nonequivalent sites in the ^{13}C and ^1H spectra. However, the factor of 5 difference in frequency of observation at comparable field strengths for the two nuclei makes it easier to observe small differences in the ^1H spectra than in the ^{13}C spectra for those cases where the proton–proton coupling pattern is relatively simple.

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Thiolato Sulfur as an Electron-Transfer Bridge. The Chromium(II)-Catalyzed Aquation of Thiolatobis(ethylenediamine)chromium(III) Complexes in Aqueous Perchloric Acid Media

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The rates of the chromium(II) reductions of the $[Cr(en)_2(SCH_2COO)]^+$, $[Cr(en)_2(SC_6H_4COO)]^+$, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, and $[Cr(en)_2(OOCCOO)]^+$ ions have been measured in aqueous perchloric acid media. All reactions proceed by inner-sphere electron transfer. Reduction of the mercaptoacetato and 2-mercaptobenzoato complexes is strongly catalyzed by acid, whereas reduction of the 2-mercaptoethylamine and oxalato complexes is essentially independent of acid. The acid-catalyzed redox path is interpreted in terms of a proton-induced cis nonbridging ligand effect. Rates of the title reactions are compared to the rates of chromium(II) reduction of the analogous thiolatobis(ethylenediamine)cobalt(III) complexes, and arguments are presented which indicate that the remarkable bridging efficiency reported for thiolato sulfur in Cr(II)–Co(III) reactions does not carry over to the analogous Cr(II)–Cr(III) reactions. It is suggested that this kinetic difference may arise from the fact that thiolato sulfur induces a ground state trans effect in the cobalt(III) complexes, but not in an analogous chromium(III) complex.

Introduction

The remarkable ability of low-valent sulfur to mediate electron transfer from chromium(II) to cobalt(III) was first noted by Bennett[2] for thiolato sulfur. Thiocyanato sulfur was shown to also efficiently bridge electron transfer from chromium(II) to cobalt(III),[3] as well as from uranium(III) to chromium(III),[4] but a study on electron transfer from cobalt(II) (as $[Co(CN)_5]^{3-}$) to cobalt(III) was inconclusive.[5] In an effort to determine if the unusually great bridging efficiency of thiolato sulfur in Cr(II)–Co(III) reactions extends to other redox systems, we have prepared, characterized, and quantified the acid-catalyzed aquation of thiolatobis(ethylenediamine)chromium(III) complexes[6] which are analogous to the thiolatobis(ethylenediamine)cobalt(III) complexes

Table I. Absorption Spectra (200–700 nm) of Selected Chromium(III) Complexes[a]

	Visible				Ultraviolet	
Complex	A λ_{sh}	B λ_{max}	λ_{min}	C λ_{max}	D λ_{max}	E λ_{max}
$[Cr(en)_2(SCH_2COO)]^+$ [b]	–	500	442	385	310	250
		(99)	(46)	(91)	(1000)	(7440)
$[Cr(en)_2(H_2O)(OOCCH_2SH)]^{2+}$ [b]	–	488	418	370	–[e]	–
		(89)	(21)	(51)		
$[Cr(en)_2(SC_6H_4COO)]^+$ [b]	–	524	448	–	332	240
		(133)	(42)		(2864)	(15200)
$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ [b]	560	468	406	–	316	256
	(39)	(99)	(63)		(1100)	(7600)
$[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$ [b]	–	474	407	354	–[f]	–
		(68)	(18)	(61)		
$[Cr(en)_2(OOCCOO)]^+$ [c]	–	495	416	370		
		(97)	(23)	(87)		
$[Cr(OH_2)_4(SCH_2COO)]^+$ [b]	–	548	490	437	–	262
		(70)	(36)	(55)		(5270)
$[Cr(OH_2)_4(SC_6H_4COO)]^+$ [b]	–	565	503	–	340	260 (sh)
		(56)	(23)		(1800)	(7500)
$[Cr(OH_2)_4(OOCCOO)]^+$ [d]	–	556		418		
		(35)		(40)		

[a] Wavelengths in nm; values inside parentheses are molar extinction coefficients ϵ (F^{-1} cm^{-1}); – signifies no band observed in that region (A, B, C, D, or E), while no entry signifies no band has been reported in that region. [b] This work. Stereochemistry of second and fifth entries is assumed to be cis. Spectra were recorded in aqueous perchlorate solutions of pH <3. The estimated error in ϵ is <5%. [c] Reference 25. [d] H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968). [e] $\epsilon < 20\ F^{-1}$ cm^{-1} at 310 nm. [f] $\epsilon < 20\ F^{-1}$ cm^{-1} at 316 nm.

studied by Bennett.[2,7,8] This paper then describes the reaction of these, and other, chromium(III) complexes with chromium(II) in aqueous perchloric acid media. Some differences between the Cr(II)–Co(III) and Cr(II)–Cr(III) systems are noted, and the bridging efficiencies of thiolato sulfur in the two systems are compared.

Experimental Section

Materials. Common laboratory chemicals, doubly distilled water, doubly distilled perchloric acid, and purified Dowex 50W-X2 ion exchange resin were obtained as previously described.[6] Lithium perchlorate, hexaaquochromium(III) perchlorate, and *p*-aminophenyl disulfide were purified as described previously.[9,10] Solutions of chromium(II) perchlorate were prepared by reduction with zinc amalgam as previously described.[9] Solutions of zinc perchlorate were prepared by treating a weighed amount of 99.999% zinc metal with a known volume of standardized perchloric acid and diluting to the desired volume. ***O,S*-Mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate**, ***N,S*-2-mercaptoethylamine)bis(ethylenediamine)chromium(III) perchlorate**, and ***O,S*-(2-mercaptobenzoato)bis(ethylenediamine)chromium(III) perchlorate** were available from previous studies.[6,11] **Oxalatobis(ethylenediamine)chromium(III) perchlorate** was prepared by a literature procedure;[12a] the spectral properties of this material were in good agreement with those previously reported.[12b] Anal. Calcd for $[Cr(en)_2(OOCCOO)]ClO_4$: C, 20.03; H, 4.49; N, 15.58; Cr, 14.45. Found: C, 19.62; H, 4.87; N, 15.12; Cr, 14.42.

Analyses. Elemental analyses of solid compounds were performed by PCR Inc. of Gainesville, Fla. Determinations of total chromium concentrations, as well as standardizations of both perchloric acid and lithium perchlorate solutions, were done as previously described.[6,9]

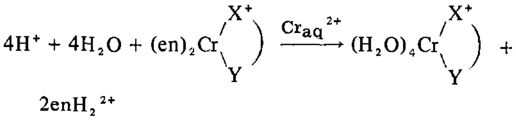
Equipment. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer at room temperature. Kinetic experiments were performed on either a Cary Model 14 or a Cary Model 16K spectrophotometer, both instruments being equipped with thermostated cell compartments that maintained the temperature of reactant solutions to better than ±0.2°. Standard linear and nonlinear least-squares calculations were conducted on an IBM System 360 located at the University of Chicago Computation Center.[13]

Kinetic Measurements. Unless specified otherwise, kinetic experiments were performed in aqueous perchloric acid solutions that were maintained at constant ionic strength 1.00 ± 0.01 or 4.00 ± 0.04 *F* with $LiClO_4$. Reactions were carried out under a nitrogen atmosphere using syringe techniques that have been previously described,[9] and precautions appropriate to the light sensitivity of the chromium(III) complexes were taken at all times. Reaction rates were monitored spectrophotometrically at an absorption maximum of the chromium(III) complex: 500 nm for $[Cr(en)_2(SCH_2COO)]^+$; 468 nm for $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$; 524 nm for $[Cr(en)_2(SC_6H_4COO)]^+$; 495 nm for $[Cr(en)_2(OOCCOO)]^+$. All reactions were monitored for at least 2 half-lives.

Calculations. Chromium(II)-catalyzed aquation of the initial reaction products, as well as in some cases acid-catalyzed aquation of the starting material, often prevented the experimental determination of A_∞, the absorbance at infinite time. Hence all A_t–t data were treated by the exponential form of the Guggenheim procedure (Kezdy time-lag method)[14] as previously described[6] to yield values of k_{obsd} and σ_k (the observed first-order rate constant and its standard deviation) for a given reaction. In several experiments the time interval used in the Kezdy procedure was varied over a wide range (0.5–2.5 half-lives), resulting in no significant variation in the calculated value of k_{obsd}. For each system under study it was possible to find a set of reaction conditions which resulted in an experimentally determinable value of A_∞; linearity of ln $(A_t - A_\infty)$ vs. t plots for these experiments verifies the first-order character of these reactions and justifies the use of the Kezdy procedure. Values of k_{obsd} obtained from these first-order plots agreed to within 2% of the values of k_{obsd} obtained from the Kezdy analysis of the same A_t–t data. In subsequent calculations, individual values of k_{obsd} were weighted as $1/\sigma_k^2$. All errors reported in this paper are standard deviations unless otherwise noted.

Results

Stoichiometry. On the time scale of interest in this paper, the net chemical reaction engendered by adding chromium(II) to aqueous perchloric acid solutions of $[Cr(en)_2(SCH_2COO)]^+$, $[Cr(en)_2(SC_6H_4COO)]^+$, or $[Cr(en)_2(OOCCOO)]^+$ may be represented by the following equation:



$$4H^+ + 4H_2O + (en)_2Cr\left(\begin{matrix} X^+ \\ Y \end{matrix}\right) \xrightarrow{Cr_{aq}^{2+}} (H_2O)_4Cr\left(\begin{matrix} X^+ \\ Y \end{matrix}\right) + 2enH_2^{2+} \qquad (1)$$

where X–Y represents either $[OOCCOO]^{2-}$, $[SCH_2COO]^{2-}$, or $[SC_6H_4COO]^{2-}$. The chromium(III) products of this reaction behave as 1+ species on Dowex 50W-X2 cation exchange resin and are further characterized by their visible–uv spectra which are given in Table I. The spectra recorded for mercaptoacetatotetraaquochromium(III) and oxalatotetraaquochromium(III) are in good agreement with those previously reported for these ions,[15,16] and the spectrum recorded for (2-mercaptobenzoato)tetraaquochromium(III) is wholly consistent with its proposed formulation. The ultraviolet bands observed in the 240–340 nm region (Table I) for all starting material and product thiolato–chromium(III) complexes are

Table III. Calculated Second-Order Rate Parameters for the Reaction of $[Cr(en)_2(SCH_2COO)]^+$ with Chromium(II) as a Function of $[H^+]$, μ, and Temperature[a,b]

$\mu = 1.00\ F$, T 11.2° [c]		$\mu = 1.00\ F$, T 14.5° [d]		$\mu = 4.00\ F$, T 25.0° [e]		$\mu = 1.00\ F$, T 25.0° [f]		$\mu = 1.00\ F$, T 39.7° [g]	
$[H^+]$, F	10^3k_{Cr}, F^{-1} sec^{-1}	$[H^+]$, F	10^3k_{Cr}, F^{-1} sec^{-1}	$[H^+]$, F	10^2k_{Cr}, F^{-1} sec^{-1}	$[H^+]$, F	10^3k_{Cr}, F^{-1} sec^{-1}	$[H^+]$, F	10^3k_{Cr}, F^{-1} sec^{-1}
0.066	0.834	0.066	0.772	0.207	2.1	0.066	2.35	0.135	9.03
0.134	1.21	0.135	1.74	0.207	2.1	0.066	2.08	0.204	13.4
0.204	1.56	0.204	2.06	0.207	2.3	0.134	4.48	0.204	13.7
0.269	2.10	0.270	2.70	0.99	3.9	0.204	6.06	0.270	16.3
0.336	3.07	0.336	3.33	0.99	3.4	0.204	5.99	0.270	14.3
0.336	3.04			1.99	3.6	0.269	7.72	0.336	20.3
				1.99	4.2	0.336	7.59	0.336	19.3
				2.75	4.0	0.336	8.41		
				2.75	5.1				
				3.55	6.3				
				3.55	6.1				
				3.55	6.8				

[a] $k_{Cr} = (k_{obsd} - k_{acid})/[Cr(II)]$; k_{obsd} and [Cr(II)] taken from Table II. [b] At $\mu = 1.00\ F$, the error in $k_{Cr} \simeq 3\%$; at $\mu = 4.00\ F$, the error in $k_{Cr} \simeq 14\%$. [c] $k_{acid} = (2.63[H^+] + 0.056) \times 10^{-4}$ sec^{-1} (ref 6). [d] $k_{acid} = (3.70[H^+] + 0.077) \times 10^{-4}$ sec^{-1} (ref 6). [e] $k_{acid} = [H^+]/(94[H^+] + 108)$ sec^{-1} (ref 6). [f] $k_{acid} = (1.11[H^+] + 0.025) \times 10^{-3}$ sec^{-1} (ref 6). [g] $k_{acid} = (3.98[H^+] + 0.078) \times 10^{-3}$ sec^{-1} (ref 6).

to be especially noted; these bands are assigned as ligand-to-metal charge transfers[11] and are characteristic of the Cr–S bond. Since the electron transfer reactions represented by eq 1 do not involve the net destruction of Cr–S bonds, but rather the aquation of four Cr–N bonds, they were monitored in the visible region of the spectrum at wavelengths sensitive to the conversion of Cr–N to Cr–O bonds (see Experimental Section and Table I).

Subsequent aquation of the chelated tetraaquochromium(III) products of reaction 1 is catalyzed by both chromium(II) and acid[9,15] and it is therefore difficult to define quantitatively the stoichiometry of this reaction. However, ion exchange analysis of an experiment in which excess $[Cr_{aq}]^{2+}$ was quenched with *p*-aminophenyl disulfide[10,17] establishes that the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ reaction proceeds *at least* 80% by the stoichiometry indicated in eq 1.

The stoichiometry of the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ reaction is even more difficult to define quantitatively because acid-catalyzed aquation of the starting material is competitive with the electron transfer reaction. However, the visible spectra of the reaction products are sufficiently distinct so that the two reaction paths may be qualitatively distinguished. Thus, in an experiment with $[Cr(II)] = 0.186\ F$, $[[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}] = 0.008\ F$, $[H^+] = 0.151\ F$, and $\mu = 1.00\ F$, as the spectral features of the starting material decay spectral features characteristic of aquochromium(III) species appear, indicating that the electron transfer reaction predominates. When the experiment is conducted with identical metal ion concentrations but $[H^+] = 3.15\ F$ and $\mu = 4.00\ F$, spectral features characteristic of $[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$ (see Table I) appear as the starting material disappears, indicating that acid-catalyzed aquation predominates. After ca. 30 hr the spectrum of the first product mixture is essentially that of $[Cr(H_2O)_6]^{3+}$ while the spectrum of the second product mixture is primarily that of $[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$ with very slow reactions still proceeding. The implications of these observations will be discussed later.

Kinetics of the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ Reaction. As noted in the Experimental Section, in this reaction the chromium(III) starting material disappears in a first-order fashion. Table II[18] lists the first-order specific rate constants (k_{obsd}) observed for this reaction as a function of temperature, ionic strength, $[H^+]$ and [Cr(II)]. At $\mu = 1.00\ F$, 25°, $[H^+] = 0.316\ F$, a plot of k_{obsd} vs. [Cr(II)] is linear over the range $[Cr(II)] = 0.024–0.121\ F$; a weighted linear least-squares treatment of these data yields a slope of $8.03 \pm 0.42 \times 10^{-3}\ F^{-1}$ sec^{-1} and an intercept of $0.35 \pm 0.03 \times 10^{-3}$ sec^{-1}. The intercept term is in excellent agreement with the value of the acid-catalyzed aquation rate constant ($k_{acid} = 0.37 \times 10^{-3}$ sec^{-1}) calculated for these conditions from parameters reported previously[6] and thus may be taken to reflect competitive acid-catalyzed aquation. The observed rate law for the $[Cr_{aq}]^{2+}$–$[Cr(en)_2)(SCH_2COO)]^+$ reaction may therefore be expressed as

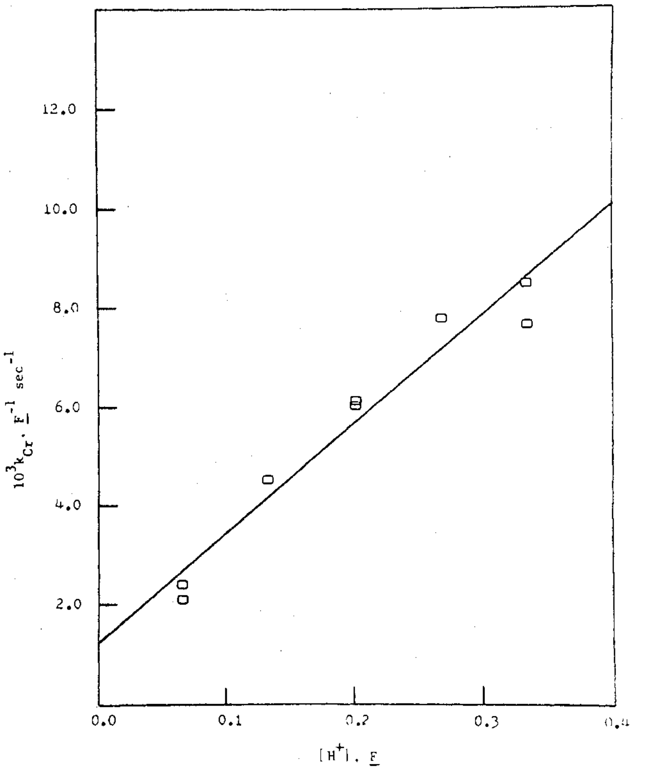


Figure 1. Plot of $10^3 \times k_{Cr}$ (F^{-1} sec^{-1}) vs. $[H^+]$ (F) for the reaction of chromium(II) with $[Cr(en)_2(SCH_2COO)]^+$ at 25°, $\mu = 1.00\ F$. Data taken from Table III.

$$-d(\ln[Cr(en)_2(SCH_2COO)])/dt = k_{obsd} = k_{Cr}[Cr(II)] + k_{acid} \qquad (2)$$

Table III lists values of k_{Cr} calculated from the data of Table II, the known values of k_{acid}[6] (as a function of $[H^+]$, ionic strength, and temperature), and the expression

$$k_{Cr} = (k_{obsd} - k_{acid})/[Cr(II)] \qquad (3)$$

For each of the temperatures studied at $\mu = 1.00\ F$, plots of k_{Cr} vs. $[H^+]$ are linear over the range $[H^+] = 0.066–0.336$

Table IV. Acid Dependence of the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SCH_2COO)}]^+$ Reaction at $\mu = 1.00\ F$ as a Function of Temperature ($k_{\mathrm{Cr}} = a + b[\mathrm{H^+}]$)

t, °C	$10^3 b$, F^{-2} sec^{-1}	$10^3 a$, F^{-1} sec^{-1}
11.2	8.34 ± 0.90	0.1 ± 0.2
14.5	8.99 ± 0.74	0.30 ± 0.16
25.0	21.7 ± 2.1	1.2 ± 0.5
39.7	50.1 ± 5.6	2.6 ± 1.5

F (see Figure 1) and therefore

$$k_{\mathrm{Cr}} = a + b[\mathrm{H^+}] \qquad (4)$$

Table IV lists values of a and b obtained from linear least-squares analyses of the k_{Cr}–$[\mathrm{H^+}]$ data at $\mu = 1.00\ F$. At $\mu = 4.00\ F$ the contribution of k_{acid} to k_{obsd} is larger than at $\mu = 1.00\ F$, resulting in a relatively larger error in the derived values of k_{Cr}. Thus, at $\mu = 4.00\ F$ the average error associated with k_{Cr} (calculated by the usual procedure for propagating errors) is 14% of its value as listed in Table III. Analysis of these data will be presented later.

Direct calculation of activation parameters (at $\mu = 1.00\ F$) within the four-parameter Eyring expression

$$k_{\mathrm{Cr}} = \frac{(kT)}{h}\,[e^{\Delta S_a{}^*/R} e^{-\Delta H_a{}^*/RT} + [\mathrm{H^+}] e^{\Delta S_b{}^*/R} e^{-\Delta H_b{}^*/RT}] \qquad (5)$$

is precluded by the large standard errors associated with the a terms (see Table IV). Therefore $\Delta H_a{}^*$ and $\Delta S_a{}^*$ have been estimated graphically ($\Delta H_a{}^* = 18.4$ kcal/mol, $\Delta S_a{}^* = -10.5$ eu) and held fixed while $\Delta H_b{}^*$ and $\Delta S_b{}^*$ are varied within eq 5. This procedure leads to values of $\Delta H_b{}^* = 9.4 \pm 0.5$ kcal/mol and $\Delta S_b{}^* = -34.8 \pm 1.6$ eu, the average deviation between calculated and observed values of k_{Cr} being 12%.

The internal consistency of the above procedures may be gauged by the following observation: the value of k_{Cr} calculated at $[\mathrm{H^+}] = 0.316\ F$ from the values of a and b given in Table IV (25°, $\mu = 1.00\ F$, $k_{\mathrm{Cr}} = (21.7[0.316] + 1.2) \times 10^{-3} = 8.0 \times 10^{-3}\ F^{-1}\ \mathrm{sec^{-1}}$) is in excellent agreement with the value of the slope found in the k_{obsd} vs. [Cr(II)] plot described earlier ($k_{\mathrm{Cr}} = 7.9 \pm 0.5 \times 10^{-3}\ F^{-1}\ \mathrm{sec^{-1}}$ at 25°, $\mu = 1.00\ F$, $[\mathrm{H^+}] = 0.316\ F$).

Kinetics of the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ Reaction. As noted in the Experimental Section, in this reaction the chromium(III) starting material disappears in a first-order fashion. Table V[18] lists the first-order specific rate constants (k_{obsd}) observed for this reaction as a function of ionic strength, $[\mathrm{H^+}]$, and [Cr(II)]. At $\mu = 1.00\ F$, 25°, $[\mathrm{H^+}] = 0.202\ F$, a plot of k_{obsd} vs. [Cr(II)] is linear over the range [Cr(II)] = 0.023–0.172 F; linear least-squares treatment of these data yields a slope of $11.2 \pm 0.4 \times 10^{-5}\ F^{-1}\ \mathrm{sec^{-1}}$ and an intercept of $0.55 \pm 0.05 \times 10^{-5}\ \mathrm{sec^{-1}}$. The intercept term is again taken to reflect competitive acid-catalyzed aquation and thus the observed rate law for the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ reaction may be expressed as

$$-\mathrm{d}(\ln\ [\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}])/\mathrm{d}t = k_{\mathrm{obsd}} = k_{\mathrm{Cr}}[\mathrm{Cr(II)}] + k_{\mathrm{acid}} \qquad (6)$$

Table VI lists values of k_{Cr} calculated from the data of Table V[18] and known values of k_{acid} by means of eq 3: at $\mu = 4.00$, values of k_{acid} (given in a footnote of Table VI) have been experimentally determined by substituting an equivalent amount of zinc perchlorate for the chromous perchlorate used in the redox reactions; at $\mu = 1.00\ F$, values of k_{acid} have been calculated using an expression which is given in a footnote of Table VI and which will be discussed later. The errors associated with the values of k_{Cr} in Table VI have been calculated by the usual procedure for propagating errors.

Table VI. Calculated Second-Order Rate Parameters for the Reaction of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ with Chromium(II) at 25° as a Function of $[\mathrm{H^+}]$ and μ[a,b]

$\mu = 1.00\ F$, T 25°		$\mu = 4.00\ F$, T 25°	
$[\mathrm{H^+}]$, F	$10^5 k_{\mathrm{Cr}}$,[c] F^{-1} sec^{-1}	$[\mathrm{H^+}]$, F	$10^5 k_{\mathrm{Cr}}$,[d] F^{-1} sec^{-1}
0.10	10.4 ± 2.0	0.50	7.7 ± 0.2
0.20	10.5 ± 2.0	0.90	7.1 ± 0.2
0.35	10.4 ± 2.1	1.30	7.2 ± 0.2
0.55	10.6 ± 2.1	1.70	7.1 ± 0.2
0.66	6.7 ± 2.2	2.07	6.5 ± 0.1
0.79	5.8 ± 2.2		

[a] $k_{\mathrm{Cr}} = (k_{\mathrm{obsd}} - k_{\mathrm{acid}})/[\mathrm{Cr(II)}]$. [b] k_{obsd} and [Cr(II)] taken from Table V. [c] $k_{\mathrm{acid}} = (7.61[\mathrm{H^+}] + 4.0) \times 10^{-6}\ \mathrm{sec^{-1}}$ (ref 6). [d] Values of $10^5 \times k_{\mathrm{acid}}$ determined at the five tabulated acidities ($\mu = 4.00\ F$, $[\mathrm{Zn(II)}] = 0.64\ F$, $[\mathrm{ClO_4^-}] = 3.36\ F$, initial $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}] = 8.65 \times 10^{-4}$, monitored at 316 nm) are, in order of increasing $[\mathrm{H^+}]$, 2.21 ± 0.02, 3.28 ± 0.02, 4.25 ± 0.03, 5.21 ± 0.03, and 6.17 ± 0.03.

Table VII. Observed and Calculated Rate Parameters for the Reaction of $[\mathrm{Cr(en)_2(SC_6H_4COO)}]^+$ with Chromium(II) as a Function of $[\mathrm{H^+}]$[a]

$[\mathrm{H^+}]$, F	$10^5 \times k_{\mathrm{acid}}$, sec^{-1}	$10^5 \times k_{\mathrm{obsd}}$,[b] sec^{-1}	$10^4 \times k_{\mathrm{Cr}}$,[c] F^{-1} sec^{-1}
0.178	0.20 ± 0.08	4.01 ± 0.08	5.4 ± 0.2
0.329	0.58 ± 0.04	6.14 ± 0.06	7.9 ± 0.1

[a] Conditions: 25°, $\mu = 1.00\ F$. [b] Initial concentration of $[\mathrm{Cr(en)_2(SC_6H_4COO)}]^+ = 0.91 \times 10^{-3}\ F$; kinetics monitored at 524 nm; $[\mathrm{Cr(II)}] = 0.0705\ F$; total perchlorate concentration = 0.923 F. [c] $k_{\mathrm{Cr}} = (k_{\mathrm{obsd}} - k_{\mathrm{acid}})/[\mathrm{Cr(II)}]$.

At $\mu = 1.00\ F$, k_{Cr} shows no acid dependence within the limits of error and thus

$$k_{\mathrm{Cr}} = a \qquad (7)$$

The average value of k_{Cr} (neglecting those values determined at the two highest acid concentrations where more than 75% of the observed reaction proceeds by acid-catalyzed aquation) for the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ reaction is 10.5 ± 2.4[19] $\times 10^{-5}\ F^{-1}\ \mathrm{sec^{-1}}$ (25°, $\mu = 1.00\ F$). This value is in good agreement with the value of $k_{\mathrm{Cr}} = 11.2 \pm 0.4 \times 10^{-5}\ F^{-1}\ \mathrm{sec^{-1}}$ (25°, $\mu = 1.00\ F$) obtained from the slope of the k_{obsd}–[Cr(II)] plot described earlier. Accepting the acid independence of this reaction, the latter value is more reliable by the nature of its origins.

At $\mu = 4.00\ F$, k_{Cr} decreases slightly with increasing $[\mathrm{H^+}]$ (see Table VI). A weighted linear least-squares analysis of these k_{Cr}–$[\mathrm{H^+}]$ data yields a slope = $-0.69 \pm 0.15 \times 10^{-5}\ F^{-2}\ \mathrm{sec^{-1}}$ and an intercept = $8.00 \pm 0.25 \times 10^{-5}\ F^{-1}\ \mathrm{sec^{-1}}$. From these values it is clear that the bulk of the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ reaction at $\mu = 4.00\ F$ proceeds via an acid-independent path. The large relative standard error associated with the slope (±22%) precludes it being used alone to assign an acid-dependent path, much less the form of this acid dependence.

Kinetics of the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(SC_6H_4COO)}]^+$ Reaction. This reaction has been briefly examined to determine whether or not it is facilitated by acid. The rate law is assumed to be analogous to that given in eq 2. Table VII lists the experimentally determined values of k_{obsd} and k_{acid} and the values of k_{Cr} calculated by means of eq 3. From these limited data it can be seen that k_{Cr} increases with $[\mathrm{H^+}]$. If the form of this dependence is assumed to be that of eq 4, then $a = 0.25 \pm 0.06 \times 10^{-3}\ F^{-1}\ \mathrm{sec^{-1}}$ and $b = 1.6 \pm 0.2 \times 10^{-3}\ F^{-2}\ \mathrm{sec^{-1}}$ where the indicated errors are calculated by the usual propagation procedures, but should be taken only as crude estimates of the true errors because of the limited number of data points used.

Kinetics of the $[\mathrm{Cr_{aq}}]^{2+}$–$[\mathrm{Cr(en)_2(OOCCOO)}]^+$ Reaction. As

Table VIII. Observed and Calculated Rate Parameters for the Reaction of $[Cr(en)_2(OOCCOO)]^+$ with Chromium(II) as a Function of [Cr(II)] and $[H^+]$[a]

[Cr(II)],[b] F	$10^4 \times k_{obsd}$, sec^{-1}	$[H^+]$,[c] F	$10^4 \times k_{obsd}$, sec^{-1}	$10^3 \times k_{Cr}$,[d] F^{-1} sec^{-1}
0.023	1.00 ± 0.02	0.20	1.78 ± 0.02	2.92 ± 0.15
0.046	1.78 ± 0.02	0.35	2.12 ± 0.06	3.66 ± 0.19
0.093	3.30 ± 0.04	0.55	2.34 ± 0.03	4.13 ± 0.17
0.139	4.73 ± 0.15	0.79	2.39 ± 0.05	4.24 ± 0.19
0.139	4.31 ± 0.02			
0.177	5.45 ± 0.15			
0.177	5.31 ± 0.06			

[a] Conditions: 25°, $\mu = 1.00$ F, initial concentration of $[Cr(en)_2(OOCCOO)]^+ \simeq 1 \times 10^{-3}$ F, kinetics monitored at 500 nm. [b] $[H^+] = 0.202$ F. [c] $[Cr(II)] = 0.0465$ F; total perchlorate concentration = 0.93 F. [d] $k_{Cr} = (k_{obsd} - k_{acid}')/[Cr(II)]$ were k_{acid}' is approximated as $(0.42 \pm 0.07) \times 10^{-4}$ sec^{-1} independent of $[H^+]$.

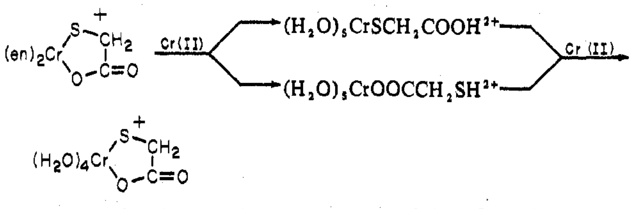
noted in the Experimental Section, in this reaction the chromium(III) starting material disappears in a first-order fashion. Table VIII lists the first-order specific rate constants (k_{obsd}) observed for this reaction as a function of $[H^+]$ and [Cr(II)]. At $\mu = 1.00$ F, 25°, $[H^+] = 0.202$ F, a plot of k_{obsd} vs. [Cr(II)] is linear over the range 0.023–0.177 F; a weighted linear least-squares treatment of these data yields a slope = $2.82 \pm 0.08 \times 10^{-3}$ F^{-1} sec^{-1} and an intercept = $0.042 \pm 0.007 \times 10^{-3}$ sec^{-1}. The intercept term is again taken to represent a competitive acid-catalyzed aquation path. Therefore the observed rate law for the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(OOCCOO)]^+$ reaction may be expressed as

$$-d(\ln [Cr(en)_2(OOCCOO)])/dt = k_{obsd} = k_{Cr}[Cr(II)] + k_{acid}' \qquad (8)$$

Table VIII also lists estimated values of k_{Cr} which are calculated as $(k_{obsd} - k_{0.202}')/[Cr(II)]$ where $k_{0.202}' = 4.2 \pm 0.7 \times 10^{-5}$ sec^{-1}, the value of k_{acid}' at $[H^+] = 0.202$ F. A weighted linear least-squares analysis of these k_{Cr}–$[H^+]$ data yields a slope = $2.32 \pm 0.66 \times 10^{-3}$ F^{-2} sec^{-1} and an intercept = $2.63 \pm 0.33 \times 10^{-3}$ F^{-1} sec^{-1}. Since the contribution to the total rate from the slope term ranges from only 15% at $[H^+] = 0.20$ F to 41% at $[H^+] = 0.79$ F, and since a portion of this slope term must arise from the acid dependence of k_{acid}' (for which we have not corrected), it is clear that the bulk of the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(OOCCOO)]^+$ reaction proceeds via an acid-independent path.

Discussion

The $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ Reaction. This reaction proceeds predominantly by bridged electron transfer. However, the stoichiometry of eq 1 does not determine whether it is the thiolato or the carboxylato group which functions as the initial electron transfer bridge since subsequent chelate closure converts both possible initial products to the same final product:



The predominant kinetic feature of the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ reaction is the dependence of k_{Cr} on $[H^+]$. Any rationale proposed to account for this acid dependence must be consistent both with the results obtained in this work and with the evidence and parameters previously reported[6] for the acid-catalyzed aquation of $[Cr(en)_2(SCH_2COO)]^+$. One such rationale is provided by the following scheme which involves the same rapid prior protonation of $[Cr(en)_2(SCH_2COO)]^+$ that was invoked in the acid-catalyzed aquation studies[6] (Scheme I).

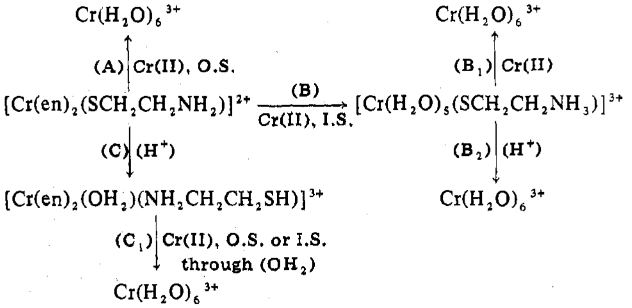
Scheme I

$$H^+ + Cr(en)_2(SCH_2COO)^+ \xrightarrow{1/K_a} [Cr(en)_2(SCH_2COO)H]^{2+}$$

$$Cr^{2+} + Cr(en)_2(SCH_2COO)^+ \xrightarrow{k_1} \text{products}$$

$$Cr^{2+} + [Cr(en)_2(SCH_2COO)H]^{2+} \xrightarrow{k_2} \text{products}$$

Scheme II



The formula $[Cr(en)_2(SCH_2COO)H]^{2+}$ represents the protonated form of the starting material, protonation possibly occurring at either of the carboxylate oxygens or at the coordinated sulfur. Scheme I leads directly to the rate expression

$$\frac{1}{[Cr(II)]} \frac{-d(\ln [Cr_T])}{dt} = k_{Cr} = \frac{k_1 + k_2[H^+]/K_a}{1 + [H^+]/K_a} \qquad (9)$$

where $[Cr_T]$ represents the total concentration of chromium(III) starting material in all forms. Equation 9 shows that k_{Cr}–$[H^+]$ plots will be linear if $[H^+]/K_a$ is small with respect to one and this is observed at all temperatures when $\mu = 1.00$ F. Correspondingly, at $\mu = 1.00$ F, the acid-catalyzed aquation is also linearly dependent on $[H^+]$.[6] Thus, the form of eq 9 appropriate to unit ionic strength is

$$k_{Cr} = k_1 + (k_2/K_a)[H^+]$$

and from eq 4, $a = k_1$ and $b = k_2/K_a$.

At $\mu = 4.00$ F, protonation of cationic complexes is more favorable than at $\mu = 1.00$ F.[6,9,20] Acid-catalyzed aquation[6] of $[Cr(en)_2(SCH_2COO)]^+$ becomes less than first order in $[H^+]$ at $\mu = 4.00$ F, presumably because a prior protonation equilibrium is being saturated at high concentrations of acid; the value of K_a determined from the acid-catalyzed aquation study[6] is 1.15 ± 0.12 F (25°, $\mu = 4.00$ F), it being uncertain whether protonation occurs at the thiolato or at the carboxylato group. The k_{Cr}–$[H^+]$ data given in Table III for $\mu = 4.00$ F are too imprecise (average error in k_{Cr} is ±14% due to large contributions of k_{acid} to k_{obsd}) and too limited in range (again due to competition from k_{acid}) to directly reflect saturation of a protonation equilibrium with $K_a = 1.15$ F. However, Scheme I demands that if saturation occurs in the acid-catalyzed aquation studies, then saturation must also occur in the redox studies, no matter which site is protonated. By taking $K_a = 1.15$ F, eq 9 may be rewritten as

$$k_{Cr}(1 + [H^+]/1.15) = k_1 + (k_2/K_a)[H^+] \qquad (9b)$$

and a plot of k_{Cr} $(1 + [H^+]/1.15)$ vs. $[H^+]$ at $\mu = 4.00$ F yields a slope = $(k_2/K_a) = 6.7 \pm 0.6 \times 10^{-2}$ F^{-2} sec^{-1} (25°). This slope is larger than the corresponding value (2.2×10^{-2} F^{-2} sec^{-1}; see Table IV) observed at $\mu = 1.00$, as expected.

The $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ Reaction. It is convenient to discuss the stoichiometry of this reaction in terms of Scheme II which delineates the major paths available for conversion of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ into $[(H_2O)_6Cr]^{3+}$

Table IX. Rate Parameters for the Reaction of Various Oxalatochromium(III) Complexes with Chromium(II) at 25° [a]

	μ, F	k, F^{-1} sec^{-1}
$[Cr(en)_2(OOCCOO)]^+$ [b]	1.0	2.8×10^{-3}
$[Cr(NH_3)_4(OOCCOO)]^+$ [c]	1.0	6.4×10^{-3}
$[Cr(H_2O)_4(OOCCOO)]^+$ [d]	2.0	1.3×10^{-1}
trans-$[Cr(H_2O)_2(OOCCOO)_2]^-$ [e]	1.2	1.1×10^{-1}
$[Cr(OOCCOO)_3]^{3-}$ [e]	1.2	1.3×10^{-1}

[a] The reactions follow the rate law $-d[Cr(III)]/dt = k[Cr(III)] \cdot [Cr(II)]$. [b] This work. [c] Reference 23. [d] T. Spinner and G. M. Harris, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1968, Paper INOR-36. [e] D. H. Huchital, *Inorg. Chem.*, 9, 486 (1970).

in the presence of acid and chromium(II). Reactions A and B are electron transfer processes, outer sphere (O.S.) and inner sphere (I.S.), respectively. Reaction C is acid-catalyzed aquation of the Cr–S bond, and it has been investigated independently.[6] Under conditions of high acid, high ionic strength, the primary reaction product is $[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$ and thus reaction C_1 destroys a negligible amount of this aquation product in a period of time which is sufficient at low acid, low ionic strength for most of the starting material to be converted to $[(H_2O)_6Cr]^{3+}$ (see Results section). Therefore reaction C_1 is slower than the initial electron transfer process, either A or B, which leads to $[(H_2O)_6Cr]^{3+}$ at low acid, low ionic strength. Since it is unreasonable that C_1 be significantly slower than A, this leaves path B as the reaction that destroys starting material at low acid, low ionic strength. Apparently initial electron transfer proceeds through a sulfur bridge and when acid-catalyzed aquation cleaves the Cr–S bond, there is no longer an efficient bridging group to mediate electron transfer. The inner sphere redox product, $[(H_2O)_5Cr(SCH_2CH_2NH_3)]^{3+}$, is not observed because under all conditions it is destroyed by the combined effect of B_2[20] and B_1[9,21] at least an order of magnitude faster than it is produced by reaction B. Thus, $[(H_2O)_6Cr]^{3+}$ is the only detectable redox product.

At $\mu = 1.00$ F, k_{Cr} for the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ reaction is independent of $[H^+]$ over the range $[H^+] = 0.10$–0.98 F. This implies that, unlike the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ reaction, there is no rate advantage gained by protonating the chromium(III) center. In fact, two pieces of evidence suggest that protonation of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ actually inhibits the rate of electron transfer: (a) by increasing the ionic strength to 4.00 F, protonation of the coordinated sulfur is favored[6] and the average value of k_{Cr} becomes *smaller* than that determined at $\mu = 1.00$ F; (b) at $\mu = 4.00$ F, k_{Cr} decreases slightly with increasing $[H^+]$. Analogous inhibition of an inner sphere electron transfer by prior protonation of the bridge has previously been reported[22] for the $[Cr_{aq}]^{2+}$–$[(NH_3)_5CoOOCCH_3]^{2+}$ reaction.

The $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SC_6H_4COO)]^+$ Reaction. Although only briefly investigated, it is clear that the rate of this reaction increases with increasing $[H^+]$. This effect is analogous to, but somewhat smaller than, that observed in the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ system. Acid-catalyzed electron transfer is therefore not limited to the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ system.

The $[Cr_{aq}]^{2+}$–$[Cr(en)_2(OOCCOO)]^+$ Reaction. This reaction is predominantly independent of $[H^+]$ under the conditions investigated in this work. This observation is in agreement with Jordan's report[23] that the rate of the $[Cr_{aq}]^{2+}$–$[Cr(NH_3)_4(OOCCOO)]^+$ reaction is acid independent over the range $[H^+] = 0.1$–0.5 F. Table IX lists values of k_{Cr} obtained for several Cr(II)–Cr(III) oxalato systems. The ordering of rates suggests that the relatively inflexible chelated ethylenediamine provides a slightly larger barrier to electron transfer than does monodentate ammonia, and the strong field ammonia provides a much larger barrier than the weak field aquo ligand.[24-27] It is also interesting to note that the last three complexes in Table IX react at very similar rates despite their differences in formal charge.

Comparisons. In the acid-catalyzed path of the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2COO)]^+$ reaction, uncertainty as to the site of protonation and as to the identity of the bridging function leads to four possible configurations for the activated complex: (1) the proton may reside on sulfur and electron transfer may occur through a sulfur bridge; (2) the proton may reside on sulfur and electron transfer may occur through a carboxylate bridge; (3) the proton may reside on a carboxylate oxygen and electron transfer may occur through a carboxylate bridge; (4) the proton may reside on a carboxylate oxygen and electron transfer may occur through a sulfur bridge. Hypothesis (1) can be dismissed since no acid catalysis is observed in the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ reaction where an equivalent configuration is possible (and in fact the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ reaction rate seems to be inhibited by protonation at sulfur). Hypothesis (3) may also be dismissed since no such path is observed in the $[Cr_{aq}]^{2+}$–$[Cr(en)_2(OOCCOO)]^+$ reaction, and furthermore, protonation of $[Co(NH_3)_5OOCCH_3]^{2+}$ actually decreases its rate of reduction by chromium(II).[22] Hence only configurations (2) and (4) are rational possibilities, both of which imply a strong cis nonbridging ligand effect caused by protonation. Such effects induced by cis ligands are well documented.[24,28,29] The origin of this acid-catalyzed path is readily rationalized within the established theories of nonbridging ligand effects,[24-26] i.e., a protonated ligand provides a weaker ligand field than the unprotonated form and therefore offers a smaller barrier to Franck–Condon reorganization.[30,31] Both hypotheses (2) and (4) are consistent with these theories and at this time we cannot distinguish between them.

The rates of the chromium(II) reductions of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ and $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ [8] have been measured under identical conditions (25°, $\mu = 1.00$ F); both reactions are independent of $[H^+]$ under these conditions, and both have been shown to proceed via an inner-sphere mechanism. Therefore the relative ability of thiolato sulfur to bridge electron transfer from chromium(II) to either cobalt(III) or chromium(III) may be calculated directly as $k(Cr^{II}\text{–}Co^{III})/k(Cr^{II}\text{–}Cr^{III}) = 3 \times 10^8$. This and similar rate ratios for various bridging ligands, along with the individual $k(Cr^{II}\text{–}Co^{III})$ and $k(Cr^{II}\text{–}Cr^{III})$ values, are listed in Table X.

The data of Table X are, unfortunately, insufficient to directly determine whether the remarkable ability of thiolato sulfur to bridge electron transfer from chromium(II) to cobalt(III)[2,32] carries over to chromium(II)–chromium(III) reactions. However, the data are sufficient to allow two indirect arguments which indicate that it does not. (1) The rate of reduction of $[Co(en)_2(SCH_2COO)]^+$ is faster than any of the halo–cobalt(III) complexes, but the rate of reduction of the analogous chromium complex is not even as fast as the chloro–chromium(III) complexes. (The $[M(en)_2(SCH_2CH_2NH_2)]^{2+}$ complexes give no information in this context since both react slower than any of the corresponding halo–M(III) complexes.) (2) The ratio $k(Cr^{II}\text{–}Co^{III})/k(Cr^{II}\text{–}Cr^{III})$ for thiolato bridging is much larger than would be anticipated from the other ratios given in Table X; i.e., $k(Cr^{II}\text{–}Co^{III})/k(Cr^{II}\text{–}Cr^{III})$ decreases by two orders of magnitude on going from a fluoride bridge to a chloride bridge and in the absence of any special effect a similar decrease would be expected on going from an oxygen bridge to a sulfur bridge. However, $k(Cr^{II}\text{–}Co^{III})/k(Cr^{II}\text{–}Cr^{III})$ either stays the same or actually increases on going from oxygen[33] to sulfur (depending on which thiolato complex is used in the com-

Table X. Rate Data for the Inner Sphere Reduction of Various Cobalt(III) and Chromium(III) Complexes by Chromium(II) at 25° [a]

Oxidant	Bridging group	$k(\mathrm{Cr^{II}\text{-}Co^{III}})$	$k(\mathrm{Cr^{II}\text{-}Cr^{III}})$	R
$M(NH_3)_5F^{2+}$	F^-	9×10^5 [b]	2.7×10^{-4}	3×10^9
$M(NH_3)_5Cl^{2+}$	Cl^-	2.6×10^6 [b]	5.1×10^{-2} [c]	5×10^6
$M(NH_3)_5Br^{2+}$	Br^-	1.4×10^6 [b]	0.32[c]	5×10^6
$M(NH_3)_5I^{2+}$	I^-	3×10^6 [b]	5.5[c]	6×10^5
cis-$M(en)_2(H_2O)F^{2+}$	F^-	1.4×10^5 [d]		
cis-$M(en)_2(H_2O)Cl^{2+}$	Cl^-	3.8×10^5 [d]	1.2×10^{-2} [e]	3×10^7
cis-$M(en)_2Cl_2^+$	Cl^-	7.7×10^5 [d]	3.9×10^{-2} [e]	2×10^7
$M(NH_3)_5OH^{2+}$	OH^-	1.5×10^6 [f]	(5×10^{-3})[g]	(3×10^8)
$M(NH_3)_4(OOCCOO)^+$	Ox^{2-}	2.0×10^5 [h]	6.4×10^{-3}[i]	3×10^7
$M(en)_2(SCH_2CH_2NH_2)^{2+}$	RS^-	3.3×10^4 [j]	1.1×10^{-4} [k]	3×10^8
$M(en)_2(SCH_2COO)^+$	RS^-	6.4×10^6 [l]	$\leqslant 1.4 \times 10^{-3}$ [k,m]	$>5 \times 10^9$

[a] The reactions follow the rate law $-\mathrm{d}(\ln[\text{complex}])/\mathrm{d}t = k[\mathrm{Cr(II)}]$; k's are given in units of F^{-1} sec^{-1} and $R = k(\mathrm{Cr^{II}\text{-}Co^{III}})/k(\mathrm{Cr^{II}\text{-}Cr^{III}})$; $\mu = 1.00\ F$ except for $[Co(NH_3)_5Br]^{2+}$, $[Co(NH_3)_5I]^{2+}$, and $[Co(en)_2(SCH_2COO)]^+$ where $\mu = 0.10\ F$. [b] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965). [c] A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958). [d] R. C. Patel, R. E. Ball, J. F. Endicott, and G. Hughes, *Inorg. Chem.*, **9**, 23 (1970). [e] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966). [f] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959). [g] Estimated from comparisons of $[Cr_{aq}]^{2+}$–$[Cr(NH_3)_5X]^{2+}$ rates (footnote *c*) with those of $[\mathrm{Cr^{II}(EDTA)}(H_2O)_5X]^{2+}$ (H. Ogino and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **41**, 2411 (1968)) and $[Cr_{aq}]^{2+}[Cr(H_2O)_5X]^{2+}$ (F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1172 (1968)). The rates for $X = OH^-$ are known for the latter two reactions. [h] C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970). [i] Reference 23. [j] Reference 8. [k] This work. [l] Reference 32. [m] Calculated at $[H^+] = 0.01\ F$ and therefore essentially represents the acid-independent rate term; listed as an upper limit for RS^- bridging since the measured rate may reflect carboxylate bridging (vide supra).

parison) implying that a special effect *is* operative and $k(\mathrm{Cr^{II}\text{-}Co^{III}})$ is unusually larger than $k(\mathrm{Cr^{II}\text{-}Cr^{III}})$ when thiolato sulfur functions as the electron transfer bridge.

Results from recent structural determinations by Elder et al.[34] may in part explain why the remarkable bridging efficiency reported for thiolato sulfur in Cr(II)–Co(III) reactions does not carry over to the analogous Cr(II)–Cr(III) reactions. In both $[Co(en)_2(SCH_2COO)]^+$ and $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, the Co–N bond trans to sulfur is significantly longer than the average of the cis Co–N bond lengths, but this effect is not observed in the $[Cr(en)_2(SCH_2COO)]^+$ complex; therefore thiolato sulfur induces a significant ground state trans effect in the cobalt(III) complexes, but not in an analogous chromium(III) complex.[34] Since for reduction of both cobalt(III) and chromium(III) the trans ligand–metal bond must be elongated within the redox transition state[24,25,35] the thiolato–cobalt(III) ground state configuration would seem to require less activation in order to attain the transition state configuration than would the thiolato–chromium(III) ground state configuration. Thus, in the cobalt(III) complexes, the bridging thiolato sulfur may be viewed as inducing its own nonbridging ligand effect by means of its ground state weakening of the trans metal–ligand bond. Further studies are currently in progress to test the validity of this hypothesis linking trans effects with electron transfer rates, as well as to examine the origins and scope of trans effects (both ground state and kinetic) in octahedral complexes.

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Registry No. $[Cr(en)_2(SCH_2COO)]^+$, 41654-60-8; $[Cr(en)_2(H_2O)(OOCCH_2SH)]^{2+}$, 51922-33-9; $[Cr(en)_2(SC_6H_4COO)]^+$, 51922-73-7; $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, 48131-66-4; $[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$, 57128-69-5; $[Cr(en)_2(OOCCOO)]^+$, 21748-30-1; $[Cr(OH_2)_4(SCH_2COO)]^+$, 32696-60-9; $[Cr(OH_2)_4(SC_6H_4COO)]^+$, 57066-24-7; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Tables II and V, giving observed first-order rate parameters for the reaction of chromium(II) with $[Cr(en)_2(SCH_2COO)]^+$ and $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ as a function of μ, $[H^+]$, [Cr(II)], and temperature, two pages. Ordering information is given on any current masthead page.

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