00	3.2 ± 0.1
0.883 ^c	25.0	10.00	3.0 ± 0.1
1.97	40.0	2.49	2.21 ± 0.08
1.97	40.0	2.98	4.28 ± 0.13
1.97	40.0	7.45	6.4 ± 0.3
1.97	40.0	9.95	8.11 ± 0.26
Reaction with $\text{trans-Au}(\text{CN})_2\text{Cl}_2^-$ ^d			
0.995	25.0	0.099	0.0287 ± 0.0012
0.995	25.0	0.825	0.207 ± 0.008
0.995	25.0	10.3	3.09 ± 0.10

^a $\lambda = 285$ nm, $C_{\text{Br}} = 0.25$ mM, $[\text{H}^+] = 2.5$ mM. ^b $C_{\text{Au(III)}} = 9.25 \times 10^{-6}$ M. ^c $C_{\text{Au(III)}} = 9.25 \times 10^{-5}$ M. ^d $\lambda = 285$ nm, $C_{\text{Cl}} = 2.5$ mM, $[\text{H}^+] = 2.5$ mM.

High-Pressure Stopped-Flow Experiments. Reactions were followed under pseudo-first-order conditions with thiocyanate in excess. The drive syringes of the high-pressure stopped-flow instrument were loaded with solutions of gold(III) complex and thiocyanate, respectively, the bomb was allowed to thermostat at 24.7 °C for approximately 30 min, and the kinetics were followed as a function of pressure between 0.1 and 200 MPa. All high-pressure data are summarized in Supporting Information Tables S3–S5.

Reaction between $\text{trans-Au}(\text{CN})_2\text{Cl}_2^-$ and thiocyanate gives rise to a decrease of absorbance at 284 nm due to reduction of $\text{trans-Au}(\text{CN})_2(\text{SCN})_2^-$ (substitution processes are too rapid to be observed). The kinetics were started by mixing equal volumes of two solutions with $C_{\text{Au}} = 1.70 \times 10^{-4}$ M and $C_{\text{SCN}} = 1.02 \times 10^{-2}$ M. Rate constants as a function of pressure are given in Figure 3a. Addition of thiocyanate to $\text{trans-Au}(\text{NH}_3)_2\text{Cl}_2^+$ results in two consecutive reactions that can be monitored at 295 nm. The first one, which gives rise to an increase of absorbance, is due to rapid substitutions of the two chloride ligands for thiocyanate, substitution of the first chloride being rate-determining.¹⁴ This reaction was monitored as a function of pressure after mixing of equal volumes of two solutions with $C_{\text{Au}} = 4.03 \times 10^{-5}$ M

(15) In *Gmelins Handbuch der Anorganischen Chemie*; Verlag Chemie: GMBH., Weinheim/Bergstrasse, Berlin, 1974; Vol. 8; p 745.

(16) Mason, W. R. *Inorg. Chem.* **1970**, *9*, 2688–2691.

(17) Skibsted, L. H. *Acta Chem. Scand. Ser. A* **1979**, *A33*, 113–123.

(18) Moensted, O.; Skibsted, L. H. *Acta Chem. Scand. Ser. A* **1984**, *A38*, 23–29.

(19) Nichols, P. J.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1983**, *22*, 3993–3995.

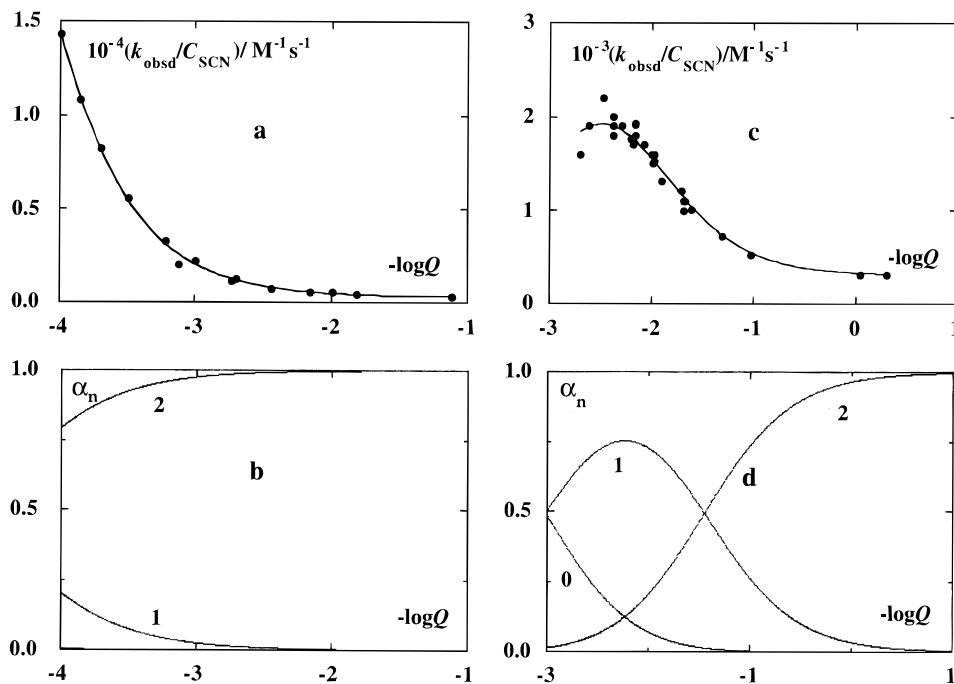


Figure 2. Second-order rate constants for reduction of $trans\text{-Au}(\text{CN})_2\text{X}_{2-n}(\text{SCN})_n^-$ ($n = 0, 1, 2$) by thiocyanate and the corresponding equilibrium distribution, both as a function of $-\log Q$: (a) Rate constants for $\text{X} = \text{Cl}$, the solid line corresponding to the function defined by eq 5 with $k_{\text{Cl},r0} = 0$, $k_{\text{Cl},r1} = 7.0 \times 10^4$, and $k_{\text{Cl},r2} = 3.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $K_{\text{X},n}$ in agreement with (b); (b) equilibrium distribution calculated by use of $K_{\text{Cl},1} = 4 \times 10^3$ and $K_{\text{Cl},2} = 3.8 \times 10^4$; (c) rate constants for $\text{X} = \text{Br}$, the solid line corresponding to the function defined by eq 5 with $k_{\text{Br},r0} = 0$, $k_{\text{Br},r1} = 3.0 \times 10^3$, and $k_{\text{Br},r2} = 3.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $K_{\text{X},n}$ in agreement with (d); (d) equilibrium distribution calculated by use of $K_{\text{Br},1} = 1 \times 10^3$ and $K_{\text{Br},2} = 1.1 \times 10^2$.

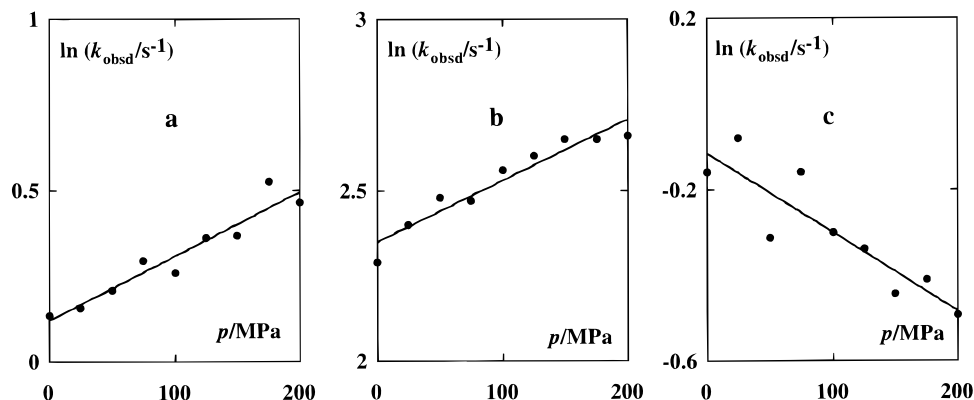


Figure 3. Pressure effect on the natural logarithm of the observed pseudo-first-order rate constants: (a) Reduction of $trans\text{-Au}(\text{CN})_2(\text{SCN})_2^-$ ($C_{\text{Au}} = 1.70 \times 10^{-4} \text{ M}$, $C_{\text{SCN}} = 1.02 \times 10^{-2} \text{ M}$); (b) substitution of the first chloride ligand for thiocyanate on $trans\text{-Au}(\text{NH}_3)_2\text{Cl}_2^+$ ($C_{\text{Au}} = 4.03 \times 10^{-5} \text{ M}$, $C_{\text{SCN}} = 8.17 \times 10^{-4} \text{ M}$); (c) reduction of $trans\text{-Au}(\text{NH}_3)_2(\text{SCN})_2^+$ ($C_{\text{Au}} = 4.03 \times 10^{-5} \text{ M}$, $C_{\text{SCN}} = 8.17 \times 10^{-3} \text{ M}$).

and $C_{\text{SCN}} = 8.17 \times 10^{-4} \text{ M}$, respectively. Results are given in Figure 3b. The subsequent, slower decrease of absorbance, due to the reduction of $trans\text{-Au}(\text{NH}_3)_2(\text{SCN})_2^+$ by thiocyanate, was followed under identical experimental conditions. Results are shown in Figure 3c.

Calculations. All kinetic runs were evaluated by use of the OLIS "Model 4000 Data System Stopped-Flow", Version 9.04, software.²⁰ Pseudo-first-order rate constants were calculated as an average of at least six independent kinetic runs. Second-order rate constants were obtained by a fit of the pseudo-first-order rate constants *vs* the concentration of free thiocyanate to a straight line by use of a least-squares routine. Enthalpies and entropies of activation for reduction of $trans\text{-Au}(\text{CN})_2(\text{SCN})_2^-$ were derived from a fit to the Eyring equation of the natural logarithm of the second-order rate constant *vs* $1/T$. Volumes of activation were obtained by a fit of the variable-pressure data to eq 1, where k_0 denotes the rate constant at 0.1 MPa and 24.7 °C.

$$\ln k = \ln k_0 - \Delta V^\ddagger P/RT \quad (1)$$

Results and Discussion

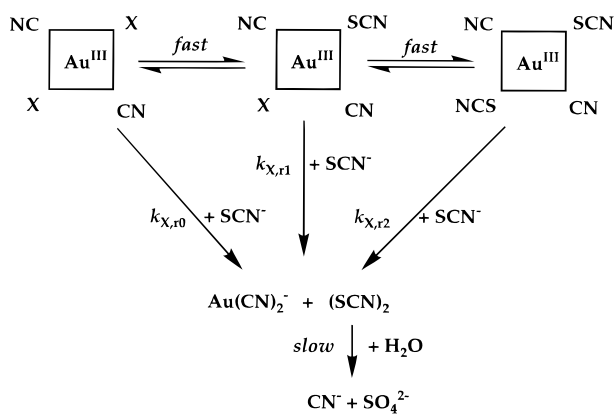
Reaction Mechanism. The stoichiometric mechanism for the reduction of $trans\text{-Au}(\text{CN})_2\text{X}_2^-$ with SCN^- is outlined in Scheme 1. The substitution reactions, which are too fast to be monitored with the stopped-flow technique, allow formation of a transient equilibrium between the complexes $trans\text{-Au}(\text{CN})_2\text{X}_{2-n}(\text{SCN})_n^-$ ($n = 0, 1, 2$) prior to the subsequent and slower redox process.

Oxidation of SCN^- in aqueous solution has previously been shown to result in formation of $(\text{SCN})_2$, which is hydrolyzed to CN^- and SO_4^{2-} in a subsequent reaction.²¹ This hydrolysis was observed to interfere with the overall process when reduction of $trans\text{-Au}(\text{NH}_3)_2\text{X}_2^+$ was studied at low concentrations of SCN^- .¹⁴ Since the dicyano complexes of gold(III) react at least 10 times faster than the diammine complexes, it is reasonable to expect that the redox process of the dicyano

(20) The OLIS 4300S Spectroscopy User's Manual; OLIS: Jefferson, GA.

(21) Söderbäck, E. *Liebigs Ann. Chem.* **1919**, 419, 217–322.

Scheme 1



complexes studied here proceeds without disturbance by the much slower hydrolysis of $(\text{SCN})_2$. The expression for the disappearance of the transient Au(III) complexes is given in eq 2. The concentration of each of the complexes *trans*-Au-

$$-d[\text{Au(III)}]_{\text{tot}}/dt = [\text{SCN}^-](k_{X,r0}[\textit{trans}\text{-Au}(\text{CN})_2\text{X}_2^-] + k_{X,r1}[\textit{trans}\text{-Au}(\text{CN})_2\text{X}(\text{SCN})^-] + k_{X,r2}[\textit{trans}\text{-Au}(\text{CN})_2(\text{SCN})_2^-]) \quad (2)$$

$(\text{CN})_2\text{X}_{2-n}(\text{SCN})_n^-$ can be related to the total concentration of gold(III) by use of overall equilibrium constants, β_n , and the ratio $Q = [\text{X}^-]/[\text{SCN}^-]$ according to eq 3 and 4, where $\beta_0 = 1$

$$[\textit{trans}\text{-Au}(\text{CN})_2\text{X}_{2-n}(\text{SCN})_n^-] = [\text{Au(III)}]_{\text{tot}}\alpha_n \quad (n = 0, 1, 2) \quad (3)$$

$$\alpha_n = \frac{\beta_n Q^{-n}}{1 + \beta_1 Q^{-1} + \beta_2 Q^{-2}} \quad (4)$$

and α_n is the mole fraction of the particular complex. The observed pseudo-first-order rate constant for excess $[\text{SCN}^-]$ is given by eq 5, which is obtained from eqs 2–4 after replacement

$$k_{\text{obsd}} = [\text{SCN}^-] \frac{k_{X,r0} + k_{X,r1}K_{X,1}Q^{-1} + k_{X,r2}K_{X,1}K_{X,2}Q^{-2}}{1 + K_{X,1}Q^{-1} + K_{X,1}K_{X,2}Q^{-2}} \quad (5)$$

$$\beta_1 = K_{X,1} \quad \beta_2 = K_{X,1}K_{X,2} \quad (6)$$

of overall stability constants by stepwise constants $K_{X,j}$ according to eq 6. The stepwise constants $K_{X,j}$ and the rate constants for the reduction, $k_{X,m}$, were derived from a least-squares fit of the second-order rate constants, $k_{\text{obsd}}/[\text{SCN}^-]$, and the values of Q to eq 5, with the separately determined rate constant for reduction of *trans*-Au(CN) $_2$ (SCN) $_2^-$, $k_{X,r2} = 310 \text{ M}^{-1} \text{ s}^{-1}$, as a fixed constant. Rate constants for reduction of *trans*-Au(CN) $_2\text{X}_2^-$ were assumed to be negligibly small in analogy with the corresponding ammine complexes.¹⁴

Reactions at Low Q . For $Q < 13$ for $\text{X} = \text{Cl}$ and $Q < 1$ for $\text{X} = \text{Br}$, addition of excess thiocyanate to *trans*-Au(CN) $_2\text{X}_2^-$ gives rise to rapid formation of a species with an absorbance maximum at 290 nm; cf. Figure 1. The rate of disappearance of this peak follows pseudo-first-order kinetics with a linear dependence on the concentration of excess thiocyanate. Furthermore, the rate is independent on which of the metal complexes ($\text{X} = \text{Cl}$ or Br) that is used as starting material; cf. Table 1. Plots of k_{obsd} as a function of C_{SCN} (data in Table 1)

Table 2. Second-Order Rate Constants for Reduction of *trans*-Au(CN) $_2$ (SCN) $_2^-$ by Thiocyanate as a Function of Temperature^a

$10^5 C_{\text{Au}}/\text{M}$	$t/^\circ\text{C}$	$k/\text{M}^{-1} \text{s}^{-1}$
2.00	2.0	40 ± 2
1.973	13.0	109 ± 11
1.973	25.0	309 ± 9
1.973	40.0	770 ± 80

^a *trans*-Au(CN) $_2\text{Br}_2^-$ used as substrate, $\lambda = 285 \text{ nm}$, $[\text{H}^+] = 2.5 \text{ mM}$.

gave the values for the second-order rate constants $k_{X,r2}$ in Table 2, i.e. the rate constant for reduction of *trans*-Au(CN) $_2$ (SCN) $_2^-$ by SCN^- that follows after the rapid initial substitutions of the two halide ligands by thiocyanate.

Activation Parameters. In Table 3, rate constants and activation parameters for reduction of *trans*-Au(NH $_3$) $_2$ (SCN) $_2^+$ and *trans*-Au(CN) $_2$ (SCN) $_2^-$ are summarized. Although the rate constants $k_{X,r2}$ are similar (220 and $310 \text{ M}^{-1} \text{ s}^{-1}$, respectively), the activation parameters differ. The ΔH^\ddagger value for the cyanide complex is significantly smaller, probably due to a decreasing electron density at the gold(III) center already in the ground state,¹ facilitating reductive elimination. Reduction of *trans*-Au(NH $_3$) $_2$ (SCN) $_2^+$ by SCN^- takes place with charge neutralization and is accompanied by positive values of ΔS^\ddagger and ΔV^\ddagger , $21 \text{ J K}^{-1} \text{ mol}^{-1}$ and $4.6 \text{ cm}^3 \text{ mol}^{-1}$, respectively. In contrast, reduction of *trans*-Au(CN) $_2$ (SCN) $_2^-$ by SCN^- results in charge formation during the activation process which gives rise to negative ΔS^\ddagger and ΔV^\ddagger , $-17.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-4.6 \text{ cm}^3 \text{ mol}^{-1}$, respectively. Apparently, the magnitudes of both ΔS^\ddagger and ΔV^\ddagger are dominated by contributions from solvation, and the switch from positive to negative sign of ΔS^\ddagger contributes to decrease the difference in reactivity between these two metal complexes. This observation fits well with an assumption of small contributions from changes in the inner coordination sphere during the activation process for the redox reaction.

The small contribution from volume changes in the first coordination sphere for reduction of *trans*-Au(NH $_3$) $_2$ (SCN) $_2^+$ with SCN^- is further indicated by a comparison with the activation parameters for the substitution reaction at the {Au(NH $_3$) $_2$ } moiety, which are also given in Table 3. As expected for an associative (I_a) substitution process,^{1,22} formation of the pentacoordinated transition state with closely bound leaving and entering ligands gives rise to a negative volume ($-4.5 \text{ cm}^3 \text{ mol}^{-1}$) and entropy ($-48 \text{ J K}^{-1} \text{ mol}^{-1}$) of activation. These negative values are obtained in spite of the charge neutralization in the activation process. This suggests a substantially more negative value of the intrinsic volume of activation for the substitution process than for the redox process, dominating over the volume changes due to solvation/electrostriction.²³

Thus, the observed entropies and volumes of activation reflect large differences in the transition states for the reductive elimination and substitution processes. The former seem to be more sensitive to solvational changes, possibly as a result of a more loosely bound transition state, not involving any large changes of the inner coordination sphere of the gold(III) center.

Reactions at High Q and Effect of Added Halide. The rate of the overall reduction of the gold(III) complexes increases with increasing halide concentration and increasing values of Q , as shown in Figure 2 (data from Supporting Information Tables S1 and S2). Addition of bromide gives rise to a shift of

(22) Cattalini, L.; Orio, A.; Tobe, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3130–3135.

(23) van Eldik, R.; Merbach, A. E. *Comments Inorg. Chem.* **1992**, *12*, 341–387.

Table 3. Rate Constants and Activation Parameters at 25.0 °C for Reactions of Gold(III) Complexes with Thiocyanate

reacn	process	$k/M^{-1} s^{-1}$	$\Delta H^\ddagger/kJ mol^{-1}$	$\Delta S^\ddagger/J K^{-1}mol^{-1}$	$\Delta V^\ddagger/cm^3 mol^{-1}$
$Au(NH_3)_2Cl_2^+ + SCN^-$	substitution ^b	$(3.3 \pm 0.2) \times 10^3$ ^a	33 ± 7^a	$-48 + 21^a$	-4.5 ± 0.5
$Au(NH_3)_2(SCN)_2^+ + SCN^-$	reduction	$(2.2 \pm 0.4) \times 10^2$ ^a	66 ± 4^a	$21 + 12^a$	4.6 ± 0.9
$Au(CN)_2(SCN)_2^- + SCN^-$	reduction	$(3.1 \pm 0.1) \times 10^2$	55 ± 3	-17.8 ± 0.8	-4.6 ± 0.5

^a Reference 14. ^b Refers to substitution of the first of the two chloride ligands for thiocyanate.

the absorbance maximum for the transient gold(III) species to shorter wavelengths, whereas addition of chloride has no such influence; see Figure 1. These features make a direct outer-sphere redox reaction similar to those observed for thiocyanate reduction of complexes of Ni(III)²⁴ and Ag(III)²⁵ unlikely. The spectral and kinetics data observed when the concentration of bromide is increased can be assigned to a change of the equilibrium distribution between the short-lived, intermediate complexes *trans*-Au(CN)₂Br(SCN)⁻ and *trans*-Au(CN)₂(SCN)₂⁻ prior to reduction. The observed pseudo-first-order overall rate constant for the reduction is a linear function of the concentration of excess thiocyanate for constant distribution between the complexes *trans*-Au(CN)₂X_{2-n}(SCN)_n⁻, *i.e.* for a fixed value of Q (data in Table S2). This fact indicates that the reduction takes place as an intermolecular process, involving attack at the complexes by outersphere thiocyanate.

The variation of the overall second-order rate constants as a function of Q was used to calculate the second-order rate constant for reduction of *trans*-Au(CN)₂X(SCN)⁻ and to estimate values for the relative stability constants $K_{X,2}$ by use of eqs 5 and 6. Systematic deviations between experimental and fitted data were observed for $K_{Br,1}/K_{Br,2} \geq 100$, and this ratio was used to estimate an upper limit of $K_{Br,1}$ (Figure S1). A least-squares fit of the experimental data to eqs 5 and 6 combined with a variation of the ratio $K_{Br,1}/K_{Br,2}$ in the interval 4–100 gave $k_{Br,r1} = (3.1 \pm 0.7) \times 10^3 M^{-1} s^{-1}$ and $K_{Br,2} = (1.1 \pm 0.4) \times 10^2$ (Table S7). $K_{Br,1}$ was estimated to $500 < K_{Br,1} < 10\,000$, with the lower limit determined by the ratio obtained for exchange of Br⁻ for SCN⁻ on diamminegold(III) complexes.¹⁴ A similar treatment of the data for the reaction of *trans*-Au(CN)₂Cl₂⁻ with SCN⁻ was also performed (Table S7). The absence of a maximum for the reduction rate in this case makes an estimation of the upper limit of $K_{Cl,1}$ impossible. A variation of the ratio $K_{Cl,1}/K_{Cl,2}$ in the interval 4–10 000 gave $k_{Cl,r1} = (6.9 \pm 1.1) \times 10^4 M^{-1} s^{-1}$ and $K_{Cl,2} = (3.8 \pm 0.8) \times 10^4$, indicating that displacement of the equilibrium between *trans*-Au(CN)₂Cl(SCN)⁻ and *trans*-Au(CN)₂(SCN)₂⁻ alone accounts for the observed variations in rate.

Plots of second-order rate constants, k_{obsd}/C_{SCN} , are given as a function of $-\log Q$ in Figure 2a,c. The solid lines correspond to a fit of the experimental data to eq 5. Figure 2b,d shows the distribution between the complexes *trans*-Au(CN)₂X_{2-n}(SCN)_n⁻ as a function of $-\log Q$. Common features for the reactivity of the two metal substrates include (i) a similar second-order rate constant for reduction at small Q values, k_{red} ca. $300 M^{-1} s^{-1}$, corresponding to reduction of *trans*-Au(CN)₂(SCN)₂⁻, and (ii) a sharp increase of the rate of reduction after addition of halide. A steadily increasing rate constant is observed after addition of chloride (Figure 2a), which is in contrast to the indication of a maximum of $k_{red} \approx 2000 M^{-1} s^{-1}$ for $Q \geq 150$ in the case of bromide (Figure 2c). The highest rate constant observed after addition of chloride exceeds the maximum value for the bromide complexes by almost 2 orders of magnitude in spite of the much smaller percentage of the mixed complex *trans*-Au(CN)₂Cl(SCN)⁻ present in solution.

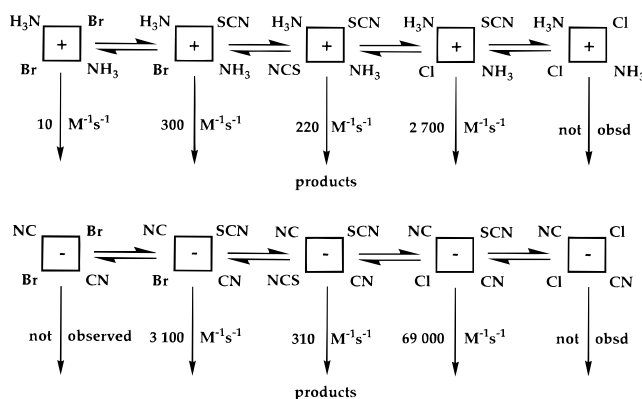
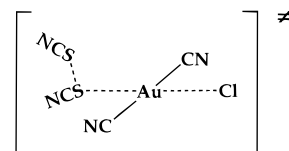


Figure 4. Second-order rate constants for reduction of gold(III) ammine and cyano complexes by thiocyanate. Data for ammine complexes are from ref 14. Products are gold(I) complexes, sulfate, and cyanide.

A summary of the derived second-order reduction rate constants is given in Figure 4 together with a comparison with the values for the corresponding ammine complexes. The relative increase of the rate observed for the complexes with an asymmetric *trans* axis X–Au–SCN is at least 1 order of magnitude larger for the cyano than for the ammine complexes.¹⁴ The effect is most pronounced for complexes containing ligands with a large difference in their ground-state *trans* influence, *viz.* Cl⁻ and SCN⁻. The more rapid rate of reduction observed for the chloride complexes (in spite of bromide being a better bridging ligand for electron transfer than chloride) is thus a strong indication that reductive elimination takes place through a transition state of the type shown involving development of an S–S interaction, possibly also comprising the metal center:



Halide-bridged electron transfer can be of only minor importance for complexes containing coordinated thiocyanate. Thus, the experimental observations based on the present systems give further support to the tentative mechanism suggested earlier.¹⁴

Stability vs Rate Constants. The kinetic method used allows an estimation of the stability constants for the short-lived gold(III) complexes present as transient intermediates for a few tenths of a second during the initial stages of the overall process. A summary of the stability constants used in the fitting procedures is given in Table 4. As expected, the change from ammine to cyano ligands increases the softness/discriminating power of the metal center. Thus, K_2 for exchange of chloride for bromide is 4 times larger for the {Au(CN)₂} moiety than for the {Au(NH₃)₂} moiety,^{16,26} ca. 10 times larger for exchange of bromide for thiocyanate, and almost 2 orders of magnitude larger for exchange of chloride for thiocyanate. The derived redox rate constants summarized in Figure 4 decrease in the order *trans*-Au(CN)₂Cl(SCN)⁻ > *trans*-Au(CN)₂Br(SCN)⁻ >

(24) Hung, M.-L.; Stanbury, D. M. *Inorg. Chem.* **1994**, *33*, 4062–4069.

(25) Kirschenbaum, L. J.; Sun, Y. *Inorg. Chem.* **1991**, *30*, 2360–2365.

(26) Kaas, K.; Skibsted, L. H. *Acta Chem. Scand.* **1985**, *A39*, 1–14.

Table 4. Relative Stepwise and Overall Stability Constants for Formation of Gold(III) Complexes with Thiocyanate at 25 °C

reacn	$K_{X,1}$	$K_{X,2}$	β_2	$K_{X,1}/K_{X,2}$	ref
<i>trans</i> -Au(NH ₃) ₂ Cl ₂ /Br ₂ ⁺	122 ± 2 ^a	29.9 ± 0.5 ^a	(3.65 ± 0.12) × 10 ³	4	25
<i>trans</i> -Au(NH ₃) ₂ Cl ₂ /(SCN) ₂ ⁺	(1.5 ± 0.5) × 10 ⁴ ^b	(4.6 ± 0.5) × 10 ² ^b	(6.9 ± 3) × 10 ⁶	33	14
<i>trans</i> -Au(NH ₃) ₂ Br ₂ /(SCN) ₂ ⁺	67 ± 12 ^a	12 ± 3 ^a	(8.0 ± 4) × 10 ²	6	14
<i>trans</i> -Au(CN) ₂ Cl ₂ /Br ₂ ⁻	1.1 × 10 ³ ^c	1.2 × 10 ² ^c	1.3 × 10 ⁵	9	16
<i>trans</i> -Au(CN) ₂ Cl ₂ /(SCN) ₂ ⁻		(3.8 ± 0.8) × 10 ⁴ ^d			this work
<i>trans</i> -Au(CN) ₂ Br ₂ /(SCN) ₂ ⁻		(1.1 ± 0.4) × 10 ² ^d			this work

^a $K_n = k_n/k_{-n}$. ^b Calculated from thermodynamic data. ^c Equilibrium measurements. ^d Calculated from redox data, eq 5.

trans-Au(CN)₂(SCN)₂⁻, which is similar to the trend obtained for the {Au(NH₃)₂} moiety. This is in agreement with an earlier assumption that a decreasing ground-state stability of the gold(III) complexes increases the rate of the redox reaction.¹⁴ It is obvious from a comparison between the redox rate constants for complexes with an identical labile *trans*-axis that the ground-state stability of the complex is not the only factor influencing the observed reactivity, however. For example, the similar reactivity of *trans*-Au(CN)₂(SCN)₂⁻ and *trans*-Au(NH₃)₂(SCN)₂⁺ is due to solvational effects, as discussed above. Further, the much higher reactivity of the *trans*-Au(CN)₂X(SCN)⁻ complexes compared to the corresponding less stable complexes *trans*-Au(NH₃)₂X(SCN)⁺ suggests that redox reactivity is not only a ground-state effect but is also strongly influenced by the energy required for orbital rearrangement during the activation process.

Conclusion. Introduction of cyano ligands instead of amines increases the soft and discriminating character of the gold(III) center. Substitution as well as redox processes with S-donor nucleophiles like thiocyanate are faster compared to complexes containing σ -donor ammine ligands. The overall reaction mechanism, substitution followed by reduction, remains unchanged, however. The observed entropies and volumes of activation depend on large contributions from solvational changes when formation of the transition state involves charge

neutralization or formation. Still, they seem to reflect the mechanistic differences between the substitution and reductive elimination reactions in these systems quite well.

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Supporting Information Available: Observed first-order rate constants for reduction of *trans*-Au(CN)₂X_{2-n}(SCN)_n⁻ (X = Cl, Br) as a function of Q (Tables S1 and S2), observed first-order rate constants for reduction of *trans*-Au(CN)₂(SCN)₂⁻ as a function of pressure (Table S3), observed first-order rate constants for reaction of *trans*-Au(NH₃)₂-Cl₂⁺ with SCN⁻ as a function of pressure (Table S4), observed first-order rate constants for reduction of *trans*-Au(NH₃)₂(SCN)₂⁺ with SCN⁻ as a function of pressure (Table S5), a summary of second-order rate constants given in Figure 4 (Table S6), examples of stability and redox rate constants obtained from redox data (Table S7), and examples of fits of experimental data to eq 5 illustrating the effect of a variation of the ratio $K_{X,1}/K_{X,2}$ (Figure S1) (6 pages). Ordering information is given on any current masthead page.

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