crease in the AuCl stretching force constant on the frequency.

With the dimeric halides, a broad band was observed at *ca.* 150 cm^{-1}. By analogy with Au_2Cl_6, it might be expected that out-of-plane bending vibrations would occur in this region. Because of the uncertainty of the assignment of the low-frequency modes and complications arising out of the redundancies in the angles about gold and in the bridge, no further analysis of the low-frequency data was attempted.

In contrast to the isoelectronic dimethylplatinum(II) moiety the dimethylgold(III) group can be stabilized with a very wide range of ligands. In general the trends in the metal–carbon and metal–X bond strengths are the same as observed for methylmercury(II) compounds.[34]

The thiocyanate $[(CH_3)_2Au(NCS)]_2$ is particularly unreactive, and this must be associated with the di-μ-thiocyanato-*N,S* bridge. Foss and Gibson[35] found that these diorganogold(III) thiocyanates were not attacked by nitrogen bases, *e.g.*, ethylenediamine, which cleaves the chloride, bromide, and iodide.[36] Sulfur-containing ligands, here thiourea by reaction 2, will break the thiocyanate bridges and give complexes where

$$[(CH_3)_2Au(SCN)]_{2(\text{hexane})} + 2SC(NH_2)_{2(\text{aq})} \longrightarrow 2(CH_3)_2Au(SCN)(SC(NH_2)_2)(\text{s}) \qquad (2)$$

both ligands are bound by sulfur. The product of reaction 2 is insoluble in water and most organic solvents, but the low melting point, 83°, is in accord with a molecular compound.

The di-μ-thiocyanato-*N,S* structure would be expected to be quite stable with the heavy d^8 transition metals. A bridge with 90° angles at the metal, 180° for M–N–C, and 90° for C–S–M should be unstrained. In addition to the gold(III) and platinum(II) complexes discussed here, it is very likely that the binuclear rhodium(I) complex $[Rh\{(p\text{-}C_6H_4CH_3O)_3P\}_2(SCN)]_2$ has a similar bridge. This compound was first reported by Vallarino,[37] who suggested bridging by the sulfur atoms alone. The reported infrared spectrum has a band at 2150 cm^{-1} consistent with the Au(III) and Pt(II) compounds.

Although the chemistries of $(CH_3)_2Au^{III}$ and $(CH_3)_2Ga^{III}$ are similar in a number of ways,[38] Dehnicke has found that dimethylgallium thiocyanate is a trimer and has assigned a structure with only sulfur bridging on the basis of the infrared spectrum.[39] This structure is not surprising, since bridging *via* both the nitrogen and sulfur ends of the thiocyanates would produce considerable strain with a tetrahedrally coordinated representative element.

The very low intensity of the Au–C stretching and C–Au–C bending vibrations in the infrared spectra of all of these compounds suggests that the Au–C bond moments are very small. This is consistent with the inertness of these bonds to attack by both electrophiles and nucleophiles.

Acknowledgment.—W. M. S. wishes to acknowledge the assistance provided by E. I. du Pont de Nemours and Co. in the form of summer research support.

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[35] M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 3074 (1949).

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[37] L. Vallarino, *J. Chem. Soc.*, 2473 (1957).

[38] Compare, for example, the behavior in aqueous solution given by ref 6 and L. Pellerito and R. S. Tobias, *Inorg. Chem.*, **9**, 953 (1970).

[39] K. Dehnicke, *Angew. Chem.*, **79**, 942 (1967).

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The Interconversion of the *trans*-Dibromo- and *trans*-Dichlorodicyanoaurate(III) Anions[1]

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The replacement of the two bromide ligands in *trans*-$Au(CN)_2Br_2^-$ by chloride has been characterized as a stepwise process involving the intermediate *trans*-$Au(CN)_2ClBr^-$ complex. The kinetics of the first and second bromide replacements were studied by stopped-flow spectrophotometry, and both are found to obey two-term rate laws containing first- and second-order terms. Rate constants at 25° and $\mu = 0.51$ *M* for the first replacement are $k_1 = 2.1$ sec^{-1} and $k_2 = 1670$ M^{-1} sec^{-1}, while those for the second are $k_1 = 2.3$ sec^{-1} and $k_2 = 143$ M^{-1} sec^{-1}. Equilibrium measurements are reported and the synthesis of *trans*-$Au(CN)_2ClBr^-$ is described.

Introduction

Ligand replacement reactions of square-planar gold(III) complexes are generally rapid in aqueous solution—considerably more so than those of isostructural and isoelectronic platinum(II) complexes.[2] This feature has been one of the chief deterrents to their systematic investigation. Even though a number of replacement reactions of gold(III) have been studied in

[1] Presented at the Fourth Great Lakes Regional Meeting of the American Chemical Society, Fargo, N. D., 1970.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 410–414.

nonaqueous solvents where rates are slow enough to be measured by conventional techniques,[3] very few data are available from aqueous solution.[4–6] The bulk of kinetic data for platinum(II) reactions, however, is from aqueous studies, and direct comparisons with the features of gold(III) are limited. The mechanistic behavior of gold(III) compared to platinum(II) is of interest because the higher charge on the metal is expected to favor a bond-making mode of activation to a greater extent. Data on a variety of gold(III) systems thus would be useful in exploring some of the details of the square-planar substitution process.

In an effort to provide kinetic data for several rapid replacement reactions of gold(III) complexes in aqueous solutions, stopped-flow spectrophotometric measurements have been employed, since many gold(III) complexes have characteristic ultraviolet and visible spectra. The present paper describes the kinetics of the first and second bromide replacements in *trans*-$Au(CN)_2Br_2^-$ by chloride, the forward reactions of eq 1 and 2. Equilibrium measurements were also made for these reactions, and the synthesis of the intermediate

$$trans\text{-}Au(CN)_2Br_2^- + Cl^- \rightleftharpoons trans\text{-}Au(CN)_2ClBr^- + Br^- \quad (1)$$

$$trans\text{-}Au(CN)_2ClBr^- + Cl^- \rightleftharpoons trans\text{-}Au(CN)_2Cl_2^- + Br^- \quad (2)$$

trans-$Au(CN)_2ClBr^-$ complex is described in the Experimental Section.

Experimental Section

Preparation of Compounds.—The starting material for the preparation of the gold complexes was potassium dicyanoaurate(I), $K[Au(CN)_2]$, which was prepared by the literature method.[7] All other chemicals were reagent grade. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Tetramethylammonium *trans*-Dibromodicyanoaurate(III), $[(CH_3)_4N][Au(CN)_2Br_2]$.[8]—Solid $K[Au(CN)_2]$ was dissolved in a minimum amount of water and treated with a large excess of bromine. Nitrogen was then bubbled through the solution to expel the unreacted bromine. A concentrated aqueous solution of $(CH_3)_4NBr$ was then added at ice-bath temperature, whereupon the golden yellow product precipitated immediately. The product was collected by filtration, washed with a small amount of ice water and ether, and finally dried under reduced pressure at room temperature. Yields were typically 90–92%. *Anal.* Calcd for $[(CH_3)_4N][Au(CN)_2Br_2]$: Au, 40.78; C, 14.92; H, 2.50; N, 8.70; Br, 33.09. Found: Au, 40.80, 40.60; C, 14.99; H, 2.45; N, 8.85; Br, 32.89.

Tetramethylammonium *trans*-Dichlorodicyanoaurate(III), $[(CH_3)_4N][Au(CN)_2Cl_2]$.[8]—This complex was prepared in a similar manner except that chlorine was bubbled through the $K[Au(CN)_2]$ solution for 2–3 min. A small amount of yellowish insoluble material was formed initially, and this was removed before a concentrated aqueous solution of $(CH_3)_4NCl$ was added at ice-bath temperature. The colorless product was washed with ice water and ether and dried under reduced pressure. *Anal.* Calcd for $[(CH_3)_4N][Au(CN)_2Cl_2]$: Au, 49.98; C, 19.29; H, 3.07; N, 10.66; Cl, 17.99. Found: Au, 49.70; C, 19.31; H, 3.19; N, 10.72; Cl, 18.16.

Tetramethylammonium *trans*-Chlorobromodicyanoaurate(III), $[(CH_3)_4N][Au(CN)_2ClBr]$.—Equimolar amounts of $[(CH_3)_4N][Au(CN)_2Br_2]$ and $[(CH_3)_4N][Au(CN)_2Cl_2]$ were dissolved together in a minimum of water at 80–90°. When all the solids were dissolved, the solution was cooled to ice-bath temperature whereupon a lemon yellow product crystallized. The product was collected, washed, and dried as before. The yield was 85% of theory. *Anal.* Calcd for $[(CH_3)_4N][Au(CN)_2ClBr]$: Au, 44.92; C, 16.43; H, 2.76; N, 9.58; Cl, 8.08; Br, 18.22. Found: Au, 44.72; C, 16.41; H, 2.65; N, 9.49; Cl, 8.23; Br, 18.03.

Spectral Measurements.—Before rate or equilibrium measurements were made, the visible and ultraviolet spectra of the gold complexes were measured using a Cary Model 1501 spectrophotometer. Solutions were prepared with dilute (0.01 *M*) $HClO_4$. No substantial changes in the spectra were noted as a function of time for periods up to about 1 hr. Isosbestic points for *trans*-$Au(CN)_2Br_2^-$ and *trans*-$Au(CN)_2ClBr^-$ and for *trans*-$Au(CN)_2Cl_2^-$ and *trans*-$Au(CN)_2ClBr^-$ were noted at 42,800 cm^{-1} (234 nm) and 45,200 cm^{-1} (221 nm), respectively. The products of reactions 1 and 2 were identified by recording the spectra of reaction mixtures and comparing with spectra of the pure complex.

Kinetic Measurements.—The kinetics of the bromide replacement reactions were studied spectrophotometrically using a Durrum–Gibson stopped-flow spectrophotometer equipped with thermostated drive syringes and mixing chamber. The temperature was controlled to within ±0.1°. Transmittance changes at a selected wavelength during the course of the reaction were displayed on a storage oscilloscope, and traces were photographed with a Polaroid camera. Duplicate experiments gave oscilloscope traces that were virtually indistinguishable. The ionic strength of the reaction mixtures was controlled at 0.51 *M* with $NaClO_4$, and all experiments were run under conditions of large excess of NaCl. Under these circumstances the kinetics are pseudo first order in gold complex, and the reactions go substantially to completion. The first bromide replacement was followed at 221 nm which corresponds to the isosbestic point for *trans*-$Au(CN)_2ClBr^-$ and *trans*-$Au(CN)_2Cl_2^-$. At this wavelength the changes in transmittance are due entirely to the first bromide replacement since the product of the first replacement has the same absorptivity as the product of the second. Similarly, the second replacement was followed at 234 nm which is the isosbestic point for *trans*-$Au(CN)_2Br_2^-$ and *trans*-$Au(CN)_2ClBr^-$. Here only the formation of *trans*-$Au(CN)_2Cl_2^-$ gives rise to a change in absorptivity.

Rate data were evaluated by means of a Gauss–Newton fit to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t)$.[9] Twenty data points spaced over 2–5 half-lives were used for each kinetic run. The standard deviations in computed values of k_{obsd} were 0.5–1.5% in almost all cases. Separate kinetic experiments generally could be reproduced to within ±5%, and rate constants reported here in many cases represent averages of several separate experiments. Rate constants for reactions 1 and 2 were evaluated by constructing least-squares plots of k_{obsd} *vs.* $[Cl^-]$. These plots were linear, and the slope corresponds to the second-order constant k_2, while the intercept corresponds to the first-order constant k_1. Values of k_2 were generally self-consistent to ±10%; the values of k_1 were less precise.

Equilibrium Measurements.—Equilibrium measurements for reactions 1 and 2 were made spectrophotometrically at 241 and 235 nm, respectively. Reaction mixtures containing *trans*-$Au(CN)_2Br_2^-$ or *trans*-$Au(CN)_2Cl_2^-$ and Br^- and Cl^- were thermostated at 25.0°, and the absorbance was determined *vs.* a blank containing only Br^- and Cl^-. The equilibrium constant

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[3] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966); L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, **5**, 1674 (1966); L. Cattalini, A. Orio, and M. L. Tobe, *ibid.*, **6**, 75 (1967); L. Cattalini, A. Orio, and M. L. Tobe, *J. Amer. Chem. Soc.*, **89**, 3130 (1967).

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[7] O. Glemser and H. Sauer, "Handbook of Preparative Inorganic Chemistry," Vol. II, G. Brauer, Ed, 2nd ed, Academic Press, New York, N. Y., 1965, p 1065.

[8] "Gmelins Handbuch der Anorganishen Chemie," Vol. 62, 8th ed, Verlag Chemie, Weinheim/Bergstrasse, Germany, 1954, p 745.

[9] The author is indebted to Dr. Ronald C. Johnson for the computer program used in calculating the rate constants.

for reaction 1 was evaluated from eq 3, where [Au(III)] is the

$$K_1 = \{[\mathrm{Au(III)}]\epsilon_{\mathrm{Br_2}} - A\}[\mathrm{Br^-}]/\{A - [\mathrm{Au(III)}]\epsilon_{\mathrm{ClBr}}\}[\mathrm{Cl^-}] \quad (3)$$

total gold(III) concentration, $\epsilon_{\mathrm{Br_2}}$ is the molar absorptivity of *trans*-$\mathrm{Au(CN)_2Br_2^-}$ at 241 nm (=34,000 M^{-1} cm^{-1}), A is the measured absorbance at 241 nm, ϵ_{ClBr} is the molar absorptivity of *trans*-$\mathrm{Au(CN)_2ClBr^-}$ at 241 nm (=17,700 M^{-1} cm^{-1}), and [Cl$^-$] and [Br$^-$] are the uncomplexed halide concentrations. Equation 3 is valid only for 1.00-cm cells. The equilibrium constant for reaction 2 was evaluated from eq 4. In this equation A is the measured absorbance at 235 nm, $[\mathrm{Br^-}]_0$ is the

$$K_2 = \frac{\{A - [\mathrm{Au(III)}]\epsilon_{\mathrm{ClBr}}\}\{[\mathrm{Br^-}]_0 D + [\mathrm{Au(III)}]\epsilon_{\mathrm{Cl_2}} - A\}}{D\{[\mathrm{Au(III)}]\epsilon_{\mathrm{Cl_2}} - A\}[\mathrm{Cl^-}]} \quad (4)$$

concentration of added NaBr, ϵ_{ClBr} is the molar absorptivity of *trans*-$\mathrm{Au(CN)_2ClBr^-}$ at 235 nm (=20,300 M^{-1} cm^{-1}), $\epsilon_{\mathrm{Cl_2}}$ is the molar absorptivity of *trans*-$\mathrm{Au(CN)_2Cl_2^-}$ at 235 nm (=4900 M^{-1} cm^{-1}), and $D = \epsilon_{\mathrm{ClBr}} - \epsilon_{\mathrm{Cl_2}} = 15{,}400\ M^{-1}$ cm^{-1}. The other symbols have the same meaning as in eq 3. Equation 4 is also valid only for 1.00-cm cells. The derivation of both eq 3 and 4 is tedious but straightforward. In both cases only a single reactant and product complex is assumed to be present at equilibrium. This assumption is supported by measurements of the spectra of several reaction mixtures for each reaction. Isosbestic points were observed at 222 and 234 nm, respectively, for reactions 1 and 2. The molar absorptivities in eq 3 and 4 were taken from experimental spectra. The values of K_1 were self-consistent to ±12%, while those for K_2 were self-consistent to ±3%.

Results

The electronic spectra of *trans*-$\mathrm{Au(CN)_2Br_2^-}$, *trans*-$\mathrm{Au(CN)_2ClBr^-}$, and *trans*-$\mathrm{Au(CN)_2Cl_2^-}$ are presented in Figure 1. The small circles denote the isosbestic points used in gathering the rate data. The points were also within experimental error of isosbestics observed in the equilibrium measurements.

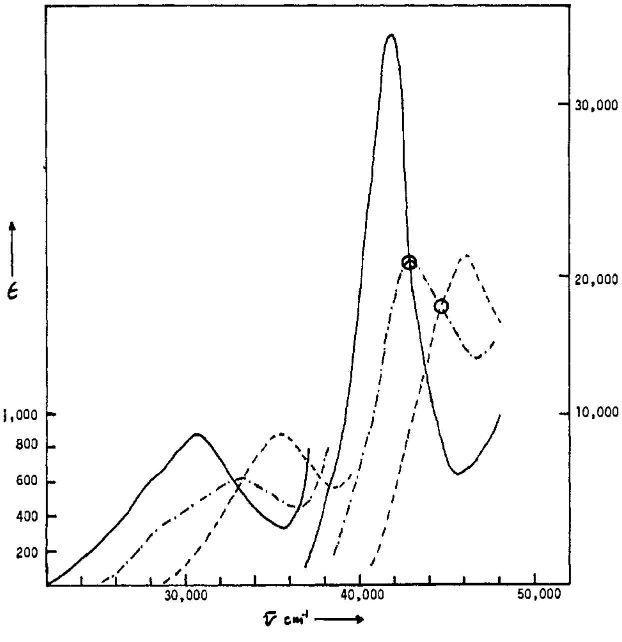

Figure 1.—Electronic spectra of the gold(III) complexes in 0.010 M $\mathrm{HClO_4}$: ——, $[\mathrm{(CH_3)_4N}][\mathrm{Au(CN)_2Br_2}]$; –·–·–, $[\mathrm{(CH_3)_4N}][\mathrm{Au(CN)_2ClBr}]$; – – – –, $[\mathrm{(CH_3)_4N}][\mathrm{Au(CN)_2Cl_2}]$.

Table I

Rate Data

trans-$\mathrm{Au(CN)_2Br_2^-}$ + $\mathrm{Cl^-}$ ⟶ *trans*-$\mathrm{Au(CN)_2ClBr^-}$ + $\mathrm{Br^-}$

[NaCl], M	$10^{-1}k_{\mathrm{obsd}}$, sec^{-1}	$10^{-3}k_2$, M^{-1} sec^{-1}	[NaCl], M	$10^{-1}k_{\mathrm{obsd}}$, sec^{-1}	$10^{-3}k_2$, M^{-1} sec^{-1}
	25.0°^{a,b}			30.0°^{a,g}	
0.125	21.2	1.68	0.040	9.45	2.22
0.050	8.23	1.61	0.020	4.71	2.08
0.020	3.57	1.68	0.010	2.92	2.37
0.010	2.06	1.85			
0.125	19.7^c	1.56		35.0°^{a,h}	
0.010	1.81^d	1.61	0.040	12.0	2.87
0.020	3.47^e	1.63	0.020	6.17	2.80
0.020	3.72^f	1.76	0.010	3.51	2.93

trans-$\mathrm{Au(CN)_2ClBr^-}$ + $\mathrm{Cl^-}$ ⟶ *trans*-$\mathrm{Au(CN)_2Cl_2^-}$ + $\mathrm{Br^-}$

[NaCl], M	$10^{-1}k_{\mathrm{obsd}}$, sec^{-1}	$10^{-2}k_2$, M^{-1} sec^{-1}	[NaCl], M	$10^{-1}k_{\mathrm{obsd}}$, sec^{-1}	$10^{-2}k_2$, M^{-1} sec^{-1}
	25.0°^{a,i}			30.0°^{a,n}	
0.500	7.41	1.44	0.250	5.39	2.05
0.250	3.83	1.44	0.125	2.59	1.85
0.125	1.93	1.36	0.050	1.41	2.27
0.050	1.02	1.58			
0.125	1.91^j	1.34		35.0°^{a,o}	
0.250	3.89^e	1.46	0.250	7.17	2.70
0.125	1.97^c	1.39	0.125	3.63	2.57
0.125	2.20^k	1.57	0.050	1.84	2.85
0.125	1.99^l	1.41			
0.125	2.03^f	1.43			
0.125	2.36^m	1.70			

[a] $[\mathrm{Au(CN)_2Br_2^-}] = 2.4 \times 10^{-5}\ M$, $[\mathrm{HClO_4}] = 0.0100\ M$, $\mu = 0.51\ M$. [b] $k_1 = 2.07$ sec^{-1}. [c] $[\mathrm{Au(CN)_2Br_2^-}] = 1.2 \times 10^{-5}\ M$. [d] $\mu = 0.20\ M$. [e] $[\mathrm{HClO_4}] = 0.030\ M$. [f] $[\mathrm{Au(CN)_2^-}] = 1.06 \times 10^{-4}\ M$. [g] $k_1 = 5.5$ sec^{-1}. [h] $k_1 = 5.7$ sec^{-1}. [i] $k_1 = 2.3$ sec^{-1}. [j] $\mu = 0.135\ M$. [k] $[\mathrm{Au(CN)_2Br_2^-}] = 3.5 \times 10^{-5}\ M$. [l] $[\mathrm{Au(III)}] = [\mathrm{Au(CN)_2ClBr^-}] = 2.4 \times 10^{-5}\ M$. [m] $[\mathrm{Fe^{2+}}] = 1.04 \times 10^{-5}\ M$. [n] $k_1 = 2.7$ sec^{-1}. [o] $k_1 = 4.2$ sec^{-1}.

Rate constants for the forward reactions 1 and 2 are given in Table I. The data for both reactions are consistent with a two-term rate law, eq 5, typical of square-planar substitution. The value of k_1 was found to be

$$\mathrm{d}[\mathrm{Au(III)}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{Cl^-}]\}[\mathrm{Au(III)}] \quad (5)$$

2.1 and 2.3 sec^{-1} for reactions 1 and 2, respectively, at 25° and $\mu = 0.51\ M$. Under the reaction conditions used in this study, the first-order path never contributed more than 20%—and usually 10% or less—to the overall rate. The rates of both reactions were essentially independent of [H$^+$] and ionic strength over the limited range studied. The rates were also essentially independent of the presence of $\mathrm{Au(CN)_2^-}$ and $\mathrm{Fe^{2+}}$ suggesting that catalytic reaction paths are not important for these reactions.

The temperature dependence of the rates permits calculation of activation parameters for the k_2 reaction path for both bromide replacements. Values of ΔH^* and ΔS^*, along with rate constants at 25°, are summarized in Table II. The values of k_1 were not suffi-

Table II

Rate Constants at 25° and μ = 0.51 M and Activation Parameters

Rate constant	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
trans-$\mathrm{Au(CN)_2Br_2^-}$ + $\mathrm{Cl^-}$ ⟶ *trans*-$\mathrm{Au(CN)_2ClBr^-}$ + $\mathrm{Br^-}$		
$k_2 = 1670\ M^{-1}$ sec^{-1}	9.2 ± 0.1	−13 ± 1
$k_1 = 2.1$ sec^{-1}	17^a	−2^a
trans-$\mathrm{Au(CN)_2ClBr^-}$ + $\mathrm{Cl^-}$ ⟶ *trans*-$\mathrm{Au(CN)_2Cl_2^-}$ + $\mathrm{Br^-}$		
$k_2 = 143\ M^{-1}$ sec^{-1}	10.8 ± 0.8	−12 ± 3
$k_1 = 2.3$ sec^{-1}	10^a	−22^a

[a] Estimated—values not precise.

ciently precise to obtain reliable values of ΔH^* and ΔS^* but estimates are also included in Table II.

Equilibrium constants for reactions 1 and 2 at 25° and $\mu = 0.51\ M$ are given in Table III.

Table III

Equilibrium Constants at 25°

$$K_1 = \frac{[trans\text{-Au(CN)}_2\text{ClBr}^-][\text{Br}^-]}{[trans\text{-Au(CN)}_2\text{Br}_2^-][\text{Cl}^-]}$$

[NaCl], M	10^2[NaBr], M	A(241 nm)	10^3K_1[a]
0.50	2.00	0.891	7.7
0.50	1.50	0.865	8.3
0.50	1.00	0.825	8.7
0.25	1.00	0.897	7.0
0.25	0.50	0.826	8.6

$$K_2 = \frac{[trans\text{-Au(CN)}_2\text{Cl}_2^-][\text{Br}^-]}{[trans\text{-Au(CN)}_2\text{ClBr}^-][\text{Cl}^-]}$$

[NaCl], M	$10^4[\text{NaBr}]_0$, M	A(235 nm)	10^4K_2[b]
0.50	1.25	0.335	9.3
0.50	2.50	0.422	9.4
0.25	2.50	0.530	9.1
0.25	1.25	0.416	9.3

[a] [Au(III)] $= 2.84 \times 10^{-5}\ M$, [HClO$_4$] $= 0.0100\ M$, $\mu = 0.51\ M$. [b] [Au(III)] $= 4.20 \times 10^{-5}\ M$, [HClO$_4$] $= 0.0100\ M$, $\mu = 0.51\ M$.

Discussion

The trans structure of the $\text{Au(CN)}_2\text{Br}_2^-$ and $\text{Au(CN)}_2\text{Cl}_2^-$ complexes has been inferred from infrared studies.[10] The structure of the $\text{Au(CN)}_2\text{ClBr}^-$ complex prepared in this study is presumed trans since its electronic spectrum is quite similar to the spectra of the $\text{Au(CN)}_2\text{Br}_2^-$ and $\text{Au(CN)}_2\text{Cl}_2^-$ complexes.

The spectrophotometric changes observed both in the equilibrium measurements and in the kinetic measurements and the existence of isosbestic points in these measurements which agree favorably with those determined from experimental spectra are consistent with the stepwise replacement of Br^- in *trans*-$\text{Au(CN)}_2\text{Br}_2^-$ by Cl^-. The kinetic behavior exhibited by the two replacements is described by a rate law that is common for many square-planar substitutions. Thus an associative type of mechanism may be presumed with the k_2 path involving the entering chloride and k_1 path involving solvent participation. The rate of the first replacement is faster than the second. This may be ascribed to the differences in "trans effect" of a Br^- *vs.* a Cl^- ligand, since the entering, leaving, and cis ligands are the same for the forward reactions 1 and 2. The relative rates at 25° and $\mu = 0.51$, corrected for the statistical advantage of the two replaceable bromides in reaction 1 compared to the single one in reaction 2, are Br > Cl: 5.8:1. The same order has been observed[11] for chloride replacement by pyridine in *cis*-$\text{Pt(NH}_3)\text{XCl}_2^-$ (X = Br, Cl) where relative rates were 3:1.

Previous studies of replacement reactions of anionic gold(III) complexes in aqueous media have been limited as has been noted. However, the present results may be compared in a qualitative way with data reported for the radiochloride exchange of AuCl_4^-, eq 6. Rate

$$\text{AuCl}_4^- + {}^*\text{Cl}^- \longrightarrow \text{Au}^*\text{Cl}_4^- + \text{Cl}^- \qquad (6)$$

constants (ΔH^*, ΔS^*) for this reaction at 20° have been reported[4,6] as $k_1 = 6 \times 10^{-3}\ \text{sec}^{-1}$ (15 kcal mol^{-1}, -16 cal deg^{-1} mol^{-1}) and $k_2 = 1.47\ M^{-1}\ \text{sec}^{-1}$ (16.5 kcal mol^{-1}, -2 cal deg^{-1} mol^{-1}). It is apparent that the bromide replacements of eq 1 and 2 are faster than the exchange of eq 6 by both the k_1 and the k_2 paths. A comparison of reactions 2 and 6 for the k_2 path (entering ligands and trans ligands are Cl^- for both reactions) reveals that the difference in rates is due primarily to the lower activation enthalpy for the bromide replacement; the activation entropy is actually more unfavorable. Differences in the reactivity of a chloride compared to a bromide leaving ligand are known to be small for platinum(II) complexes.[12] Thus it is plausible to ascribe a large part of the reactivity difference between reactions 2 and 6 to the presence of the cis cyano ligands in reaction 2. Both chloride and cyano ligands are good σ donors, but the π-acceptor ability of CN^- permits delocalization of electronic charge away from the metal. Consequently it is likely that the gold has a higher positive charge in the cyano complexes than in AuCl_4^-, and the reactivity differences can be rationalized in terms of greater bond making (charge neutralization) in the cyano complexes, resulting in a more stable activated complex. Consistent with this point of view is the less positive activation enthalpy and more negative activation entropy for reaction 2 than for reaction 6, although differences in solvation could be partly responsible for such changes.

The equilibrium data (Table III) indicate a strong preference of Au(III) for bromide compared to chloride. This is consistent with the "soft" character of Au(III). It is interesting that the ratio $K_1/K_2 = 9:1$ is somewhat greater than the statistical ratio of 4:1.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supporting this research.

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[10] L. H. Jones, *Inorg. Chem.*, **3**, 1581 (1964).

[11] Reference 2, p 382.

[12] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 4200 (1960).