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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2674.

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Synthesis, Characterization, and Aquation Kinetics of Thiolatobis(ethylenediamine)chromium(III) Complexes

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A general procedure for the synthesis of thiolatobis(ethylenediamine)chromium(III) complexes has been developed. These compounds exhibit an intense absorption in the near-ultraviolet spectrum which is characteristic of metal-sulfur bonding. The rates of aquation of two specific complexes, $[Cr(en)_2(SCH_2COO)]^+$ and $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, in aqueous perchloric acid media are reported as a function of acid concentration, ionic strength, and temperature. Aquation of both complexes is formulated as an approach to equilibrium between chelated and monodentate thiolato ligands, equilibrium being attained *via* the making and breaking of Cr-S bonds. This reaction proceeds predominantly through acid-catalyzed Cr-S bond fission, although the rates of acid-independent Cr-S and Cr-N bond cleavage are also competitive. The rates of Cr-S bond breaking are at least 10^4 times greater than the rates of Co-S bond breaking in the analogous cobalt(III) compounds $[Co(en)_2(SCH_2COO)]^+$ and $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$. This effect is in part attributed to the different Bronsted basicities of thiolato sulfur coordinated to cobalt(III) and chromium(III).

Introduction

Recent reports[1,2] that low-valent sulfur functions as a remarkably efficient bridge for electron transfer from chromium(II) to cobalt(III) have generated considerable interest in the chemistry of thiolato complexes of cobalt(III) and chromium(III).[3,4] In order to investigate the efficiency of electron transfer through a thiolato bridge to chromium(III), we have prepared certain thiolatobis(ethylenediammine)chromium(III) complexes by the reduction of organic disulfides with ethylenediamine-chromium(II) mixtures. Since these are the first examples of thiolatoamminechromium(III) compounds and because Cr^{III}-S bonds are well known to be more labile than Co^{III}-S bonds,[5] we felt it necessary to investigate thoroughly the thermal aquation of two specific complexes, $[Cr(en)_2(SCH_2COO)]^+$ and $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, before commencing redox studies. These investigations have not only aided in characterizing this new class of complexes but, since detailed kinetic studies of metal-sulfur bond cleavage are relatively rare,[3] they have also significantly extended the range of experimental results pertaining to ligand substitution reactions. Therefore in this paper we report on acid-catalyzed Cr-S bond fission, which for the above two complexes is generally faster than, but competitive with, acid-independent Cr-S and Cr-N bond fission. Cleavage of the Cr-S linkage in these complexes may be generally classified as an acid-catalyzed replacement of a basic multidentate ligand; evidence is also presented for the reverse of this reaction *via* Cr-S bond formation. The corresponding cobalt(III) complexes, $[Co(en)_2(SCH_2COO)]^+$ and $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, are shown to be completely inert to Co-S bond fission under the conditions employed in this study.

Experimental Section

Equipment. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer at room temperature, infrared spectra were recorded on a Beckman IR-10 spectrophotometer, and molecular weights were obtained with a Model 115 Hitachi Perkin-Elmer molecular weight apparatus. Kinetic experiments were followed on a Cary Model 16K spectrophotometer equipped with a thermostated cell compartment that maintained the temperature of reacting solutions to better than ±0.2°. Computer calculations were performed on an IBM System 360 located at the University of Chicago Computation Center. The standard Los Alamos nonlinear least-squares program was adapted to this system and used for all data analyses.[6]

Materials. All common laboratory chemicals were of reagent grade. Water was distilled two times in Pyrex equipment. G. Frederick Smith doubly distilled perchloric acid was used for all kinetic experiments. Dowex 50W-X2 ion-exchange resin, 200–400 mesh, was kindly donated by Dow Chemical Co. and was cleaned by a previously outlined procedure.[7] **Cystamine dihydrochloride** (97%) and **dithiodiglycolic acid** (96%) were obtained from Aldrich Chemical Co. and were used in preparative procedures without further purification. Chromium metal (99.999%) was purchased from Apache Chemicals. Salts of ***O,S*-mercaptoacetatobis(ethylenediamine)cobalt(III)** and ***N,S*-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III)**[8] were prepared by the method of Lane and Bennett[1] and were recrystallized three times before use.

Analyses. Elemental analyses of solid compounds were performed by PCR Inc. of Gainesville, Fla. Molecular weights were

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determined in water by an isopiestic method; the water calibration curve was obtained with sodium chloride solutions of known concentrations. The total chromium content of a sample was measured spectrophotometrically as chromate (ϵ_{373} 4815 F^{-1} cm^{-1}) after oxidation of the appropriate aqueous solution with basic hydrogen peroxide.[9] Solutions of perchloric acid and lithium perchlorate were standardized by usual procedures,[4,8,10] and in addition lithium perchlorate solutions were also standardized by controlled evaporation of aliquots to yield defined hydrates[11] which were subsequently weighed.

Preparation of *O,S*-Mercaptoacetatobis(ethylenediamine)chromium(III) Perchlorate. A concentrated solution of chromium(II) perchlorate was prepared by dissolving 99.999% chromium metal in a slight excess of 20% perchloric acid under anaerobic conditions.[12] To this solution were successively added a deaerated 10% (v/v) solution of ethylenediamine and a deaerated 30% (w/v) solution of dithiodiglycolic acid in proportions such that the molar ratio of chromium:ethylenediamine:disulfide was 2:6:1. Oxidation of the chromium(II) occurred rapidly; all transfers up to this point were conducted under an inert atmosphere, and all operations after this point were performed in darkness or in dim light because of the photosensitivity of this class of compounds. Chromium(III) hydroxide was removed and the resulting solution acidified with perchloric acid and cooled to give red crystals of **_O,S_-mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate** (yield usually about 30%). This product was twice recrystallized from water before being used in kinetic experiments. *Anal.* Calcd for $[Cr(en)_2(SCH_2COO)]ClO_4$: C, 19.92; H, 5.03; N, 15.49; S, 8.86; O, 26.53; Cr, 14.37. Found: C, 19.66; H. 4.99; N, 15.37; S, 9.73; O, 28.16; Cr, 14.01. The molecular weight was determined to be 335 ± 30 compared to a calculated value of 362. The composition of this compound was further confirmed by the single-crystal X-ray structure analysis reported in the following paper.[13]

Preparation of *N,S*-(2-Mercaptoethylamine)bis(ethylenediamine)chromium(III) and Bis[*N,S*-(2-mercaptoethylamine)]ethylenediaminechromium(III) Salts. When cystamine dihydrochloride was reduced according to the above procedure, two different chromium(III) complexes containing cysteamine (2-mercaptoethylamine) were obtained. These two products could be separated by ion-exchange chromatography or by fractional crystallization of the perchlorate salts from dilute sodium perchlorate. The product with apparent 1+ charge (determined by comparing ion-exchange elution characteristics with those of complexes of known charge) is red and may be formulated as $[Cr(en)(SCH_2CH_2NH_2)_2]^+$, while the 2+ product is brown and may be formulated as $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$. It was shown that the proportion of 1+ species in the product mixture could be increased by using excess disulfide in the original redox reaction or by injecting the disulfide into the en–Cr^{II} mixture. Formation of the 2+ product was favored when the en–Cr^{II} mixture was injected into the disulfide solution. Both salts were twice recrystallized from water. *Anal.* Calcd for $[Cr(en)(SCH_2CH_2NH_2)_2]ClO_4$: C, 19.81; H, 5.54; N, 15.40; S, 17.63; Cr, 14.29. Found: C, 20.08; H, 5.56; N, 15.31; S, 17.73; Cr, 13.99. Calcd for $[Cr(en)_2(SCH_2CH_2NH_2)](ClO_4)_2$: C, 16.12; H, 4.96; N, 15.66; S, 7.17; Cr, 11.63. Found: C, 15.98; H, 5.01; N, 15.27; S, 7.51; Cr, 11.52. The molecular weight of the perchlorate salt was determined to be 447 ± 30 compared to a calculated value of 447. Recrystallization of the 2+ product from excess sodium iodide yielded the iodide salt. *Anal.* Calcd for $[Cr(en)_2(SCH_2CH_2NH_2)]I_2$: C, 14.35; H, 4.42; N, 13.95; S, 6.38. Found: C, 14.29; H, 4.45; N, 13.63; S, 6.19.

Kinetic Measurements and Calculations. All kinetic experiments were performed in aqueous acidic solutions that were maintained at constant ionic strength 1.00 ± 0.01 or 4.00 ± 0.04 F with $LiClO_4$. Precautions appropriate to the light sensitivity of these reactions were taken at all times. However, no precautions were taken to exclude oxygen from reaction solutions[4] since a comparison of kinetic experiments under aerobic and anaerobic conditions showed no discernible difference in rate for either of the two complexes investigated in this work. Likewise, identical kinetic parameters were obtained when solutions were prepared directly from crystalline starting material or from starting material which had been eluted from an ion-exchange column immediately prior to the aquation experiment. The rate of chromium–sulfur bond fission was monitored spectrophotometrically at 310 nm for $[Cr(en)_2(SCH_2COO)]^+$ and at 314 nm for $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$. For the former complex it was also possible to follow aquation at 385 nm, the observed rate constant being independent of the wavelength employed.

Three different methods were employed to calculate k^{obsd}. (1) At $\mu = (H^+) = 4.00\ F$, for $[Cr(en)_2(SCH_2COO)]^+$, k^{obsd} could directly be obtained from the usual plots of ln $(A_t - A_\infty)$ *vs.* t (the subscript on A denotes the time of that reading). These plots were linear for more than 90% of the reaction, thus providing the rationale for assuming that the reaction being followed is a first-order process under all the conditions used in this study. This assumption is a prerequisite to the following two treatments. (2) If A_∞ did not remain at a constant value but instead slowly drifted to lower values, an exponential form of the Guggenheim treatment (Kezdy time-lag method[14]) was employed. All reactions treated by this method were followed for at least 2 half-lives. In several experiments the time interval chosen was varied over a wide range (0.5–2.5 half-lives), resulting in no significant variation in the calculated k^{obsd}. The data described above ($\mu = (H^+) = 4.00\ F$, for $[Cr(en)_2(SCH_2COO)]^+$) were also treated in this fashion and in all cases the calculated values of k^{obsd} agreed to within 2% of those obtained from first-order plots. The slope of each individual time-lag plot was determined by a linear least-squares calculation[15] which also yielded the standard deviation of the slope (σ_{slope}). The standard deviation of k^{obsd} (σ_k) was calculated from σ_{slope} *via* the expression[16]

$$\sigma_k = \frac{\sigma_{slope}}{(\text{slope})(\text{time interval})}$$

and $1/(\sigma_k)^2$ was later used to weight individual kinetic runs for the determination of activation parameters and Harned coefficients. In order to maintain internal consistency, all of the rate constants in Table I, as well as those obtained at $\mu = 4.00\ F$ in Table II, were obtained by the time-lag treatment. (3) In the aquation of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ at $\mu = 1.00\ F$, an initial rate treatment which never considered more than the first 5% of the reaction was employed (see Table II). In these experiments the spectrophotometer was zeroed on a 1.00 F $HClO_4$ solution in order to provide absolute absorbance readings, and A_∞ was assumed to be exactly zero; the error introduced into the calculated rate constant by this assumption is less than 2%. During the initial portion of these reactions (usually 0–3% reaction) A_t decreased linearly with t, and the slope of this plot was calculated *via* the linear least-squares analysis previously described.[15] Division of this slope by A_0 (obtained by extrapolation) directly yielded k_{ir}^{obsd} (initial first-order rate constant), the standard deviation in this parameter (σ_k) being calculated from the standard deviation of the slope (σ_{slope}) by the relationship

$$\sigma_k = \sigma_{slope}/A_0$$

Again, $1/(\sigma_k)^2$ was used to weight individual kinetic runs for the determination of activation parameters.

All errors reported in this paper are standard deviations unless otherwise noted.

Results and Discussion

Synthesis and Characterization of Thiolatobis(ethylenediamine)chromium(III) Complexes. The successful synthesis of this class of compounds is due to four aspects of chromium chemistry. (1) In aqueous solution, chromium(II) is readily complexed by one or two ethylenediamine ligands but has very little tendency to add a third ethylenediamine.[17] (2) Coordination of polyamines to chromium(II) markedly enhances its reducing ability.[18,19] (3) Chromium(II) usually reduces both organic and inorganic substrates *via* an inner-sphere mechanism.[20-22] (4) Upon oxidation from the labile

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Table I. Rate Data for Aquation of $[Cr(en)_2(SCH_2COO)]^{+\ a,b}$

$\mu = 1.00\ F, T = 10.0°$		$\mu = 1.00\ F, T = 25.0°$		$\mu = 1.00\ F, T = 39.3°$		$\mu = 4.00\ F, T = 25.0°$			
$[H^+]$, F	10^4k_{obsd}, sec^{-1}	$[H^+]$, F	10^4k_{obsd}, sec^{-1}	$[H^+]$, F	10^4k_{obsd}, sec^{-1}	$[H^+]$, F	10^4k_{obsd}, sec^{-1}	$[H^+]$, F	10^4k_{obsd}, sec^{-1}
0.050	0.183 ± 0.002	0.026	0.309 ± 0.006	0.050	2.74 ± 0.03	0.050^c	4.48 ± 0.04	2.00^c	63.1 ± 0.5
0.050	0.197 ± 0.002	0.050	0.714 ± 0.007	0.050	2.73 ± 0.03	0.050	4.32 ± 0.07	2.25^c	64.9 ± 0.9
0.088	0.290 ± 0.002	0.050	0.733 ± 0.007	0.088	4.40 ± 0.05	0.050	4.50 ± 0.06	2.50^c	64.8 ± 0.3
0.088	0.291 ± 0.002	0.088	1.12 ± 0.02	0.088	4.61 ± 0.03	0.070^c	5.74 ± 0.09	2.75^c	71.0 ± 0.6
0.202	0.627 ± 0.004	0.088	1.15 ± 0.01	0.202	10.02 ± 0.06	0.10^c	8.14 ± 0.06	2.75^c	69.5 ± 0.6
0.202	0.616 ± 0.004	0.202	2.54 ± 0.01	0.202	10.09 ± 0.06	0.10^c	10.3 ± 0.1	3.00^c	76.4 ± 0.8
0.328	0.990 ± 0.004	0.202	2.54 ± 0.02	0.328	16.4 ± 0.1	0.15^c	12.3 ± 0.1	3.25^c	80.6 ± 0.8
0.497	1.463 ± 0.009	0.328	3.91 ± 0.03	0.328	16.4 ± 0.1	0.30^c	21.4 ± 0.3	3.50^c	83.4 ± 0.6
0.497	1.48 ± 0.01	0.328	3.87 ± 0.02	0.497	24.7 ± 0.1	0.30^c	22.6 ± 0.2	3.50^c	75.6 ± 0.2
1.00	2.69 ± 0.01	0.605	7.33 ± 0.02	0.497	24.4 ± 0.1	0.50^c	33.0 ± 0.4	3.75^c	82.7 ± 0.3
1.00	2.73 ± 0.01	0.605	7.45 ± 0.02	1.00	45.6 ± 0.2	0.75^c	43.3 ± 0.3	4.00^c	88.2 ± 0.7
		0.806	9.54 ± 0.03	1.00	43.4 ± 0.3	1.00^c	50.7 ± 0.2	4.00^c	85.7 ± 0.4
		0.806	9.68 ± 0.03			1.25^c	52.9 ± 0.3	4.00^c	84.8 ± 1.1
		1.00	11.6 ± 0.1			1.50^c	55.2 ± 0.5	4.00	85.1 ± 0.9
		1.00	10.6 ± 0.1			1.75^c	58.8 ± 0.6	4.00	85.5 ± 0.5
		1.00	10.6 ± 0.1						
		1.00	11.6 ± 0.1						
		1.00	11.3 ± 0.1						
		1.00	11.3 ± 0.1						

[a] Typical range of initial concentrations of $[Cr(en)_2(SCH_2COO)]^+$ was $(0.5–8.0) \times 10^{-4}\ F$. [b] Unless otherwise noted, kinetics were followed at 310 nm. [c] Kinetics were followed at 385 nm; the initial concentration of $[Cr(en)_2(SCH_2COO)]^+$ was as high as $2.0 \times 10^{-2}\ F$.

Table II. Rate Data for Aquation of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+\ a,b}$

$\mu = 1.00\ F, T = 25.0°$		$\mu = 1.00\ F, T = 34.1°$		$\mu = 1.00\ F, T = 44.3°$		$\mu = 4.00\ F, T = 25.0°$			
$[H^+]$, F	$10^6k_{ir}^{obsd}$, sec^{-1}	$[H^+]$, F	$10^6k_{ir}^{obsd}$, sec^{-1}	$[H^+]$, F	$10^6k_{ir}^{obsd}$, sec^{-1}	$[H^+]$, F	$10^6k_{ir}^{obsd}$, sec^{-1}	$[H^+]$, F	$10^6k_{ir}^{obsd}$, sec^{-1}
0.20	2.80 ± 0.03	0.20	9.91 ± 0.17	0.20	31.6 ± 0.3	0.33	26.8 ± 0.8	2.67	105 ± 2
0.20	2.85 ± 0.03	0.20	9.69 ± 0.08	0.20	30.2 ± 0.3	0.67	40.0 ± 0.5	2.67	106 ± 1
0.40	4.62 ± 0.07	0.40	14.4 ± 0.1	0.40	49.4 ± 0.5	1.00	54.7 ± 0.6	3.00	114 ± 2
0.40	4.14 ± 0.04	0.40	15.6 ± 0.3	0.40	42.2 ± 0.4	1.34	63.6 ± 0.4	3.00	119 ± 1
0.60	5.93 ± 0.08	0.60	18.5 ± 0.2	0.60	67.8 ± 1.1	1.34	67.6 ± 1.1	3.34	127 ± 2
0.60	5.69 ± 0.06	0.60	19.7 ± 0.4	0.60	58.7 ± 0.5	1.68	75.1 ± 0.3	3.34	130 ± 1
0.80	7.51 ± 0.08	0.80	25.3 ± 0.2	0.80	79.5 ± 1.2	1.68	72.7 ± 0.9	3.68	139 ± 2
0.80	7.23 ± 0.07	0.80	22.6 ± 0.1	0.80	79.2 ± 0.5	2.00	84.6 ± 0.3	3.68	145 ± 1
1.00	8.97 ± 0.12	1.00	28.0 ± 0.5	1.00	91.5 ± 1.6	2.00	83.6 ± 2.2	3.99	157 ± 1
1.00	8.91 ± 0.10	1.00	27.2 ± 0.5	1.00	89.0 ± 1.1	2.33	96.8 ± 1.0	3.99	161 ± 3
				1.00	99.6 ± 1.3	2.33	94.2 ± 1.7		

[a] Typical range of initial concentrations of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ was $(4.0–13) \times 10^{-4}\ F$. [b] Kinetics were followed at 314 nm.

2+ state to the substitution-inert 3+ state, chromium has a strong tendency to capture whatever ligands are in its first coordination sphere at the instant of electron transfer.[20,23] While these facts suggest a simple mechanism for the reduction of organic disulfides by ethylenediamine-chromium(II) solutions, the actual situation must be fairly complicated since the reduction of cystamine dihydrochloride yields two cysteamine-chromium(III) products in a ratio dependent upon reaction conditions. Despite the complexity and unknown mechanism of the reduction of organic disulfides by metal ions, the synthetic method made possible by these reactions is practicable and reasonably general, having now been employed to prepare several chromium(III)- and cobalt(III)-thiolato complexes.[1,4,8,19]

The three complexes reported in this paper are characterized by (1) their preparative chemistry, (2) the elemental analyses and molecular weight determinations reported in the previous section, (3) the single-crystal X-ray structure determination of *O,S*-mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate which is reported in the following paper,[13] (4) their elution characteristics on cation-exchange resins which are consistent with their proposed formal charges, (5) the absence of an S-H absorption at about 2500 cm^{-1} in their infrared spectra and their lack of reaction with Benedict's solution,[24] both lines of evidence indicating the absence of a free thiol function, and (6) their visible-ultraviolet spectra which are listed in Table III along with spectra of other complexes relevant to this discussion.

There is one distinct feature of the spectra of the three thiolatobis(ethylenediamine)chromium(III) complexes prepared in this study which is common to all thiolatochromium(III) and thiolatocobalt(III) complexes prepared to date[1,3,4,8,25] and which seems to be characteristic of thiolato coordination. The intense band observed in the near-ultraviolet region for all these complexes may reasonably be assigned as a ligand-to-metal charge transfer resulting from coordination of low-valent sulfur to a potentially oxidizing center. A similar assignment has been made for the intense near-ultraviolet bands observed in a variety of S-bonded thiocyanato com-

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(19) Chromium(II) in aqueous acidic solution does not reduce cystamine dihydrochloride but does reduce dithiodiglycolic acid to yield, among other products, the *O,S*-mercaptoacetatotetraaquochromium(III) ion. The presence of a suitable chelating function in alkyl disulfides seems to be necessary for their reduction by hexaaquochromium(II) and ethylenediamine-cobalt(II) mixtures.[8]

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Table III. Selected Cr(III) Absorption Spectra (200-700 nm)[a]

	Visible				Ultraviolet	
	λ_{sh}	λ_{max}	λ_{min}	λ_{max}	λ_{max}	λ_{max}
$[Cr(en)_2(SCH_2COO)]^+$ [b]	. . .	500 (99)	442 (46)	385 (91)	310 (1000)	250 (7440)
$[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ [b]	560 (39)	468 (99)	406 (63)	. . .	316 (1100)	256 (7600)
cis-$[Cr(en)(SCH_2CH_2NH_2)_2]^+$ [b]	. . .	528 (157)	467 (74)	424 (117)	282 (15,600)	213 (12,000)
$[Cr(en)_2(H_2O)(OOCCH_2SH)]^{2+}$ [b]	. . .	488 (89)	418 (21)	370 (51)	. . .[c]	. . .
$[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$ [b]	. . .	474 (68)	407 (18)	354 (61)	. . .[d]	. . .
$[Cr(en)_3]^{3+}$ [e]	. . .	438 (73)	395 (14)	350 (60)	. . .	
$[Cr(SCH_2COO)_3]^{3-}$ [f]		632 (202)		476 (202)		
$[Cr(S_2P(OC_2H_5)_2)_3]^{3-}$ [f]		697 (380)		536 (270)		280 (15,200)
cis-$[Cr(en)_2(H_2O)_2]^{3+}$ [e]	. . .	485 (68)	417 (17)	366 (44)		
cis-$[Cr(en)_2(C_2O_4)]^+$ [e]	. . .	495 (97)	416 (23)	370 (87)		
cis-$[Cr(en)_2(H_2O)(enH)]^{4+}$ [g]	. . .	475 (56)	410 (17)	360 (44)		

[a] Wavelengths in nm; values inside parentheses are molar extinction coefficients ϵ (F^{-1} cm^{-1}); ". . ." signifies no band observed, while no entry signifies no band has been reported. [b] This work. Spectra recorded in aqueous perchlorate solutions at pH <3. [c] ϵ <20 at 310 nm. [d] ϵ <20 at 316 nm. [e] C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 59 (1970). [f] C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968). [g] E. Jorgensen and J. Bjerrum, *Acta Chem. Scand.*, **13**, 2075 (1959).

plexes.[26,27] Hence, the rate of chromium-sulfur bond fission was monitored spectrophotometrically at these charge-transfer peaks, the thiolato complexes having much greater extinction coefficients (ϵ >1000) than the aquation products which do not contain a Cr-S bond (ϵ <20). For $[Cr(en)_2(SCH_2COO)]^+$ it was also possible to follow aquation at 385 nm. However, it was not feasible to monitor Cr-S bond fission at wavelengths further into the visible portion of the spectrum since in this region the starting materials and *initial* aquation products (*i.e.*, those produced by Cr-S bond cleavage, but containing a full complement of Cr-N bonds) have similar extinction coefficients. Thus, the rate of absorbance decrease in this region of the spectrum is determined almost exclusively by the rate of Cr-N bond fission.

It is also of interest that the energies of the observed visible absorption bands of $[Cr(en)_2(SCH_2COO)]^+$ agree very well with values calculated from the rule of average environment[27,28] and the known spectra[29,30] of $[Cr(SCH_2COO)_3]^{3-}$ and $[Cr(en)_3]^{3+}$ (20.5 *vs.* 20.0 kK for ν_1 and 26.0 *vs.* 26.0 kK for ν_2). A similar calculation cannot be done directly for $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ since the spectrum of $Cr(SCH_2CH_2NH_2)_3$ has not been reported. However, Jorgensen[27] has had success in using the spectrum of $Cr(S_2P(OC_2H_5)_2)_3$ as a crude model for calculating the spectral effects of monodentate thiolato coordination to chromium(III), and in the same manner we calculate[31] ν_1 to be 21.4 kK (observed, 21.4 kK) and ν_2 to be 27.0 kK (ν_2 is obscured by the tail of the charge-transfer absorption). The spectral characteristics of $[Cr(en)(SCH_2CH_2NH_2)_2]^+$ (*i.e.*, no observable splitting and relatively high intensities of visible bands) cause us tentatively to assign the cis configuration to this complex.[32]

Aquation of the *O,S*-Mercaptoacetatobis(ethylenediamine)chromium(III) Ion. The aquation of $[Cr(en)_2(SCH_2COO)]^+$ in aqueous perchloric acid solutions proceeds *via* several successive steps with the first being sufficiently more rapid than succeeding ones so that it can be studied independently. The product of this first step behaves as a doubly charged cation on Dowex 50X2 resin and gives a positive test for reducing power with Benedict's solution.[24] These properties, along with its visible-ultraviolet spectrum (*i.e.*, lack of charge-transfer band in the near-ultraviolet region and similarity of visible spectrum to that of $[Cr(en)_2(C_2O_4)]^+$ and that of *cis*-$[Cr(en)_2(OH_2)_2]^{3+}$—see Table III), support identification of this initial product as *cis*-$[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$ showing that the first aquation step involves Cr-S bond cleavage. That the initial Cr-S aquation step is reversible is demonstrated by the following experiment. A sample of $[Cr(en)_2(SCH_2COO)]^+$ was allowed to undergo Cr-S bond fission in 4.00 *F* $HClO_4$ and the product was adsorbed on a cation-exchange column. The initial aquation product, $[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$, was eluted with a chilled 1.00 *F* $NaClO_4$-0.001 *F* $HClO_4$ solution, and then the spectrum of the product, in this solution, was immediately determined. Initially this solution exhibited no absorbance in the 290-350-nm region, but in less than 15 min a peak at 310 nm, which is diagnostic of Cr-S bonding, became discernible. The absorbance at this wavelength continued to increase with time, confirming that in low acid concentration the Cr-S linkage is re-formed.[33] Furthermore, from the time-lag calculation used to obtain k^{obsd} one can also obtain a hypothetical infinite-time absorbance that would have resulted if Cr-S bond cleavage were the only reaction effecting the absorbance change. At 310 nm, where the extinction coefficient of the product is less than 2% of that of the starting material (see Table III), this calculated infinite-time absorbance (A_∞^{calcd}) should be effectively zero if the reaction goes to

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(31) *E.g.*, $\nu_1 = [2.5(22.83) + 0.5(14.40)]/3$.

(32) C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 117 (1970).

(33) Competitive Cr-N bond fission precludes a direct determination of the rate of Cr-S bond formation by this procedure.

completion. However, it is observed that this parameter is zero only at high acid concentration, and in fact A_∞^{calcd} increases as (H$^+$) decreases, reaching a value of about 30% of the initial absorbance at the lowest acid concentration investigated, (H$^+$) = 0.050 *F*. Thus the initial aquation of $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$ may be formulated as an approach to an acid-dependent equilibrium between closed (O,S-chelated) and open (monodentate, carboxylate bound) mercaptoacetate ligands. Unfortunately, since A_∞^{calcd} values are obtained by what is essentially an extrapolation procedure, they are not precise enough to be used to calculate equilibrium parameters. It can only be estimated that in 0.050 *F* HClO_4, at $\mu = 1.00$ *F* and 25°, the equilibrium ratio of open to chelated forms is approximately 2.

Subsequent aquation steps presumably first involve Cr-N bond fission, since oxalato complexes of polyamminechromium(III) ions[34] and the acetatopentaamminechromium(III) ion[35] are known to aquate *via* initial Cr-N bond fission. Then at some later time aquation of the carboxylate function must occur since $[\text{Cr(en)(OH}_2)_4]^{3+}$ is the predominant product isolated from extensively hydrolyzed solutions. The slowly drifting infinite-time readings discussed in the Experimental Section are considered to result from Cr-N bond breaking which competes only marginally with Cr-S bond fission. At μ = (H$^+$) = 4.00 *F*, the acid-catalyzed Cr-S bond cleavage of $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$ proceeds so much more rapidly than the acid-independent Cr-N bond fission that an A_∞ for the former process can be obtained directly.

Table I lists the first-order specific rate constants (k^{obsd}) observed for Cr-S bond fission in $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$ as a function of acid concentration. At 25° and $\mu = 4.00$ *F*, a plot of k^{obsd} *vs.* (H$^+$) over the range (H$^+$) = 0.050-4.00 *F* gives a curve of continuously decreasing slope, whereas when $1/k^{\text{obsd}}$ is plotted *vs.* 1/(H$^+$), a straight line is obtained with slope = 107.9 ± 1.3 *F* sec and intercept = 94 ± 10 sec (30 data points, see Table I). At 25° and $\mu = 1.00$ *F*, a plot of k^{obsd} *vs.* (H$^+$) is linear over the range (H$^+$) = 0.050-1.00 *F*. Thus the acid dependence of k^{obsd} has the form

$$k^{\text{obsd}} = \frac{a(\text{H}^+) + b}{1 + c(\text{H}^+)}$$

where at $\mu = 4.00$ *F*, $b \ll a(\text{H}^+)$ even for (H$^+$) = 0.050 *F*, and at $\mu = 1.00$ *F*, $c(\text{H}^+) \ll 1$ even for (H$^+$) = 1.00 *F*. Of the many possible aquation mechanisms that are consistent with this acid dependence, as well as with the overall approach to equilibrium, two seem sufficiently plausible to warrant comment. Mechanism I is simply that which has been proposed

Mechanism I

$$\text{H}_2\text{O} + \text{Cr(en)}_2(\text{SCH}_2\text{COO})^+ \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} \text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{S})^+$$

$$\text{H}^+ + \text{Cr(en)}_2(\text{OH}_2)(\text{OOCH}_2\text{S})^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{SH})^{2+}$$

for the acid-catalyzed aquaton of $[\text{Fe(bipy)}_3]^{2+}$ (and which by analogy is presumed to operate in the aquation of $[\text{Ni(en)}_3]^{2+}$ and $[\text{Ni(bipy)}_3]^{2+}$)[36] and $[\text{Cr(tetren)(C}_2\text{O}_4)]^+$ [34b] with the addition of a k_{-2} path to allow attainment of equilibrium. However, the undesirability of including a protonation reaction (k_2) which does not proceed at the diffusion-controlled rate limit has been commented on[34b,37] and an alternate mechanism, which is not applicable to the systems studied in this work, has been proposed for the aquation of $[\text{Co(bipy)}_3]^{2+}$ [37] (and by analogy $[\text{Fe(bipy)}_3]^{2+}$, etc.). In addition, Mechanism I seems unlikely since aquations of all the thiolatochromium(III) complexes studied to date, including the $[(\text{H}_2\text{O})_5\text{CrSC}_6\text{H}_4\text{NH}_3]^{3+}$ ion,[4] are catalyzed by acid. It is difficult to rationalize a rate-determining proton-transfer reaction operating in the aquation of monodentate ligand, and since there is no reason to expect different aquation mechanisms to govern acid-catalyzed Cr-S bond fission in $[(\text{H}_2\text{O})_5\text{CrSC}_6\text{H}_4\text{NH}_3]^{3+}$ and $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$, all further discussion is presented in terms of Mechanism II.

Mechanism II

$$\text{H}^+ + \text{Cr(en)}_2(\text{SCH}_2\text{COO})^+ \overset{1/K_\text{a}}{=} [\text{Cr(en)}_2(\text{SCH}_2\text{COO})\text{H}]^{2+}$$

$$\text{Cr(en)}_2(\text{SCH}_2\text{COO})^+ + \text{H}_2\text{O} \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} \text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{S})^+$$

$$[\text{Cr(en)}_2(\text{SCH}_2\text{COO})\text{H}]^{2+} + \text{H}_2\text{O} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{SH})^{2+}$$

$$\text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{S})^+ + \text{H}^+ \overset{1/K_\text{p}}{=} \text{Cr(en)}_2(\text{OH}_2)(\text{OOCCH}_2\text{SH})^{2+}$$

Mechanism II is essentially that which has been proposed for the acid-catalyzed aquation of many chromium(III) and cobalt(III) complexes of basic ligands such as acetate, fluoride, azide, etc. In several cases, *e.g.*, $[(\text{H}_2\text{O})_5\text{CrOOCCH}_3]^{2+}$,[7] $[(\text{H}_2\text{O})_5\text{CrN}_3]^{2+}$,[38] and $[(\text{NH}_3)_5\text{CoOOCCH}_3]^{2+}$,[39] protonation of the metal complex has been confirmed spectrophotometrically and we attempted to obtain similar evidence. The absorbances of equimolar $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$ solutions at 310 nm (when extrapolated back to the time of mixing) are approximately 7% lower when 4 *F* HClO_4, rather than 4 *F* LiClO_4 (pH 4), is used as the solvent. This change in absorbance is in the direction expected for protonation of sulfur; *e.g.*, at the Co-S charge-transfer peak, the extinction coefficient of $[\text{Co(en)}_2(\text{S(CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ is less than that of $[\text{Co(en)}_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$,[8] but the small magnitude of the change, which presumably results from the protonated and unprotonated forms having similar extinction coefficients, precludes a definitive confirmation of protonation. Despite the lack of absolute proof of protonation of $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]^+$, the prevalence of acid-catalyzed aquations that proceed *via* prior protonation argues strongly for the generality of the scheme and thus for the specific conclusion that Mechanism II operates in our system. Mechanism II consists of a rapid protonation equilibrium involving the chelated starting material, followed by a much slower chelation equilibrium attained by the making and breaking of Cr-S bonds *via* zero-order and first-order acid paths. For completeness, a rapid protonation equilibrium involving the monodentate product is also included. The formula $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})\text{H}]^{2+}$ represents the protonated form of the starting material, protonation possibly occurring at either of the carboxylate oxygens or at the coordinated sulfur. While the

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thermodynamically favored site of protonation cannot be determined from our present data, the observation that Cr-S bond fission in both $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ and $[(H_2O)_5CrSC_6H_4N(CH_3)_3]^{3+}$ [4] is acid catalyzed (and in these complexes there is no ambiguity as to the site of protonation) argues for protonation of the coordinated sulfur in the kinetically active form of $[Cr(en)_2(SCH_2COO)H]^{2+}$. Mechanism II leads directly to the rate expression

$$-\mathrm{d}\ln\left[\frac{A_t - A_\infty}{A_0 - A_\infty}\right]/\mathrm{d}t = k^{\mathrm{obsd}} = \frac{k_1(\mathrm{H}^+) + k_0K_\mathrm{a}}{K_\mathrm{a} + (\mathrm{H}^+)} + \frac{k_{-1}(\mathrm{H}^+) + k_{-0}K_\mathrm{p}}{K_\mathrm{p} + (\mathrm{H}^+)} \quad (1)$$

if, at the wavelength employed, the extinction coefficients of the protonated and unprotonated forms of the starting material are identical and if the monodentate products do not have a significant absorption. The latter condition is verified by the data in Table III, while the former is established by the spectrophotometric observations just described. These conditions also lead to the following expressions for the equilibrium quotient which is defined as the total equilibrium concentration of monodentate products divided by the total equilibrium concentration of chelated species

$$Q = \frac{A_0 - A_\infty}{A_\infty} = \frac{\dfrac{k_1}{k_{-1}}\left[\dfrac{(\mathrm{H}^+)}{K_\mathrm{a}}\right] + \dfrac{k_0}{k_{-0}}}{1 + (\mathrm{H}^+)/K_\mathrm{a}} = \frac{k_1}{k_{-1}}\left[\frac{(\mathrm{H}^+) + K_\mathrm{p}}{(\mathrm{H}^+) + K_\mathrm{a}}\right] \quad (2)$$

since $K_\mathrm{p}[k_{-0}/k_0] = K_\mathrm{a}[k_{-1}/k_1]$. The equilibrium described by K_p probably involves loss of a proton from the thiol function, as depicted in Mechanism II, but may also involve loss of a proton from the coordinated water of $[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$. In the former case K_p may reasonably be estimated as 10^{-9} F from the pK_2 of free mercaptoacetic acid (10.55 at 25°)[40] and the observation[41] that the pK_a of coordinated glycine in $[(NH_3)_5Co(OOCCH_2NH_3)]^{3+}$ is lowered only 1.3 units from that of free glycine. In the latter case K_p may be estimated as 10^{-5} F in accord with acid ionization constants observed for comparable aquoamminechromium(III) complexes.[42] For either situation $K_\mathrm{p} \ll (\mathrm{H}^+)$ at all acid concentrations used in this work and thus eq 1 and 2 may be rewritten as

$$k^{\mathrm{obsd}} = \frac{k_1(\mathrm{H}^+)/K_\mathrm{a} + k_0}{1 + (\mathrm{H}^+)/K_\mathrm{a}} + k_{-1} + k_{-0}K_\mathrm{p}/(\mathrm{H}^+) \quad (1\mathrm{a})$$

$$Q = \frac{k_1}{k_{-1}}\left[\frac{(\mathrm{H}^+)}{(\mathrm{H}^+) + K_\mathrm{a}}\right] \quad (2\mathrm{a})$$

The linearity of the $1/k^{\mathrm{obsd}}$-$1/(\mathrm{H}^+)$ plot implies the chemically reasonable situation that at $\mu = 4.00$ F ring closure by both possible paths, k_{-1} and $k_{-0}K_\mathrm{p}/(\mathrm{H}^+)$, and ring opening by the acid-independent path k_0, are always much slower than ring opening by the acid-dependent path $k_1(\mathrm{H}^+)/K_\mathrm{a}$. Thus the relationship

$$\frac{1}{k^{\mathrm{obsd}}} = \frac{1}{k_1} + \frac{K_\mathrm{a}}{k_1(\mathrm{H}^+)} \quad (1\mathrm{b})$$

holds, and the observed slope corresponds to K_a/k_1 while the observed intercept corresponds to $1/k_1$. From these parameters, k_1 and K_a are calculated to be (1.06 ± 0.11) × 10^{-2} sec^{-1} and 1.15 ± 0.12 F, respectively. The linear k^{obsd}-(H^+) plot of the $\mu = 1.00$ F data implies that under these conditions ring closure *via* the $k_{-0}K_\mathrm{p}/(\mathrm{H}^+)$ path is ineffectual over the entire range $(\mathrm{H}^+) = 0.050$-1.00 F, and $(\mathrm{H}^+)/K_\mathrm{a} \ll 1$ even at $(\mathrm{H}^+) = 1.00$ F. Thus at unit ionic strength K_a must be greater than 10 F. Since protonation of a positively charged species is expected to be favored at high ionic strength, this minimum tenfold increase in K_a on going from $\mu = 4.00$ to 1.00 F is entirely reasonable. It is also in agreement with the tenfold increase observed[39] for the comparable K_a of $[(NH_3)_5Co(HOOCCH_3)]^{3+}$ and the qualitative increase reported[7] for the K_a of $[Cr(OH_2)_5(HOOCCH_3)]^{3+}$, when ionic strength is decreased from 4.00 to 1.00 F. From the form of eq 1 appropriate to unit ionic strength

$$k^{\mathrm{obsd}} = \frac{k_1(\mathrm{H}^+)}{K_\mathrm{a}} + k_0 + k_{-1} + \frac{k_{-0}K_\mathrm{p}}{(\mathrm{H}^+)} \quad (1\mathrm{c})$$

where the last term is too small to be detected experimentally, it is seen that the slopes of k^{obsd}-(H^+) plots correspond to k_1/K_a. At 10, 25, and 39.3° the values of these slopes are respectively (0.266 ± 0.004) × 10^{-3} (11 data points), (1.11 ± 0.02) × 10^{-3} (19 data points), and (4.42 ± 0.09) × 10^{-3} F^{-1} sec^{-1} (12 data points). These three plots all have small positive intercepts with large standard deviations, to wit (0.81 ± 0.19) × 10^{-5}, (2.5 ± 1.4) × 10^{-5}, and (11.9 ± 4.4) × 10^{-5} sec^{-1} respectively. These intercepts could reflect the rate term $(k_0 + k_{-1})$ or they may result from changes in activity coefficients induced by substituting H^+ for Li^+ in the ionic medium.[43] Since there is no definitive method to distinguish directly between minor rate terms and activity effects, the unit ionic strength data of Table I were successively treated within each hypothesis. First, all 42 rate constants at each (H^+) and temperature were weighted and then fitted according to the expression

$$k^{\mathrm{obsd}} = [e^{(\mathrm{H}^+)(P_1 + P_2\theta)}]\frac{kT}{h}(\mathrm{H}^+)e^{\Delta S^*_\mathrm{s}/R}e^{-\Delta H^*_\mathrm{s}/RT} \quad (3)$$

where θ is the temperature in degrees centigrade, $-(P_1 + P_2\theta)$ is just the standard Harned factor β separated into temperature-independent and -dependent portions, and the subscript "s" refers to the slopes of the k^{obsd}-(H^+) plots. The values of the four parameters that best describe the data within eq 3 are $\Delta H^*_\mathrm{s} = 15.8 \pm 0.3$ kcal/mol, $\Delta S^*_\mathrm{s} = -18.5 \pm 0.9$ eu, $P_1 = -0.28 \pm 0.07$ F^{-1}, and $P_2 = -0.0105 \pm 0.0074$ F^{-1} deg^{-1}, the average deviation between calculated and observed rate constants being 5.3%. The value of β at 25° calculated from P_1 and P_2 is 0.54 F^{-1}. This is much larger than 0.1 F^{-1} which is generally considered to be the upper limit for β expected for H^+-Li^+ solutions.[43b] This observation mitigates against the activity effect hypothesis and indicates that the intercept terms should be interpreted as real kinetic parameters. It is worthwhile noting that reasonable estimates of k_0 (from the rate of Cr-N bond breaking) and k_{-1} (from the value of Q at $(\mathrm{H}^+) = 0.050$ F) at 25° are $k_0 = k_{-1} = 1 \times 10^{-5}$ sec^{-1} and thus the magnitude of the intercept term at 25° is consistent with the hypothesis that it reflects real kinetic

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paths. When the weighted rate data are fitted to the standard Eyring expression

$$k^{\mathrm{obsd}} = \frac{kT}{h}\left[e^{\Delta S^*_{\mathrm{int}}/R}e^{-\Delta H^*_{\mathrm{int}}/RT} + (\mathrm{H}^+)e^{\Delta S^*_{\mathrm{s}}/R}e^{-\Delta H^*_{\mathrm{s}}/RT}\right] \tag{4}$$

where the subscripts "int" and "s" refer respectively to intercept and slope terms, chemically unreasonable values of $\Delta H^*_{\mathrm{int}}$ and $\Delta S^*_{\mathrm{int}}$ are obtained ($\Delta H^*_{\mathrm{int}} = 2.0 \pm 4.5$ and $\Delta H^*_{\mathrm{s}} = 16.8 \pm 0.2$ kcal/mol, $\Delta S^*_{\mathrm{int}} = -75 \pm 16$ and $\Delta S^*_{\mathrm{s}} = -15.7 \pm 0.7$ eu, average deviation between calculated and observed rate constants is 5.5%). These unreasonable results presumably arise since the contribution of k_0 and k_{-1} to the Eyring expression are of the same exponential form. Equation 4 should contain two acid-independent terms of identical form but *not* identical parameters; the solution of such an equation is not computationally feasible. In order to obtain meaningful activation parameters for the acid-dependent rate term, $\Delta H^*_{\mathrm{int}}$ and $\Delta S^*_{\mathrm{int}}$ were fixed at their graphically estimated values ($\Delta H^*_{\mathrm{int}} = 15.7$ kcal/mol and $\Delta S^*_{\mathrm{int}} = -27$ eu) and ΔH^*_{s} and ΔS^*_{s} were varied within eq 4 to determine their values which best fit the observed rate data. This approach leads to what we consider to be the best values of $\Delta H^*_{\mathrm{s}} = 16.2 \pm 0.3$ kcal/mol and $\Delta S^*_{\mathrm{s}} = -17.6 \pm 0.9$ eu, the average deviation between calculated and observed rate constants being 6.5%.

Aquation of the *N,S*-(2-Mercaptoethylamine)bis(ethylenediamine)chromium(III) Ion. The aquation of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ in 4.00 *F* $\mathrm{HClO_4}$ yields a product which behaves as a triply charged cation on Dowex 50W-X2 resin. This product exhibits negligible absorption in the near-ultraviolet region where the starting material has an intense absorption band characteristic of the Cr-S bond, and its visible spectrum is nearly identical with that of $[\mathrm{Cr(en)_2(OH_2)(enH)}]^{4+}$ (see Table III). From this evidence the primary aquation product is identified as $[\mathrm{Cr(en)_2(OH_2)(NH_2CH_2CH_2SH)}]^{3+}$ again indicating that the initial aquation step involves Cr-S bond cleavage.

At $\mu = 4.00$ *F* and 25°, the absorbance-time data for the aquation of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ were treated by the time-lag method as described for $[\mathrm{Cr(en)_2(SCH_2COO)}]^+$. Again it is observed that the $A_\infty^{\mathrm{calcd}}$ values obtained by this method increase with decreasing acidity. Furthermore, a solution of the 3+ product ion, isolated from an ion-exchange column in 4.0 *F* $\mathrm{NaClO_4}$-0.001 *F* $\mathrm{HClO_4}$, exhibits increasing absorbance at 314 nm. As in the case of the mercaptoacetato complex, these observations indicate that an equilibrium between the monodentate aquation product and the chelated starting material is operative. Thus a mechanism completely analogous to Mechanism II discussed for $[\mathrm{Cr(en)_2(SCH_2COO)}]^+$ is proposed for the aquation of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$, and since K_p is still $\ll(\mathrm{H}^+)$ for all acid concentrations, the appropriate rate expression will again be eq 1a. A plot of k^{obsd} ($\mu = 4.00$ *F*) *vs.* (H^+) is linear over the range $(\mathrm{H}^+) = 0.33$-4.00 *F* in contrast to the curvature observed under similar conditions for the mercaptoacetato complex. Thus for $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ at $\mu = 4.00$ *F*, $(\mathrm{H}^+)/K_\mathrm{a} \ll 1$ for all values of (H^+) studied, implying that $K_\mathrm{a} > 40$ *F*, and eq 1c is the appropriate form of the rate law. If the thiol function is the site of protonation in both complexes, the different K_a's for the protonated cysteamine and the protonated mercaptoacetato complexes may be rationalized in terms of electrostatic considerations. However, it is possible that the respective values of K_a may instead reflect different protonation sites in the two complexes (thiol *vs.* carboxylate function).

A linear least-squares treatment of the k^{obsd}-(H^+) plot gives a slope (k_1/K_a) of $(3.42 \pm 0.07) \times 10^{-5}$ F^{-1} sec^{-1} and an intercept ($k_0 + k_{-1}$) of $(1.68 \pm 0.18) \times 10^{-5}$ sec^{-1}. The large value of the intercept strongly indicates that it reflects a real rate term rather than a Harned activity effect.

At $\mu = 1.00$ *F*, the absorbance-time data for the aquation of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ may no longer be treated by the time-lag method since the k^{obsd} obtained from this method depends upon the time interval used in the calculation, indicating that the process is not first order during the entire time that it is being monitored. Presumably this effect arises from competition between Cr-S and Cr-N bond cleavage. By analogy to the mercaptoacetao equation, it is reasonable to expect the rate of Cr-S bond fission in $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$ to be slower at $\mu = 1.00$ *F* than it is at $\mu = 4.00$ *F* (larger K_a at lower ionic strength) whereas it has been shown[44,45] that the rate of Cr-N bond fission is relatively insensitive to ionic strength. Even though the kinetics are being monitored at a wavelength specific for Cr-S bonds, Cr-N bond fission may easily complicate the observed kinetics by producing a species that undergoes Cr-S bond fission at a different rate than does the starting material. This problem may be circumvented by looking at only the first few per cent of the aquation reaction, during which time there will be have been no significant buildup of the Cr-N aquation product, and thus the observed absorbance change results from Cr-S bond fission in the starting material (see Experimental Section for details). This approach is feasible in this system since it has been shown[34a,45] that the rate of the first Cr-N bond fission in similar complexes occurs at a specific rate of about 1×10^{-5} sec^{-1} (25°) independent of the nature of the other ligands coordinated to chromium, and thus Cr-N bond fission is never significantly faster than Cr-S bond fission. The specific rates of Cr-S bond breaking calculated from this initial rate treatment ($k_{\mathrm{ir}}^{\mathrm{obsd}}$) are listed in Table II. At all temperatures studied, plots of $k_{\mathrm{ir}}^{\mathrm{obsd}}$ *vs.* (H^+) are linear and thus $(\mathrm{H}^+)/K_\mathrm{a} \ll 1$ even at $(\mathrm{H}^+) = 1.00$ *F*. From eq 1 it is seen that

$$k_{\mathrm{ir}}^{\mathrm{obsd}} = \frac{k_1(\mathrm{H}^+)}{K_\mathrm{a}} + k_0 \tag{1d}$$

Linear least-squares analyses of the $k_{\mathrm{ir}}^{\mathrm{obsd}}$-$(\mathrm{H}^+)$ plots at 25 (10 data points), 34.1 (10 data points) and 44.3° (11 data points) respectively give slopes of $(7.61 \pm 0.18) \times 10^{-6}$, $(22.3 \pm 1.0) \times 10^{-6}$, and $(79 \pm 4) \times 10^{-6}$ F^{-1} sec^{-1} and intercepts of $(1.30 \pm 0.12) \times 10^{-6}$, $(5.73 \pm 0.68) \times 10^{-6}$, and $(15 \pm 3) \times 10^{-6}$ sec^{-1}. Again the large values of the intercepts are strongly indicative of a real rate term rather than of an activity effect.[43] All 31 rate constants in Table II at $\mu = 1.00$ *F* were weighted by the inverse square of their standard deviations and then were fitted to eq 4 by means of the previously described[6] nonlinear least-squares program. The activation parameters that best describe these data are $\Delta H^*_{\mathrm{int}} = 23.0 \pm 1.3$ and $\Delta H^*_{\mathrm{s}} = 22.3 \pm 0.6$ kcal/mol and $\Delta S^*_{\mathrm{int}} = -8 \pm 4$ and $\Delta S^*_{\mathrm{s}} = -7.2 \pm 1.8$ eu. The rate constants calculated from these activation parameters agree with the experimentally determined values with an average deviation of 4.0%.

Summary

A summary of the rate data presented in the previous sec-

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Table IV. Summary of Kinetic Parameters for Aquation of Thiolatobis(ethylenediamine)chromium(III) Complexes in Terms of Mechanism II and Eq 1

Complex	μ, F	K_a,[a] F	s ($\equiv k_1/K_a$),[a,b] F^{-1} sec^{-1}	ΔH^*_s, kcal/mol	ΔS^*_s, eu	int,[a,b] sec^{-1}
Cr(tga)[c]	1.00	>10	$(1.11 \pm 0.02) \times 10^{-3}$	16.2 ± 0.3	-17.6 ± 0.9	$(0.025 \pm 0.014) \times 10^{-3} \equiv k_0 + k_{-1}$
Cr(tga)[c]	4.00	1.15 ± 0.14	$(9.27 \pm 0.11) \times 10^{-3}$			$<0.2 \times 10^{-3} \equiv k_0 + k_{-1}$
Cr(cys)[d]	1.00		$(7.61 \pm 0.18) \times 10^{-6}$	22.3 ± 0.6	-7.2 ± 1.8	$(1.30 \pm 0.12) \times 10^{-6} \equiv k_0$[e]
Cr(cys)[d]	4.00	>40	$(34.2 \pm 0.7) \times 10^{-6}$			$(16.8 \pm 1.8) \times 10^{-6} \equiv k_0 + k_{-1}$

[a] At 25°. [b] "s" and "int" refer respectively to the slope and intercept of the acid-dependence plot. [c] Cr(tga) ≡ $[Cr(en)_2(SCH_2COO)]^+$. [d] Cr(cys) ≡ $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$. [e] $\Delta H^*_{int} \equiv \Delta H^*_0 = 23.0 \pm 1.3$ kcal/mol; $\Delta S^*_{int} \equiv \Delta S^*_0 = -8 \pm 4$ eu.

tion is given in Table IV. Within the framework of Mechanism II, there are common kinetic arguments which favor the aquation of $[Cr(en)_2(SCH_2COO)]^+$ relative to that of $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$ (subsequently referred to as Cr(tga) and Cr(cys), respectively). If for both complexes k_1 reflects Cr-S bond cleavage of the protonated complex, k_1 should be greater for Cr(tga) since the cis carboxylate function of this complex has unshared p-orbital electrons which can overlap with the empty d^2sp^3 orbital of the Cr(III) trigonal-bipyramidal transition state.[46] The k_0 term is affected in the same manner; k_0 should also be favored for Cr(tga) since the lower charge of this complex promotes separation of an anionic moiety.[47] In addition, the observed rates are inversely dependent on the parameter K_a, *i.e.*, on the relative tendencies of the complexes to be protonated. Whether it is because of electrostatic reasons or because of the fact that different sites are being protonated, K_a for Cr(tga) is smaller than for Cr(cys), thus favoring the more rapid aquation of the former. Also, K_a decreases with increasing ionic strength,[7,39] and at $\mu = 4.00\ F$, K_a for Cr(tga) becomes small enough (and the range of acid concentrations is large enough) that saturation of the protonation equilibrium occurs; the inherently larger K_a of Cr(cys) prevents saturation under these conditions. This domination of the observed rate by the value of K_a means that k_0 carries a significant portion of the reaction only when K_a is large, *e.g.*, Cr(cys) at $\mu = 1.00\ F$. Correspondingly, when K_a is small, *e.g.*, for Cr(tga) at $\mu = 4.00\ F$, the contribution from k_0 is not observed at all.

Lane and Bennett[3] have studied Cr-S bond fission in $[Cr(OH_2)_4(SCH_2COO)]^+$ as a function of acid at $\mu = 0.25\ F$ and 25°. They concluded that a mechanism analogous to Mechanism II is operative and calculated $k_1/K_a = 7.0 \times 10^{-5}\ F^{-1}$ sec^{-1}. This is to be compared with $k_1/K_a = 1.11 \times 10^{-3}\ F^{-1}$ sec^{-1} at $\mu = 1.00\ F$ and 25° for Cr(tga). The significantly smaller value of k_1/K_a observed by Lane and Bennett can reasonably be accounted for since (1) in general the rates of aquation of amminechromium(III) complexes are greater than those of comparable aquochromium(III) complexes[48,49] and (2) the value of K_a for $[Cr(OH_2)_4(SCH_2COO)]^+$ at $\mu = 0.25\ F$ is larger than it would be at $\mu = 1.00\ F$. Lane and Bennett also determined K_{eq}, equal to $Q/(H^+)$, to be 10.3 F^{-1}. Thus at $(H^+) = 0.050\ F$, Q for $[Cr(OH_2)_4(SCH_2COO)]^+$ is 0.5, which should be increased by a statistical factor of 4 in order to be directly compared to the value of $Q = 2$ observed for Cr(tga) in 0.050 F acid.

The difference between enthalpies governing the k_1/K_a aquation path for Cr(tga) and Cr(cys) (see Table IV) is consistent with the previous discussion. However, the effect of this enthalpy difference on the observed rate is partially offset by the activation entropy for Cr(tga) being more negative than that for Cr(cys) (see Table IV). This phenomenon presumably arises from the presence of the cis carboxylate of Cr(tga). One possible explanation for the effect is that, in the transition state, the carboxylate forms a specific hydrogen bond to a solvent molecule (possibly that solvent molecule which is also bound to the protonated sulfur). This would decrease the entropy of the transition state relative to the comparable Cr(cys) transition state in which there is no carboxylate function available to bind solvent. It is also possible that the entropy difference reflects different transition-state geometries or different protonation sites.

The cobalt(III) compounds analogous to Cr(tga) and Cr(cys), *i.e.*, $[Co(en)_2(SCH_2COO)]^+$ and $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, do not undergo significant aquation under the conditions used in this work (half-lives in 1 F $HClO_4$, at 25°, are greater than 4 months). This observation coincides with the phenomenology of metal-sulfur bond cleavage; *e.g.*, tris(thiooxalato)chromate(III) racemizes much more rapidly than tris(thiooxalato)cobaltate(III),[5] but it is not clear exactly what chemical factors lead to this greater lability for the Cr-S bond. The single-crystal X-ray structure determinations of Cr(tga) and Co(tga), which are reported in the following paper,[13] provide data which eliminate one possible cause. The difference in bond lengths [(Cr-X) − (Co-X)] for X = N (average of those cis to sulfur), S, and O are 0.125, 0.094, and 0.048 Å, respectively. The nitrogens are coordinatively saturated and have no low-lying orbitals capable of π bonding, and thus the M-N bond length difference provides a reasonable estimate of the inherently different radii of Cr(III) and Co(III). Since the M-S bond difference is less than this value, it would seem that the Cr-S bond is significantly shortened with respect to the Co-S bond (and the Cr-O bond is even further shortened). This implies[50] that the Cr-S bond strength is actually greater than the Co-S bond strength and therefore the greater lability of the chromium-sulfur linkage cannot be attributed to the weakness of this bond. Nor can it be attributed to the relative strengths of the nascent metal-oxygen bonds since both chromium(III) and cobalt(III) complexes are considered to aquate *via* predominantly dissociative mechanisms.[51,52] Certainly a significant portion of the rate difference arises from the larger crystal field activation energy associated with a d^6 ion relative to a d^3 ion.[53,54] However, in comparable compounds this effect leads only to a factor of 10-100 decrease in rate constant[53,54] and therefore crystal field activation energies do not alone account for the observed labilities. It may be possible that the enhanced lability of the Cr-S bond is due to a greater tendency of

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sulfur to be protonated when it is coordinated to chromium, relative to when it is coordinated to cobalt. This would strongly favor the efficient acid-dependent aquation path for the chromium compound. The direction of this proposed variation in the Bronsted basicity of coordinated thiolato sulfur with the nature of the central metal ion is in accord with the observation that methyl iodide reacts more rapidly with the sulfur of $Ni(NH_2CH_2CH_2S)_2$ than with the sulfur of $Pd(NH_2CH_2CH_2S)_2$[55] and with the observation that Cr(tga) and Cr(cys) salts are much more soluble than the corresponding cobalt compounds. These considerations, as well as relevant X-ray structural data, will be related to the rates of electron transfer through thiolato sulfur in a future communication.

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Registry No. $[Cr(en)_2(SCH_2COO)]ClO_4$, 41212-24-2; $[Cr(en)(SCH_2CH_2NH_2)_2]ClO_4$, 41777-29-1; $[Cr(en)_2(SCH_2CH_2NH_2)](ClO_4)_2$, 41777-30-4; $[Cr(en)_2(SCH_2CH_2NH_2)]I_2$, 41777-31-5; $[Cr(en)_2(H_2O)(OOCCH_2SH)]^{2+}$, 41777-32-6; $[Cr(en)_2(H_2O)(NH_2CH_2CH_2SH)]^{3+}$, 41777-33-7.

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Crystal Structure Studies of Sulfur Trans Effects

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The single-crystal structures of mercaptoacetatobis(ethylenediamine)cobalt(III) chloride monohydrate, $[Co(en)_2(SCH_2COO)]Cl \cdot H_2O$, mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate, $[Cr(en)_2(SCH_2COO)]ClO_4$, and β-mercaptoethylaminebis(ethylenediamine)cobalt(III) dithiocyanate, $[Co(en)_2(SCH_2CH_2NH_2)](SCN)_2$, have been determined using the methods of X-ray crystallography. The unit cells and space groups are: $[Co(en)_2(SCH_2COO)]Cl \cdot H_2O$, monoclinic, $a = 12.071$ (8) Å, $b = 14.876$ (9) Å, $c = 7.539$ (5) Å, $\beta = 110.41$ (5)°, $P2_1/a$, $Z = 4$; $[Cr(en)_2(SCH_2COO)]ClO_4$, monoclinic, $a = 12.250$ (4) Å, $b = 10.155$ (3) Å, $c = 11.265$ (3) Å, $\beta = 95.21$ (4)°, $P2_1/n$, $Z = 4$; $[Co(en)_2(SCH_2CH_2NH_2)](SCN)_2$, orthorhombic, $a = 15.418$ (7) Å, $b = 11.563$ (6) Å, $c = 17.454$ (10) Å, $Pbca$, $Z = 8$. All intensity data were measured using a Syntex $P\bar{1}$ automated diffractometer. The structures have been refined by least-squares methods using anisotropic thermal parameters and including hydrogen atoms to final conventional R factors of 0.033, 0.037, and 0.032, respectively. All three complex cations are pseudo-octahedral six-coordinate species. Both mercaptoacetate and β-mercaptoethylamine anions chelate to form five-membered rings. The mercaptoacetate complexes both exhibit $\Delta\lambda\delta$ and $\Lambda\delta\lambda$ configurations in their centric crystals. The β-mercaptoethylamine complex adopts the $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$ configurations. All complexes appear weakly hydrogen bonded. In both cobalt complexes, the trans (to sulfur) Co–N distance is 0.04 Å longer than the average cis Co–N bond. The trans lengthening does not appear to occur in the chromium complex. The implications of the structural trans effect are discussed relative to the electron-transfer reactions of the three complexes with chromous ion.

Introduction

Sulfur-containing ligands have been the subject of intense study in recent years. New synthetic techniques have been discovered which allow the preparation of stable metal complexes[2,3] whose free ligands are not stable. The peculiar effects of the sulfur-containing ligand on the geometric and electronic structures of dithiolate, dithiocarbamate, and β-dithioketonate complexes[2,4-6] are now well documented. The reactions of complexes of sulfur-containing ligands offer interesting contrasts. Thus, electron-transfer reactions of cobalt(III) complexes containing a thiolato ligand, β-mercaptoethylamine[7] or mercaptoacetate,[8] are extremely rapid; those of the analogous chromium(III) complexes[7] are not. The aquation of these chromium complexes is found to proceed *via* chromium–sulfur and also chromium–nitrogen bond fission at rates convenient for kinetic study,[9] whereas the cobalt(III) analogs do not aquate.

To provide structural information on which to base an understanding of these reactions, we have determined the structures of a series of mixed ligand complexes of the type thiolato-X-bis(ethylenediamine)metal(III), $[M(en)_2(SRX)]^{n+}$, where the metal atom, M, is either cobalt or chromium and where thiolato-X is either β-mercaptoethylamine or mercaptoacetate. We wished to determine (a) if the complexes are all six coordinate with metal-bonded sulfur atoms, (b) the characteristic value of the metal–sulfur bond length, (c) whether some unusual structural detail such as a ground state trans effect, a peculiar conformation, or a set of unusual bond lengths (and presumably bond strengths) is present, and (d) whether the replacement of the carboxylate group of mercaptoacetate (tga) by methylenamine in β-mercaptoethylamine (cys) and the consequent change in charge of the complex cation led to significant changes in structure. We report here the single-crystal structural determinations of mercaptoacetatobis(ethylenediamine)cobalt(III) chloride monohydrate, mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate, and β-mercapto-

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