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Effect of Added Ligands on the Rate of Chromium–Sulfur Bond Fission in Thiolatopentaaquochromium(III) Complexes. Evidence for a Sulfur-Induced Trans Effect in Chromium(III) Chemistry

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Both neutral and anionic ligands are shown to enhance the rate of chromium–sulfur bond fission in thiolatopentaaquochromium(III) complexes by factors ranging from 20 to 4800 and in turn are themselves stoichiometrically incorporated into the chromium(III) product coordination sphere. The generation of ligated product is 10^3–10^4 times faster for $(H_2O)_5CrSR^{3+}$ than for $(H_2O)_6Cr^{3+}$ and thus thiols have a strong labilizing effect in the pentaaquochromium(III) system. The detailed kinetics of this process (with $HSCH_2CH_2NH_3^+$ and p-$HSC_6H_4NH_3^{3+}$ as leaving thiols and Cl^-, Br^- (alkyl thiol only), HF, and CH_3COOH as entering ligands) are accounted for by a modification of the Moore–Basolo–Pearson trans labilization scheme in which the coordinated thiol both effects the original trans labilization and also affects the net observed rate by the involvement of its chemistry in the chromium–sulfur bond fission step. Linear free energy relationships show that the observed rate is also dependent upon the nature of the incoming ligand, and this dependence is remarkably similar to that observed in ligation of $(H_2O)_6Cr^{3+}$. The increased rate of chloride-catalyzed aquation over normal aquation is entirely due to increased values of ΔS^*, implying that in this case the catalytic effect arises primarily from the lower formal charge and concomitant decreased requirement for solvent reorientation of the trans-substituted intermediate *trans*-$(H_2O)_4Cr(Cl)SR^{2+}$. The synthetic utility of these reactions is noted and also exemplified by the clean and reproducible synthesis of $(H_2O)_5CrSH^{2+}$ from H_2S and $(H_2O)_5CrSC_6H_4NH_3^{3+}$.

Introduction

The observation, quantification, systematization, prediction, and raison d'etre of trans effects in octahedral complexes continue to be of great interest to inorganic chemists.[2] Considerable attention has recently been given to the ground state and kinetic trans effects induced by coordinated sulfur in cobalt(III) complexes.[2,3] During our investigations into the chemistry of coordinated thiols[4] we observed that added free ligands catalyze the rate of chromium–sulfur bond fission in thiolatopentaaquochromium(III) complexes and are themselves efficiently incorporated into the chromium(III) product, i.e.

$$H^+ + L^{n-} + (H_2O)_5CrSR^{3+} \rightarrow (H_2O)_5CrL^{(3-n)+} + RSH^+ \qquad (1)$$

where $RSH^+ = HSCH_2CH_2NH_3^+$ or p-$HSC_6H_4NH_3^+$. These observations may be understood if coordinated sulfur induces a trans effect in chromium(III) chemistry analogous to that which it induces in cobalt(III) chemistry,[3] thus allowing the Moore–Basolo–Pearson (MBP) scheme[5] (originally proposed for iodide as the trans-labilizing ligand) to be operative, i.e.

$$L^{n-} + (H_2O)_5CrSR^{3+} \overset{K_{os}}{\rightleftharpoons} (H_2O)_5CrSR,L^{(3-n)+} \qquad (2a)$$

$$(H_2O)_5CrSR,L^{(3-n)+} \xrightarrow{k} trans\text{-}(H_2O)_4Cr(L)SR^{(3-n)+} + H_2O \qquad (2b)$$

$$H_3O^+ + trans\text{-}(H_2O)_4Cr(L)SR^{(3-n)+} \xrightarrow{\text{fast}} (H_2O)_5CrL^{(3-n)+} + RSH^+ \qquad (2c)$$

Since the number of ligands previously known to induce trans labilization in chromium(III) chemistry is very small (and only labilization by iodide has been studied in any detail)[6] and since the efficient production of $(H_2O)_5CrL^{(3-n)+}$ species via reaction 1 could have considerable synthetic utility, it seemed worthwhile to investigate the detailed kinetics of reaction 1. In this paper we report the results of these studies and discuss these results with regard to the intimate mechanism of the MBP scheme and trans effects in general.

Nomenclature

The following symbols and nomenclature are used in this paper (first- and second-order rate parameters are in units of s^{-1} and $M^{-1}\ s^{-1}$, respectively, and unless otherwise specified they refer to the rate of chromium–sulfur bond fission):

k_{obsd}	Observed first-order rate parameter under conditions of added L (free ligand)
k_A	Observed first-order rate parameter under conditions of no added L
k_{obsd}^{cor}	$k_{obsd} - k_A$ = observed first-order rate parameter which has been corrected for normal (no added L) aquation
k_L	Apparent second-order rate parameter governing L catalysis
k_L^{alkyl}	k_L for reaction of $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$
k_L^{aryl}	k_L for reaction of $(H_2O)_5CrSC_6H_4NH_3^{3+}$
$k_{obsd,0}$, $k_{obsd,1}$	Where appropriate, the acid dependence of k_{obsd} is expressed as $k_{obsd} = k_{obsd,0} + k_{obsd,1}[H^+]$;
$k_{L,0}$, $k_{L,1}$, $k_{L,-1}$	Where appropriate, the acid dependence of k_L is expressed as $k_L = k_{L,0} + k_{L,1}[H^+] + k_{L,-1}[H^+]^{-1}$
$k_{A,0}$, $k_{A,1}$	Where appropraite, the acid dependence of k_A is expressed as $k_A = k_{A,0} + k_{A,1}[H^+]$
K_L	Equilibrium constant governing association of L and $(H_2O)_5CrSR^{3+}$ (units of M^{-1})
k_L'	Calculated first-order rate parameter = k_L/K_L
$k_{aq,L}$	First-order rate parameter governing aquation of $(H_2O)_5CrL^{q+}$
$k_{an,L}$	Second-order rate parameter governing ligation of $(H_2O)_6Cr^{3+}$ by L
$K_{eq,L}$	Equilibrium constant governing formation of $(H_2O)_5CrL^{q+}$ from L and $(H_2O)_6Cr^{3+}$ (units of M^{-1})
σ_k	Standard deviation of k_{obsd}
σ_k^{cor}	Standard deviation of k_{obsd}^{cor}
$[Cr_T]$	Total concentration of starting thiolato complex in all of its equilibrium-controlled forms
$\%_{obsd}$	Observed percent yield of ligated product(s)
$\%_{cor}$	Percent yield of ligated product(s) corrected for aquation of the ligated product(s)
$\%_{calcd}$	Theoretical percent yield of ligated product(s) calculated from kinetic data

Experimental Section

Unless otherwise noted, reagents, equipment, procedures, complex preparations, chemical analyses, computer programs, and data analyses were as previously specified.[4,7] Reagent grade lithium chloride and lithium bromide were purified by two crystallizations from triply distilled water. Stock solutions of these reagents were standardized by titration with silver nitrate using dichlorofluorescein as indicator. Hydrofluoric, hydrochloric, hydrobromic, and acetic acids were of reagent grade; stock solutions of these reagents were standardized by titration with sodium hydroxide using phenolphthalein as indicator. Duplicate kinetic experiments using hydrobromic acid and lithium perchlorate, or lithium bromide and perchloric acid, yielded identical results within experimental error.

For many of the reactions studied in this work, an experimental infinite-time optical density (OD_∞) could not be obtained because of subsequent interfering reactions (e.g., aquation of the $(H_2O)_5CrL^{q+}$ product). Therefore, for all reactions the previously described[4,7,8] LASL nonlinear least-squares program was employed to determine the values of k_{obsd}, OD_0, and OD_∞ which best fit the OD_t–t data within the first-order exponential form.[4b] Tests performed to show that the monitored reactions were indeed first order and that the first-order rate law adequately described the OD_t–t data satisfied the same criteria as previously reported.[4b] All reactions were monitored for at least 4 half-lives, and for most reactions values of k_{obsd} were calculated from an analysis of at least 4 half-lives of data. In a few experiments interference by subsequent reactions was sufficiently large that values of k_{obsd} calculated from 2 half-lives and from 4 half-lives of data differed slightly (always less than 5%); in these few cases the k_{obsd} calculated from 2 half-lives of data is reported.

The rate of disappearance of the thiolatopentaaquochromium(III) starting complexes was usually monitored at two different wavelengths, i.e., at the position of the ligand-to-metal charge transfer (LTMCT) band in the ultraviolet region and at the position of a d–d transition in the visible region.[4,7] In some systems, interference by subsequent aquation of product complexes was too severe to allow monitoring in the visible region and data were obtained only at the LTMCT band which is characteristic for the Cr–S bond.[9] In almost all systems where two monitoring wavelengths were employed, resulting values of k_{obsd} were independent of wavelength to within experimental error. However, some preparations of the $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ ion contained small amounts (less than 2% by spectrophotometric analysis) of other species[10] which led to a small apparent wavelength dependence of k_{obsd}. Most studies were performed with preparations which did not lead to this apparent wavelength dependence; however, it was difficult always to obtain such pure solutions. Since in no case is the wavelength dependence of k_{obsd} greater than 10% and our limit of reproducibility for replicate runs is only 5%, those few experiments exhibiting wavelength dependence are weighted equally with all others and are recorded in the appropriate tables.

Unless otherwise noted, all errors reported in this work are standard deviations, and in all analyses values of k_{obsd} and k_{obsd}^{cor} are weighted as the inverse square of their standard deviations. Values of σ_k were obtained directly from the LASL nonlinear least-squares analysis.[4,7,8] Values of σ_k^{cor} were assumed to be equal to the corresponding σ_k if k_A comprised less than 10% of k_{obsd}. If k_A was greater than 10% of k_{obsd}, then σ_k^{cor} was estimated[11] as $[(\sigma_k)^2 + (0.05k_A)^2]^{1/2}$. In all calculations of derived parameters, errors were propagated by standard procedures.

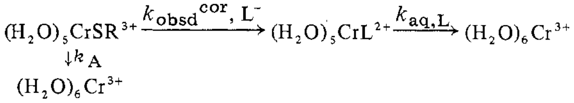
Preparation of the Thiolopentaaquochromium(III) Ion. Hydrogen sulfide gas was bubbled through a solution of pentaaquo(4-thioanilinium-*S*)chromium(III)[4c] ($[HClO_4] = 0.001$ M) which was cooled to 0 °C. The reaction vessel was sealed, allowed to warm to room temperature, and let stand under the resulting pressure for about 14 h; the pressure was then released and the reaction solution was appropriately diluted and added to a Dowex 50W-X2 (200-400 mesh) ion-exchange column. The band of 2+ formal charge was readily separated by standard techniques[4,7] and was collected in 21% yield. The visible–uv spectrum of this material showed peaks at 570, 433, and 266 nm (ϵ 26.6, 41.5, and 7000 M^{-1} cm^{-1}, respectively) in excellent agreement with the parameters reported by Ardon and Taube[12] for $(H_2O)_5CrSH^{2+}$.

Stoichiometry Experiments. Aquation product mixtures were separated on Dowex 50W-X2 (200–400 mesh) ion-exchange columns by standard techniques.[4,7] Species of 1+, 2+, and 3+ formal charge were eluted with 0.1, 0.5, and 1.0 M $NaClO_4$ solutions (pH 2 with $HClO_4$), respectively. The last traces of 3+ bands were removed with 2.0 M $NaClO_4$ (pH 2).

Results

The addition of free ligands to solutions of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ or $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ results in significant enhancement of the rate of loss of the thiolato moiety from the chromium(III) coordination sphere and concomitant incorporation of the added ligand into the product chromium(III) coordination sphere (eq 1). The product complexes, $(H_2O)_5CrL^{(3-n)+}$, are identified by their visible–uv absorption spectra[12–16] and their ion-exchange elution characteristics. Incorporation of NCS^-, Br^-, H_2S, Cl^-, HF, and CH_3COOH has been qualitatively noted for both thiolato complexes; quantitative product yields have been determined for reaction of the latter three ligands with $(H_2O)_5CrSC_6H_4NH_3^{3+}$. Increased rates of Cr–S bond cleavage (relative to the system where perchlorate and water are the only extraneous ligands present) are observed upon addition of Cl^-, Br^-, HF, NCS^-, and CH_3COOH (no attempt was made to monitor the H_2S system). The kinetics of the Cl^-, Br^- ($(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ only), HF, and CH_3COOH systems have been studied quantitatively.

Scheme I



$$\begin{tikzcd}(H_2O)_5CrSR^{3+} \arrow[r, "k_{obsd}^{cor}, L^-"] \arrow[d, "k_A"] & (H_2O)_5CrL^{2+} \arrow[r, "k_{aq,L}"] & (H_2O)_6Cr^{3+} \\ (H_2O)_6Cr^{3+} & & \end{tikzcd}$$

Table I. Observed and Calculated Stoichiometries for Ligand-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSC_6H_4NH_3^{3+}$ [a]

Free ligand	[L], M	$[H^+]$, M	$\%_{obsd}$	$\%_{cor}$	$\%_{calcd}$
Cl^-	0.105[b]	1.00	42	42.4	50
Cl^-	0.70	1.00	70	70.6	84
Cl^-	0.80	1.00	81.5	82.1	86
Cl^-	0.90	1.00	81.5	82.1	87
Cl^-	0.90[b]	0.102	67.5	69.3	84
Cl^-	0.90[b]	0.149	71.6	73.0	85
Cl^-	0.90[b]	0.149	65.5	66.8	85
Cl^-	1.44	1.00	83	83.4	91
HF	0.490	0.109	99	99	99
HF	0.490	0.109	96	96	99
HF	0.490	1.00	97	97	97
HF	0.490	1.00	94	94	97
CH_3COOH	1.00	0.054	93	94.4	98
CH_3COOH	1.00	0.054	90	91.4	98

[a] Studies performed at $\mu = 2.00$ M ($LiClO_4$) and 25.0 °C unless otherwise noted; $[(H_2O)_5CrSC_6H_4NH_3^{3+}]_0 = 0.01$ M; $\%_{obsd}$ is the percent yield of ligated product(s); $\%_{cor}$ and $\%_{calcd}$ are defined in the text. [b] Study performed at 34.3 °C.

Stoichiometry. The reaction of thiolatopentaaquochromium(III) complexes with added ligands leads to ligated product(s) via Scheme I and to $(H_2O)_6Cr^{3+}$ via normal acid-catalyzed aquation[4b,c] as well as via subsequent hydrolysis of the primary ligated product(s). Table I lists the percent yields ($\%_{obsd}$) of ligated product(s) resulting from the catalysis of chromium–sulfur bond fission in $(H_2O)_5CrSC_6H_4NH_3^{3+}$ by added Cl^-, HF, and CH_3COOH. For Cl^- and CH_3COOH catalysis, the ligated product is exclusively (greater than 98%) the monosubstituted species $(H_2O)_5CrL^{2+}$. For the HF reaction, considerable yields (ca. 30%) of $(H_2O)_4CrF_2^{2+}$ are observed in the experiments at $[H^+] = 0.109$ M. In all cases the only other detectable reaction product is $(H_2O)_6Cr^{3+}$; there is no evidence for the existence of a mixed $(H_2O)_4(L)CrSC_6H_4NH_3^{2+}$ product. Values of $\%_{obsd}$ are corrected, in order to account for aquation of the primary $(H_2O)_5CrL^{2+}$ product which occurs during the stoichiometry experiment, via the expression

$$\%_{cor} = \%_{obsd}\left[\frac{k_{obsd} - k_{aq}}{k_{obsd} - k_A}\right] \times \left[\frac{1 - k_A/k_{obsd} - (1 + k_A/k_{obsd})\exp(-k_{obsd}\tau)}{\exp(-k_{aq}\tau) - \exp(-k_{obsd}\tau)}\right] \quad (3)$$

Table IV. Calculated Parameters Describing the Chloride Dependence of the Chloride-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSR^{3+}$ [a]

Complex	Temp, °C	10^4k_A,[b] s^{-1}	$10^4k_{Cl}'$, s^{-1}	K_{Cl}, M^{-1}
$(H_2O)_5CrSC_6H_4NH_3^{3+}$	25.0	0.150	2.31 ± 0.11	0.486 ± 0.034
	34.3	0.562	10.3 ± 0.62	0.515 ± 0.050
	44.4	2.24	46.9 ± 2.7	0.558 ± 0.046
$(H_2O)_5CrSCH_2CH_2NH_3^{3+}$	25.0	1.8	18.4 ± 2.0	0.324 ± 0.048
	35.0	6.41	62.8 ± 3.8	0.493 ± 0.050
	46.3	25.1	248 ± 5	0.692 ± 0.027

[a] $[HClO_4] = 1.00$ M; $\mu = 2.00$ M ($LiClO_4$); $k_{obsd} = (k_A + k_{Cl}' \cdot K_{Cl}[Cl^-])/(1 + K_{Cl}[Cl^-])$. [b] Reference 11.

where τ is taken as the time for 99% of the $(H_2O)_5CrSC_6H_4NH_3^{3+}$ to react and k_{aq} values are taken from the literature.[17] The resulting values of $\%_{cor}$ are listed in Table I and in no case is $\%_{cor}$ more than 2% larger than $\%_{obsd}$.

Blank experiments with $(H_2O)_6Cr^{3+}$ and either HF or Cl^- show that negligible (less than 1%) ligated product is formed under the conditions (and time intervals) of the above experiments.

$Cl^- + (H_2O)_5CrSR^{3+}$ Kinetics. Tables II[18] and III[18] list, for $-R = -C_6H_4NH_3$ and $-CH_2CH_2NH_3$, respectively, the dependence of k_{obsd} on $[Cl^-]$ (at constant $[H^+] = 1.00$ M), $[H^+]$ (at constant $[Cl^-] = 0.900$ M), and temperature. Figures 1 and 2 show plots of the chloride dependence of k_{obsd} for the two reactions at 25.0 °C. Such plots with continuously decreasing slopes are often indicative of a mechanism involving a rapid prior equilibrium. For economy of nomenclature, this mechanistic interpretation (and associated rate law) is used here to identify reaction parameters, i.e.

$$Cl^- + (H_2O)_5CrSR^{3+} \overset{K_{Cl}}{\rightleftharpoons} (H_2O)_5CrSR,Cl^{2+} \tag{4a}$$

$$H^+ + (H_2O)_5CrSR^{3+} \xrightarrow{k_A} (H_2O)_6Cr^{3+} + RSH^+ \tag{4b}$$

$$H^+ + (H_2O)_5CrSR,Cl^{2+} \xrightarrow{k_{Cl}'} (H_2O)_5CrCl^{2+} + RSH^+ \tag{4c}$$

$$-d(\ln [Cr_T])/dt = k_{obsd} = \frac{k_A + k_{Cl}'K_{Cl}[Cl^-]}{1 + K_{Cl}[Cl^-]} \tag{4d}$$

$$k_{Cl} = k_{Cl}'K_{Cl} \tag{4e}$$

Possible formulations of the complex introduced in eq 4a will be discussed later. Nonlinear least-squares minimization of the k_{obsd}–$[Cl^-]$ data of Tables II[18] and III[18] according to eq 4d leads to optimized values of k_{Cl}' and K_{Cl} at each temperature investigated;[11] these optimized values are listed in Table IV. The smooth curves drawn in Figures 1 and 2 are obtained from these optimized values (at 25.0 °C), indicating that eq 4d adequately describes the k_{obsd}–$[Cl^-]$ data.

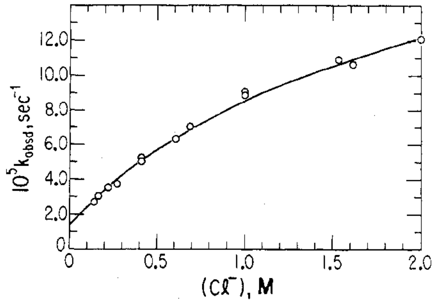


Figure 1. Plot of 10^5k_{obsd} (s^{-1}) vs. $[Cl^-]$ (M) for chloride catalysis of chromium–sulfur bond breaking in $(H_2O)_5CrSC_6H_4NH_3^{3+}$ at 25.0 °C, $[H^+] = 1.00$ M, $\mu = 2.00$ M ($LiClO_4$). The smooth curve is that calculated from the optimized parameters of the nonlinear least-squares analysis.

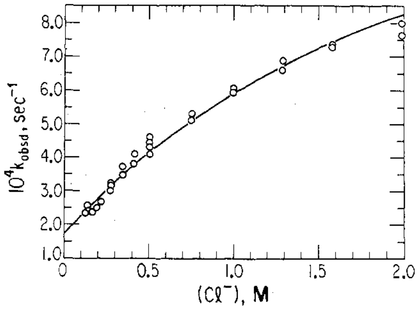


Figure 2. Plot of 10^4k_{obsd} (s^{-1}) vs. $[Cl^-]$ (M) for chloride catalysis of chromium–sulfur bond breaking in $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ at 25.0 °C, $[H^+] = 1.00$ M, $\mu = 2.00$ M ($LiClO_4$). The smooth curve is that calculated from the optimized parameters of the nonlinear least-squares analysis.

Plots of the k_{obsd}–$[H^+]$ data of Tables II[18] and III[18] are straight lines with positive intercepts (typical range of $[H^+] = 0.10$–2.00 M) and thus at constant $[Cl^-]$

$$-d(\ln [Cr_T])/dt = k_{obsd} = k_{obsd,0} + k_{obsd,1}[H^+] \tag{5}$$

Standard linear least-squares treatment of the k_{obsd}–$[H^+]$ data at each temperature investigated[11] leads to the values of $k_{obsd,0}$ and $k_{obsd,1}$ listed in Table V.

The linear acid dependence expressed in eq 5 requires that K_{Cl} not be significantly dependent on $[H^+]$ (see eq 4). Therefore the $[Cl^-]$ and $[H^+]$ dependencies expressed by eq 4 and 5, along with the known[4b,c] paths for normal acid-

Table V. Calculated Parameters for the Acid Dependence of the Chloride- and Bromide-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSR^{3+}$ [a]

L	R	Temp, °C	$10^4k_{A,0}$,[b] s^{-1}	$10^4k_{A,1}$,[b] M s^{-1}	$10^4k_{obsd,0}$, s^{-1}	$10^4k_{obsd,1}$, M s^{-1}
Cl^-	$C_6H_4NH_3$	25.0	0.040 ± 0.002	0.110 ± 0.006	0.141 ± 0.016	0.70 ± 0.01
Cl^-	$C_6H_4NH_3$	34.3	0.190 ± 0.010	0.37 ± 0.02	0.69 ± 0.04	3.0 ± 0.6
Cl^-	$C_6H_4NH_3$	44.4	0.917 ± 0.045	1.32 ± 0.07	4.2 ± 0.2	12.5 ± 0.4
Cl^-	$CH_2CH_2NH_3$	25.0	0.42 ± 0.02	1.39 ± 0.07	0.70 ± 0.04	5.04 ± 0.08
Cl^-	$CH_2CH_2NH_3$	35.0	1.97 ± 0.10	4.44 ± 0.22	3.36 ± 0.12	20.0 ± 0.3
Cl^-	$CH_2CH_2NH_3$	46.3	10.0 ± 0.5	15.1 ± 0.8	19.5 ± 1.1	92 ± 1.9
Br^-	$CH_2CH_2NH_3$	25.0	0.42 ± 0.02	1.39 ± 0.07	0.409 ± 0.006	1.93 ± 0.02

L	R	Temp, °C	$10^4k_{L,0}$, M^{-1} s^{-1}	$10^4k_{L,1}$, M^{-2} s^{-1}	$10^4k_{L,0}'$, s^{-1}	$10^4k_{L,1}'$, M^{-1} s^{-1}
Cl^-	$C_6H_4NH_3$	25.0	0.181 ± 0.026	0.99 ± 0.03	0.37 ± 0.06	2.04 ± 0.16
Cl^-	$C_6H_4NH_3$	34.3	0.91 ± 0.07	4.4 ± 0.9	1.77 ± 0.22	8.5 ± 1.9
Cl^-	$C_6H_4NH_3$	44.4	5.96 ± 0.37	19.4 ± 0.9	10.7 ± 1.1	34 ± 3
Cl^-	$CH_2CH_2NH_3$	25.0	0.53 ± 0.07	5.7 ± 0.3	1.64 ± 0.33	17 ± 3
Cl^-	$CH_2CH_2NH_3$	35.0	3.20 ± 0.28	27.1 ± 1.1	6.5 ± 0.9	55 ± 6
Cl^-	$CH_2CH_2NH_3$	46.3	24.1 ± 2.1	150 ± 4	35 ± 3	217 ± 10
Br^-	$CH_2CH_2NH_3$	25.0	0.012 ± 0.023	0.60 ± 0.08		

[a] $\mu = 2.00$ M ($LiClO_4$). [b] Reference 11.

Table VI. Nonlinear Least-Squares Optimized Parameters Describing the Temperature Dependence of the Chloride-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSR^{3+}$ [a]

	$-R = -C_6H_4NH_3$	$-R = -CH_2CH_2NH_3$
$\Delta S^*_{Cl,0}{}'$, eu	27.4 ± 4.0	15.7 ± 4.3
$\Delta H^*_{Cl,0}{}'$, kcal/mol	31.7 ± 1.2	27.4 ± 1.3
$\Delta S^*_{Cl,1}{}'$, eu	11.7 ± 3.5	3.9 ± 3.0
$\Delta H^*_{Cl,1}{}'$, kcal/mol	25.9 ± 1.1	22.4 ± 0.9
$\Delta S^\circ_{K_{Cl}}$, eu	9.7 ± 5.0	17.8 ± 4.6
$\Delta H^\circ_{K_{Cl}}$, kcal/mol	3.4 ± 1.5	5.9 ± 1.4
No. of independent values of k_{obsd}	59	80
Av % dev[b]	3.4	3.1
Max % dev[b]	12.5	12.3

[a] Temperature parameters optimized using the LASL nonlinear least-squares program.[8] Data taken from Tables II[18] and III.[18] Individual values of k_{obsd} weighted as $(1/k_{obsd})^2$. $\Delta H^*_{A,0}$, $\Delta S^*_{A,0}$, $\Delta H^*_{A,1}$, $\Delta S^*_{A,1}$ held fixed at their previously determined[4b,c] values. [b] Percent deviation = $100|k_{obsd} - k_{calcd}|/k_{obsd}$ where k_{calcd} is calculated from the optimized parameters listed in this table (plus the temperature parameters held fixed as noted above) according to eq 6a, 7a, and 7b.

catalyzed aquation, may be combined to give the overall rate expression

$$k_{obsd} = \frac{k_{A,0} + k_{A,1}[H^+] + K_{Cl}[Cl^-](k_{Cl,0}{}' + k_{Cl,1}{}'[H^+])}{1 + K_{Cl}[Cl^-]} \quad (6a)$$

and thus

$$k_{obsd,0} = \frac{k_{A,0} + K_{Cl}k_{Cl,0}{}'[Cl^-]}{1 + K_{Cl}[Cl^-]} \quad (6b)$$

and

$$k_{obsd,1} = \frac{k_{A,1} + K_{Cl}k_{Cl,1}{}'[Cl^-]}{1 + K_{Cl}[Cl^-]} \quad (6c)$$

Data from Tables IV and V may be combined with eq 6b and 6c to yield values of $k_{Cl,0}{}'$ and $k_{Cl,1}{}'$ at each of the temperatures investigated. These calculated parameters are listed in Table V.

Nonlinear least-squares minimization of all 59 independently determined values of k_{obsd} of Table II[18] and all 80 independently determined values of k_{obsd} of Table III[18] within eq 6a, with each rate parameter expressed in terms of the Eyring formalism

$$k = (k_BT/h)\exp(\Delta S^*_k/R)\exp(-\Delta H^*_k/RT) \quad (7a)$$

and K_{Cl} expressed in the usual form for an equilibrium parameter

$$K_{Cl} = \exp(\Delta S^\circ_{K_{Cl}}/R)\exp(-\Delta H^\circ_{K_{Cl}}/RT) \quad (7b)$$

(values of $\Delta H^*_{A,0}$, $\Delta H^*_{A,1}$, $\Delta S^*_{A,0}$, and $\Delta S^*_{A,1}$ fixed at their previously determined[4b,c] values), leads to the enthalpy and entropy values listed in Table VI.

Br^- + $(H_2O)_5CrSR^{3+}$ Kinetics. Added bromide ion catalyzes the rate of chromium–sulfur bond breaking in both $(H_2O)_5CrSC_6H_4NH_3^{3+}$ and $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$, but in the former system subsequent aquation of the $(H_2O)_5CrBr^{2+}$ product is too rapid to allow quantitative determination of the catalyzed rate. The $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ system is not so severely affected by $(H_2O)_5CrBr^{2+}$ aquation because of the inherently faster rate of chromium–sulfur bond breaking in this complex.[19] Table III[18] lists for $-R = -CH_2CH_2NH_3$ the dependence of k_{obsd} on $[Br^-]$ ($[Br^-]$ = 0.10–1.99 M; $[H^+]$ constant at 1.00 M) and $[H^+]$ ($[H^+]$ = 0.10–1.99 M; $[Br^-]$ constant at 0.90 M) at 25.0 °C. A plot of the k_{obsd}–$[Br^-]$ data is a straight line with a large positive intercept. Linear least-squares analysis of this data yields an intercept, $(1.74 \pm 0.02) \times 10^{-4}$ s^{-1}, equal to the independently determined[11] value of k_A, $(1.81 \pm 0.09) \times 10^{-4}$ s^{-1}, under these conditions. Therefore at constant $[H^+]$

$$-d(\ln [Cr_T])/dt = k_{obsd} = k_A + k_{Br}[Br^-] \quad (8)$$

and $k_{Br} = (6.0 \pm 0.3) \times 10^{-5}$ M^{-1} s^{-1} ($[H^+]$ = 1.00 M).

A plot of the k_{obsd}–$[H^+]$ data of Table VII[18] is also linear and thus

$$k_{obsd} = k_{obsd,0} + k_{obsd,1}[H^+] = k_{A,0} + k_{Br,0}[Br^-] + (k_{A,1} + k_{Br,1}[Br^-])[H^+] \quad (9)$$

Linear least-squares analysis of this data gives the $k_{obsd,0}$ and $k_{obsd,1}$ values listed in Table V; subsequent analysis within eq 9 leads to the values of $k_{Br,0}$ and $k_{Br,1}$ also given in Table V. It should be noted that $k_{Br,0}$ is equal to zero within experimental error.

HF + $(H_2O)_5CrSR^{3+}$ Kinetics. Table VIII[18] lists the dependence of k_{obsd} on [HF] and $[H^+]$ at 25.0 °C. For both systems k_{obsd} is independent of $[H^+]$ ($[H^+]$ = 0.05–1.00 M for $-R = -CH_2CH_2NH_3$ and 0.11–1.00 M for $-R = -C_6H_4NH_3$) and linearly dependent on [HF] ([HF] = 0.49–0.99 M for $-R = -CH_2CH_2NH_3$ and 0.25–2.44 M for $-R = -C_6H_4NH_3$), leading to the rate law

$$-d(\ln [Cr_T])/dt = k_{obsd} = k_A + k_{HF}[HF] \quad (10)$$

Linear least-squares treatment of the $k_{obsd}{}^{cor}$–[HF] data of Table VIII[11,18] yields $k_{HF}{}^{alkyl} = (3.05 \pm 0.12) \times 10^{-3}$ M^{-1} s^{-1} and $k_{HF}{}^{aryl} = (1.18 \pm 0.06) \times 10^{-3}$ M^{-1} s^{-1}; the intercepts of these plots are $(-0.4 \pm 0.7) \times 10^{-4}$ s^{-1} and $(-0.1 \pm 0.4) \times 10^{-4}$ s^{-1}, respectively.

CH_3COOH + $(H_2O)_5CrSR^{3+}$ Kinetics. Table IX[18] lists the dependence of k_{obsd} on $[CH_3COOH]$ and $[H^+]$ at 25.0 °C. For both systems plots of $k_{obsd}{}^{cor}/[CH_3COOH]$ vs. $1/[H^+]$ are straight lines with large intercepts ($[CH_3COOH]$ = 0.30–1.00 M for $-R = -C_6H_4NH_3$ and 0.44–1.48 M for $-R = -CH_2CH_2NH_3$; $[H^+]$ = 0.05–1.00 M for both systems). Thus the rate law may be written as

$$-d(\ln [Cr_T])/dt = k_{obsd} = k_A + (k_{CH_3COOH,0} + k_{CH_3COOH,-1}[H^+]^{-1})[CH_3COOH] \quad (11)$$

Linear least-squares analysis of the above plots yields the following parameter values: $k_{CH_3COOH,0}{}^{alkyl} = (2.34 \pm 0.03) \times 10^{-4}$ M^{-1} s^{-1}; $k_{CH_3COOH,0}{}^{aryl} = (0.22 \pm 0.01) \times 10^{-4}$ M^{-1} s^{-1}; $k_{CH_3COOH,-1}{}^{alkyl} = (1.15 \pm 0.03) \times 10^{-5}$ s^{-1}; $k_{CH_3COOH,-1}{}^{aryl} = (1.58 \pm 0.01) \times 10^{-5}$ s^{-1}.

Discussion

Stoichiometry and Synthesis. The competition between normal aquation and ligand-catalyzed aquation depicted in Scheme I leads to the following expressions for the theoretical percent yield of ligated product(s)

$$\%_{calcd} = \frac{k_{obsd}{}^{cor}}{k_{obsd}} = \frac{k_L}{k_A + k_L} \quad (12a)$$

for HF and CH_3COOH and

$$\%_{calcd} = \frac{k_{Cl}{}'K_{Cl}[Cl^-]}{k_A + k_{Cl}{}'K_{Cl}[Cl^-]} \quad (12b)$$

for Cl^-. Values of $\%_{calcd}$, calculated from the appropriate data of Tables IV, VIII,[18] and IX,[18] are listed in Table I for each of the tabulated stoichiometry experiments. These values are seen to be reasonably equivalent to the corresponding values of $\%_{cor}$; i.e., the percent yield of ligated product(s) corresponds well to the percent of reaction that proceeds by the ligand-catalyzed path. Thus the incorporation of L into the chro-

Table X. Comparison of Calculated Rate and Equilibrium Parameters Describing the Ligation of $(H_2O)_6Cr^{3+}$ and the Ligand-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSR^{3+}$ [a]

L	$K_{eq,L}$ [b]	$10^4k_{an,L}$ [b]	$10^4k_L^{alkyl}$ [c]	$k_L^{alkyl}/k_{H_2O}^{alkyl}$	$10^4k_L^{aryl}$ [c]	$k_L^{aryl}/k_{H_2O}^{aryl}$
H_2O		0.004 5[d]	0.032[d]		0.0027[d]	
Br^-	0.0022	0.000 09	0.64	20		
Cl^-	0.11	0.000 29	6.0	188	1.12	410
HF	26	0.005 6	31.0	969	13.0	4800
CH_3COOH			2.83	88	0.38	140

[a] Rate constants in units of $M^{-1}\ s^{-1}$, $K_{eq,L}$ in units of M^{-1}. Conditions: 25.0 °C, $[H^+] = 1.00$ M, $\mu = 2.00$ M ($LiClO_4$ where data are available; $NaClO_4$ otherwise). [b] Values are taken from D. Thusius, *Inorg. Chem.*, **10**, 1106 (1971), and represent the acid-independent path for ligation. [c] This work. [d] Tabulated second-order parameter obtained by dividing the observed first-order parameter by the concentration of water (taken as 55.5 M).

mium(III) coordination sphere via eq 1 is essentially stoichiometric. The fact that $\%_{cor}$ is consistently somewhat smaller than $\%_{calcd}$ most probably results from aquation of the ligated product during ion-exchange separation of the product mixture.

Regardless of the mechanism (see below) by which free ligands are incorporated into the coordination sphere of chromium(III) upon aquation of $(H_2O)_5CrSR^{3+}$ species, the yield data of Table I show that the chemistry described by eq 1 has considerable synthetic utility. For example, the addition of H_2S to a solution of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ (see Experimental Section) allows the clean and reproducible synthesis of the $(H_2O)_5CrSH^{2+}$ ion; we have not been able to reproduce the literature preparation of this species.[4c,12] Use of the chemistry of eq 1 should provide a general route for the synthesis of other pentaaquochromium(III) complexes not readily prepared by conventional techniques.

Kinetics and Mechanism. There has been considerable interest and controversy concerning the mechanism of free ligand (hereafter referred to as L while the leaving ligand is referred to as X) incorporation upon aquation of $(H_2O)_5CrX^{n+}$ species,[5,20–26] and this subject is treated in Swaddle's recent review.[6] Five mechanistic schemes have been advanced, or inferred, to account for ligand incorporation and ligand-catalyzed aquation but none of these is sufficient to account for our experimental data.

(I) Cis activation by coordinated oxy anions (e.g., nitrate, acetate, *O*-sulfite) is now well documented[6,27–31] but is not relevant to our systems.

(II) Ardon[20] originally proposed that incorporation proceeds via the discrete five-coordinate intermediate $(H_2O)_5Cr^{3+}$ which scavanges free ligands from solution. This mechanism has been discounted by several lines of evidence[5,6] and our observation that chloride is much more efficiently incorporated upon aquation of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ than upon aquation of $(H_2O)_5CrI^{2+}$ and $(H_2O)_5CrBr^{2+}$ (ca. 75% for SR vs. 19% and 35% for I and Br[6,24]) further argues against the operation of a common five-coordinate intermediate. In addition, evidence presented later shows that ligand-catalyzed aquations of $(H_2O)_5CrSR^{3+}$ species have considerable associative character, inconsistent with the dissociative generation of a five-coordinate intermediate.

(III) Carey, Jones, and Swaddle[24] originally proposed that incorporation proceeds via associative interchange of X and L, but the arguments initially offered[24] in support of this interpretation have been discounted[6] and the experimental data rationalized in terms of mechanism I and the Moore–Basolo–Pearson (MBP) scheme (eq 2).[6] In addition, data listed in Table X may be used to generate a persuasive, although indirect, argument against the direct interchange of L and X in our systems. Both ligation and aquation reactions at chromium(III) centers are considered to involve transition states with considerable associative character.[6] Table X shows that the ligation reactions of Br^- and Cl^- on $(H_2O)_6Cr^{3+}$ are slower than the rate of water exchange on this same substrate, whereas the rates of the hypothetical direct replacement of X (thiolato ligand) by these same ligands are all faster than the rate of replacement of X by water (normal aquation). Since the replacement of X by water must proceed by direct interchange of X and H_2O and since the anation reactions indicate water to be the most effective incoming ligand, the fact that ligand-induced aquation is *faster* than normal aquation strongly argues that direct interchange of L and X is *not* the mechanism for ligand-catalyzed aquation.

(IV) It is possible that ion pairing plays the essential role in rate enhancement and incorporation. However, while ion pairing has been shown to cause significant rate enhancements in some substitution reactions,[32,33] it is apparently not a necessary condition for the thiolatopentaaquochromium(III) systems. The neutral species HF and CH_3COOH both have large effects on the rate of chromium–sulfur bond fission, and both are efficiently incorporated into the chromium(III) product coordination sphere, even at high concentrations of $HClO_4$. To maintain that these species are effective through ion-pair formation of their respective anions would require invocation of excessively high specific rates for the anions, and thus ion-pair formation does not have to be involved in ligand-catalyzed aquation.

(V) The basic trans-labilization concept of the Moore–Basolo–Pearson (MBP) scheme (eq 2) has received considerable experimental support[5,6,23,25,34] and is generally accepted,[6] even to the extent of being used to account for unexpected experimental obsevations such as the catalyzed aquations of alkylpentaaquochromium(III) species.[35,36] However, it is clear that the originally proposed MBP scheme,[5] in which the only effect of X is labilization of the trans water in a rate-determining step (eq 2b), cannot adequately describe our ligand-catalyzed aquation data since the observed rates are strongly dependent upon the nature and chemistry of the leaving thiolato ligand (these effects are documented more specifically below). Thus, in order to account for our detailed kinetic data, the MBP scheme must be modified so that the observed rates reflect *both* the contributions of Cr–L bond formation and the contributions of Cr–X bond fission.

Contributions of Cr–X Bond Fission. The kinetic profiles for ligand-catalyzed aquation of $(H_2O)_5CrSR^{3+}$ species are remarkably similar to those observed[4b,c] for normal aquation, which of course exclusively involve Cr–X bond fission. For example, in both ligand-catalyzed and normal aquation $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$ consistently reacts faster than does $(H_2O)_5CrSC_6H_4NH_3^{3+}$ (see Table X). Also, just as in normal aquation, acid catalysis is a predominant feature of the bromide- and chloride-catalyzed aquations of $(H_2O)_5CrSR^{3+}$ (see Table V); this acid catalysis presumably reflects the fact that in both reactions HSR^+ is a much better leaving group than SR.[4b,c] The lack of significant acid-catalyzed pathways for HF- and CH_3COOH-induced aquations is consistent with the previously established[4b] "tautomeric" character of the transition state represented by $k_{A,0}$; i.e., in the transition state HF (or CH_3COOH) itself donates the proton required by the leaving SR group; thus

Table XI. Comparison of Rate and Activation Parameters for Normal and Chloride-Catalyzed Chromium–Sulfur Bond Fission in $(H_2O)_5CrSR^{3+}$ [a]

	-R = $-C_6H_4NH_3$	-R = $-CH_2CH_2NH_3$
$k_{Cl,0}'/k_{A,0}$	9.2 ± 1.6	3.9 ± 0.8
$\Delta S^*_{Cl,0}{}' - \Delta S^*_{A,0}$, eu	11 ± 5	2 ± 5
$\Delta H^*_{Cl,0}{}' - \Delta H^*_{A,0}$, kcal/mol	1.9 ± 1.4	−0.2 ± 1.4
$k_{Cl,1}'/k_{A,1}$	18 ± 2	12 ± 2
$\Delta S^*_{Cl,1}{}' - \Delta S^*_{A,1}$, eu	14 ± 5	11 ± 3
$\Delta H^*_{Cl,1}{}' - \Delta H^*_{A,1}$, kcal/mol	2.3 ± 1.3	1.8 ± 0.9

[a] Data taken from Table VI and ref 4b and 4c.

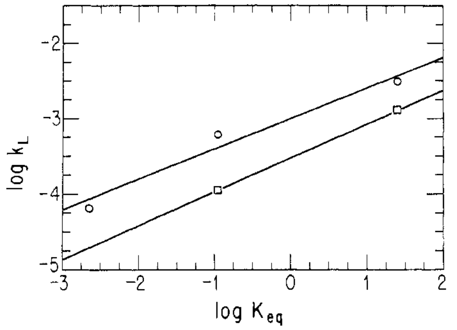


Figure 3. Plots of log k_L vs. log $K_{eq,L}$; the circles denote log k_L^{alkyl} while the squares denote log k_L^{aryl}. Data taken from Table X.

there is no net acid catalysis manifested in the observed rate law. Finally, for both $(H_2O)_5CrSC_6H_4NH_3^{3+}$ and $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$, activation enthalpies for chloride-catalyzed aquation paths are very similar to the analogous parameters for normal aquation (see Table XI) implying that similar bond deformations are involved in achieving the respective transition states. These several observations establish that the transition state for ligand-catalyzed aquation has many of the same characteristics of the transition state for normal aquation and, therefore, Cr–X bond breaking must be important in the net activation process for ligand catalysis.

Contributions of Cr–L Bond Formation. Table X summarizes the rate parameters observed (25.0 °C, $[H^+] = 1.00$ M, $\mu = 2.00$ M) for free ligand-catalyzed chromium–sulfur bond fissions and lists for comparison the anation rates of these same ligands (if available) onto $(H_2O)_6Cr^{3+}$ as well as the formation constants for the product complexes $(H_2O)_5CrL^{2+}$. It is clear that these three parameters qualitatively depend in the same fashion on the nature of the incoming ligands. These data are treated more quantitatively in Figure 3 wherein log k_L^{aryl} and log k_L^{alkyl} are plotted vs. log $K_{eq,L}$. These points can be construed to lie on two parallel lines, one for each complex. Linear least-squares treatment of the three k_L^{alkyl} data points yields a slope of 0.41 ± 0.08, while the two k_L^{aryl} data points define a line of slope 0.45. These slopes are in remarkable agreement with the slope of 0.44 obtained by Swaddle and Guastalla[37,38] upon plotting log $k_{an,L}$ vs. log $K_{eq,L}$ for these same ligands. This agreement implies that the two reactions, anation of $(H_2O)_6Cr^{3+}$ by L and ligand-catalyzed aquation of $(H_2O)_5CrSR^{3+}$, proceed by similar mechanisms; also, the slope values of ca. 0.5 imply the operation of a mechanism with considerable associative character.[6,37] Thus, the contribution of L to the net activation process of catalyzed aquation would seem to be analogous to its contribution to the direct anation reaction, i.e., associative displacement of coordinated water. Of course, in order to account for the magnitude of the ligand-catalyzed rates, the coordinated water molecule being displaced must be labilized, relative to water in $(H_2O)_6Cr^{3+}$, by the coordinated thiolato ligand.

The combined contributions of Cr–L bond formation and Cr–X bond fission to the observed rates of ligand-catalyzed aquation of $(H_2O)_5CrSR^{3+}$ species may readily be accounted for by a modification of the original MBP scheme[5]

$$L^{n-} + (H_2O)_5CrSR^{3+} \overset{K_{os}}{=\!=} (H_2O)_5CrSR,L^{(3-n)+} \tag{13a}$$

$$(H_2O)_5CrSR,L^{(3-n)+} \underset{k_{-t}}{\overset{k_t}{\rightleftarrows}} trans\text{-}(H_2O)_4Cr(SR)L^{(3-n)+} + H_2O \tag{13b}$$

$$H_3O^+ + trans\text{-}(H_2O)_4Cr(SR)L^{(3-n)+} \xrightarrow{k_p} (H_2O)_5CrL^{(3-n)+} + HSR^+ \tag{13c}$$

$$k_{obsd}{}^{cor} = \frac{k_p k_t K_{os}[L]}{(k_p + k_{-t})(1 + K_{os}[L])} \tag{14}$$

In this scheme step 13a represents the equilibrium-controlled formation of an outer-sphere complex, step 13b represents the formation of a steady-state-controlled, trans-substituted intermediate, and step 13c represents formation of the ligated product with concomitant Cr–S bond fission. Competitive normal aquation has not been included. Equation 14 shows how the observed rates reflect contributions both from Cr–L bond formation (k_t) as well as from Cr–X bond fission (k_p). The relative magnitudes of the three rate parameters k_t, k_{-t}, and k_p will determine the kinetics and chemistry observed in any given system: if $k_p \gg k_{-t}$, then the original MBP scheme results; if k_t is significantly larger than k_{-t} and k_p, then significant amounts of the trans-substituted intermediate could be generated during the reaction. This latter situation has apparently been encountered by Schilt and Schaap,[26] who reported the isolation of small yields of $(H_2O)_4Cr(SCN)CN^+$ during the SCN^--catalyzed aquation of $(H_2O)_5CrCN^{2+}$. In the thiolato systems k_p is expected to be acid catalyzed, as observed in normal aquation;[4b,c] since simple acid catalysis is observed for the bromide- and chloride-catalyzed aquations, it is apparent that at least for these systems $k_p \ll k_{-t}$ (if it were not, a complicated acid dependence would have been observed). Therefore, for at least bromide and chloride catalysis the predicted rate law reduces to

$$k_{obsd}{}^{cor} = \frac{k_p(k_t/k_{-t})K_{os}[L]}{1 + K_{os}[L]} \tag{15}$$

The observed chloride dependence of catalyzed chromium–sulfur bond fission (see Figures 1 and 2 and eq 4d) shows that at high chloride concentrations the term $K_{os}[Cl]$ becomes significant with respect to one. The calculated values of K_{os} for chloride ($=K_{Cl}$; see Table IV) are in good agreement with values of outer-sphere association constants measured and calculated[32,39] for (3+)–(1−) systems. The effect of outer-sphere complexation with bromide is presumably not detected because $k_{Br} \ll k_{Cl}$ and thus even at the highest bromide concentrations investigated the bulk of the observed reaction proceeds via k_A making it difficult to detect any curvature in the k_{obsd}–$[Br^-]$ plot. The values of K_{os} for HF and CH_3COOH are presumably so small that $K_{os}[L] \ll 1$ even at the highest ligand concentrations investigated. The lack of first-order acid dependences (and concomitant large acid-independent terms) in the HF and CH_3COOH catalyses is understood in terms of a "tautomeric" transition state (vide supra). The inverse acid term in CH_3COOH catalysis could arise from the greater effectiveness of CH_3COO^- as an entering ligand or from the implied acid catalysis of k_{-t} in this system (since hydrolysis of $[(H_2O)_5CrOOCCH_3]^{2+}$ is known[16] to be acid catalyzed) which would be manifested in an overall inverse acid dependence for $k_{obsd}{}^{cor}$ (see eq 15).

The data of Table X show that added free ligands enhance the rate of Cr–S bond fission in $(H_2O)_5CrSR^{3+}$ species by factors of 20–4800 (k_L/k_{H_2O} at the conditions tabulated). It should be noted that for any given entering ligand this enhancement factor is larger for $(H_2O)_5CrSC_6H_4NH_3^{3+}$ than for $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$, consistent with the proposition that more oxidizable ligands[4b,c] exert greater trans effects.[40] Some insight into the driving force underlying these rate enhancements is given by the data in Table XI which show that for chloride as the entering ligand the rate enhancement is entirely due to more favorable activation entropies for the chloride-catalyzed paths. This can be understood if the net activation processes for the two systems are similar, i.e., stretching of the Cr–S bond in $(H_2O)_5CrSR^{3+}$ and in *trans*-$(H_2O)_4Cr(Cl)SR^{2+}$, leading to similar ΔH^* values but more favorable ΔS^* values for the lower charged activated complex which requires less solvent reorientation.[41] Thus it appears as though the major underlying cause for chloride-catalyzed aquation is the lower net charge on the *trans*-$(H_2O)_4Cr(Cl)SR^{2+}$ intermediate; of course trans labilization of coordinated water by SR is necessary for the generation of this intermediate.

The data of Table X may also be used to calculate the factors by which ligation of the chromium(III) center is enhanced by the coordinated thiolato ligand (i.e., $k_L/k_{an,L}$). These ligation rate enhancements are in the range 10^3–10^4 which are slightly larger than those observed for ligation of $(H_2O)_5CrI^{2+}$ [25] (ca. 10^2–10^3) and somewhat smaller than that preliminarily reported for ligation of $(H_2O)_5CrCH_2Cl^{2+}$ [42] (ca. 10^5). All of these ligations are presumed to proceed via some variation of the modified MBP trans-labilization scheme, and thus the order of trans-labilizing ability of these groups within the pentaaquochromium(III) center is $-CH_2Cl > -SR > -I$.[43]

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Registry No. $[(H_2O)_5CrSH]^{2+}$, 18518-22-4; $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$, 38833-30-6; Cl^-, 16887-00-6; HF, 7664-39-3; CH_3COOH, 64-19-7; $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$, 59033-97-5; Br^-, 24959-67-9.

Supplementary Material Available: Tables II, III, and VII–IX giving observed rates of catalyzed aquations of $(H_2O)_5CrSC_6H_4NH_3^{3+}$ and $(H_2O)_5CrSCH_2CH_2NH_3^{3+}$, as a function of ligand, ligand concentration, μ, $[H^+]$, and temperature (8 pages). Ordering information is given on any current masthead page.

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(18) Supplementary material.

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