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Thioether Sulfur as an Electron-Transfer Bridge. Kinetics and Mechanism of the Chromium(II) Reduction of (Alkyl 2-aminoethyl thioether-*N*,*S*)bis(ethylenediamine)cobalt(III) Complexes

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The rates of chromium(II) reductions of a series of 12 $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes with R = methyl, ethyl, cyclohexylmethyl, benzyl, 4-fluorobenzyl, 4-methylbenzyl, carboxymethyl, methylcarboxymethyl, carboxyethyl, carboxypropyl, 1-naphthylmethyl, and 2-naphthylmethyl have been measured in aqueous perchlorate media. Reduction follows the simple second-order rate law $-d[Co^{III}]/dt = k_2[Co^{III}][Cr^{II}]$. Detection and characterization of the relatively labile thioether–chromium(III) products, as well as observed reactivity patterns, show conclusively that thioether sulfur functions as an electron-transfer bridge. For complexes with simple R groups the rate of reduction depends primarily on the steric bulk of the R group, this effect being manifested in ΔH^*; varying R from methyl to cyclohexylmethyl reduces k_2 from 0.34 to 0.013 $M^{-1}\ s^{-1}$ (25 °C, $\mu = 1.00$ M) with a concomitant increase in ΔH^* from 4.9 to 7.6 kcal/mol. For those complexes with R = $(CH_2)_nCOOH$ the rate of reduction increases with decreasing acid concentration, presumably reflecting O,S-chelation of chromium(II) in the precursor complex. For $n = 1$, $k_2 = a/(1 + b[H^+])$ while for $n = 2$ and 3, $k_2 = c + d/[H^+]$. Stability of the chelate ring in the deprotonated precursor complex, and the concomitant overall reaction rate, decreases in the order $1 > 2 > 3$ for n which corresponds to the ordering of ring size $5 > 6 > 7$.

Introduction

The possible modes of participation of thioether sulfur in 1-equiv electron transfer between metal centers have recently generated considerable interest. To a large extent this interest has arisen because of the coordination of a thioether sulfur (methionine-80) to the iron of the electron-transfer protein cytochrome *c*[1] and because of the presumed presence of coordinated thioether groups in the blue copper proteins[2] which are also involved in biological electron-transport systems.[3] While metal complexes containing coordinated thioethers have been known and studied for some time,[4-8] it has only been recently that well-defined cobalt(III) complexes suitable for mechanistic studies have become available.[9-12]

Most mechanistic work to date has focused on the roles that *nonbridging* thioether sulfur may play in electron-transfer reactions. Gould[13] and, more recently, Balahura[14] have shown that the rate of inner-sphere electron transfer from chromium(II) to cobalt(III) is only modestly affected by the presence of a pendant (i.e., noncoordinated) thioether group on the cobalt(III) complex. Worrell[15-17] has shown that coordinated, but nonbridging, thioether groups can markedly affect the rate of inner-sphere electron transfer from iron(II) to cobalt(III).

However, in light of the biological systems noted above, it is of special interest to understand the potential role of thioether sulfur as a *bridging* ligand in electron-transfer reactions. In order to function as an electron-transfer bridge, a coordinated thioether sulfur atom must attain a coordination number of 4 in the transition state. While many organic compounds containing four-coordinate sulfur are well-known (e.g., sulfones), the bonding of two octahedral metal complexes and two organic moieties to the same sulfur atom may be sterically inaccessible. Linck[18] has noted that OH^- but *not* OH_2 can bridge electron transfer from chromium(II) to cobalt(III), implying that for the smaller group 6 congener, oxygen, a four-coordinate transition state is sterically inaccessible even when two of the four moieties bonded to oxygen are relatively small hydrogen atoms. Countering this steric argument are the observations that electron-transfer reactions (especially those involving chromium(II)) tend to proceed via inner-sphere mechanisms whenever possible[19] and that coordinated thiolato sulfur appears to be an exceptionally efficient bridge for electron transfer to cobalt(III).[11,14] Bennett[20] first examined whether or not thioether sulfur can function as a bridge by investigating the chromium(II) reduction of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$; from the lack of observation of a thioether–chromium(III) product it was tentatively concluded that this reaction proceeds via an outer-sphere mechanism.[11,20] Since this conclusion is based on negative evidence, and since our experience with thiolato–chromium(III) complexes[21-24] led us to expect that the inner-sphere thioether–chromium(III) product would be transitory and difficult to observe, we decided to reexamine Bennett's conclusion by means of a more extended and systematic study. To this end we prepared and characterized a series of 12 thioether complexes of general formula $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ [12] and in this paper report on the reduction of these complexes by chromium(II). In the course of this work we have obtained direct and positive evidence that thioether sulfur can indeed function as an electron-transfer bridge.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. Triply distilled water was from two sources: (a) a sample kindly supplied by J. C. Sullivan of Argonne National Laboratory; (b) house distilled water (from a tin-lined still) which was filtered through charcoal, distilled through a continuous all-Pyrex still, and then redistilled in a batch process in an all-Pyrex still. Duplicate kinetic experiments showed no detectable difference between the two sources and, thus, they were used interchangeably in this work. Streams of nitrogen and argon gas were deoxygenated and equilibrated with water vapor by passage through two glass scrubbing towers filled with a solution 0.1 M in chromium(II) and 1.0 M in HCl; the chromium was kept in its reduced state by amalgamated zinc in the bottom of the tower. Doubly vacuum-distilled perchloric acid (70–72%, G. F. Smith) was used for all final crystallizations and for kinetics experiments. Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate as previously described.[22] Hexaaquochromium(III) perchlorate was prepared and purified by reported procedures;[25] solutions of chromium(II) perchlorate were prepared by reduction over zinc amalgam as previously described.[25] Dowex 50W-X2 (200–400 mesh) cation-exchange resin was cleaned as previously detailed,[25] then stirred in 6 M $HClO_4$ for 12 h in order to remove ultraviolet absorbing impurities, and then washed with water until the wash was neutral. Purified resin was stored under water.

Oxalatotetraamminecobalt(III) Perchlorate, $[(NH_3)_4Co(C_2O_4)]ClO_4$. A water solution of equimolar amounts (0.147 mol) of carbonatotetraamminecobalt(III) nitrate[26] and oxalic acid dihydrate was heated at 60 °C for 1 h, during which time it changed color from violet to carmine. Filtration of the hot solution, addition of saturated $NaClO_4$ solution, and cooling to 4 °C led to crystallization of the desired product. This material was recrystallized from a hot aqueous $NaClO_4$ solution, and this final product was washed and then dried in vacuo over P_2O_5 (yield 27.0 g). Anal. Calcd for $[(NH_3)_4Co(C_2O_4)]ClO_4$: C, 7.64; H, 3.85; N, 17.81; Cl, 11.27; Co, 18.74. Found: C, 7.64; H, 4.03; N, 17.58; Cl, 11.09; Co, 18.52. Since this material was to be used to quench chromium(II) in stoichiometry experiments, its

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purity was further confirmed by two ion-exchange experiments. (1) Elution from a Dowex 50W-X2 cation-exchange column with 0.5 M HCl showed only one detectable band. (2) Reduction of excess $[(NH_3)_4Co(C_2O_4)]^+$ by chromium(II), and separation of the product mixture by ion exchange, quantitatively (98.6 ± 1.4%) yielded the $[(H_2O)_4Cr(C_2O_4)]^+$ ion (λ_{max} (ϵ) 556 (35.4) and 416 (39.9) nm (M^{-1} cm^{-1}); Price and Taube[27] report 556 (34.8) and 418 (40.1)) in agreement with the results of previous studies on this system.[28] The only other column species detectable in this experiment were $[Co(aq)]^{2+}$ and excess $[(NH_3)_4Co(C_2O_4)]^+$.

(Alkyl 2-aminoethyl thioether-*N,S*)bis(ethylenediamine)cobalt(III) Perchlorates, $[(en)_2Co(S(R)CH_2CH_2NH_2)](ClO_4)_3$. The syntheses and characterization of these complexes have been detailed previously.[12] Complexes with R = methyl, ethyl, cyclohexylmethyl, benzyl, 4-fluorobenzyl, 4-methylbenzyl, carboxymethyl, methylcarboxymethyl, carboxyethyl, and carboxypropyl were recrystallized three times from water–perchloric acid or water–sodium perchlorate solutions, the last crystallization being from triply distilled water and doubly distilled $HClO_4$. Complexes with R = 1-naphthylmethyl and 2-naphthylmethyl were recrystallized three times from 50% (v/v) ethanol–water and $HClO_4$. Perchlorate salts were routinely checked for the presence of halide ion, arising from the synthetic procedure,[12] which is difficult to remove by successive recrystallizations but which may be removed as described previously.[12]

Benzyl 2-Aminoethyl Thioether Hydrochloride, $C_6H_5CH_2SCH_2CH_2NH_2 \cdot HCl$. To 0.486 mol of benzylmercaptan (Evans Chemetics) in 400 mL of toluene at 2 °C was slowly added 0.44 mol of ethylenimine (Dow Chemical; *warning*! *carcinogen*) with stirring, and the resulting mixture was refluxed (60–65 °C) for 72 h. To this mixture was added 100 mL of 4 M HCl, and the protonated thioether was extracted into 150 mL of 1.0 M HCl; this solution was brought to pH 12 with 50% NaOH, and the resulting yellow oil was extracted into diethyl ether. This acid–base extraction procedure was repeated two more times. The final ether layer was evaporated to yield a yellow oil containing some white solid. To this product was added 60 mL of distilled water, just enough 2 M HCl to bring everything into solution, and finally 100 mL of 37% HCl. When cooled to 4 °C, this solution yielded fine white crystals which were collected and recrystallized from 100 mL of water and 75 mL of 37% HCl. Collection and drying over P_2O_5 in vacuo yielded 33.6 g of white plates: mp 109–111 °C; ^1H NMR (Me_2SO-d_6, Me_4Si internal standard) δ values for $C_6H_{5c}CH_{2b}S(CH_{2a})_2NH_{3d}Cl$ 2.80 (a, br, 4 H), 3.90 (b, s, 3 H), 7.42 (c, s, 5 H), 8.50 (d, br, 3 H); UV (1.00 M $HClO_4$) λ_{max} (ϵ) 267 (205), 260 (301) nm (M^{-1} cm^{-1}); R_f values (Eastman Kodak Silica Gel 6060 Chromagram TLC sheets, I_2 development) 0.60 with 95% ethanol, 0.22 with 2-propanol. Anal. Calcd for $C_9H_{14}SNCl$: C, 53.06; H, 6.93; N, 6.87; S, 15.74; Cl, 17.40. Found: C, 52.98; H, 6.85; N, 6.84; S, 15.80; Cl, 17.59.

(Benzyl 2-aminoethyl thioether-*N,S*)bis(ethylenediamine)chromium(III) Perchlorate, $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)](ClO_4)_3$. This complex was prepared by alkylation of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)chromium(III) perchlorate[29] with benzyl chloride according to the procedure outlined for the analogous cobalt(III) complex.[12] Characterization of this complex is deferred to the Results section.

Equipment. Melting points (Thomas-Hoover apparatus) were determined in open-end capillaries and are uncorrected. Visible–UV spectra were recorded on a Cary Model 14 spectrophotometer at room temperature. Kinetic experiments with a half-life greater than ca. 10 s were monitored on a Cary Model 118B recording spectrophotometer equipped with a thermostated cell compartment, automatic turret sample changer, and a Hewlett-Packard 5150A thermal printer. Temperature was monitored with a USC Model 581C digital thermometer which had been calibrated against a NBS certified mercury thermometer; it is estimated that during any given experiment the temperature was held constant to ±0.1 °C and was known to an accuracy of ±0.3 °C. Kinetic experiments in which the half-life was less than ca. 10 s were monitored on a Durrum D-110 stopped-flow apparatus that was interfaced to a Lockheed MAC-16 minicomputer for data collection and storage on magnetic tape.[30-32] The Durrum instrument was further modified by installation of Plexiglas boxes around the drive and storage syringes; these boxes were continuously purged with argon in order to keep all reagents under an anaerobic atmosphere during a series of experiments. Circulation of thermostated water kept the temperature of the drive syringes constant to ±0.2 °C. All computer calculations were performed on the SWORCC IBM 370 system located at the University of Cincinnati.

Table I. Equivalent Weights and pK_a Values for $[(en)_2Co(S((CH_2)_nCOOH)CH_2CH_2NH_2)]^{3+}$ (n = 1, 2, 3) Complexes at μ = 1.00 ± 0.01 M ($LiClO_4$), 25 °C

		equiv wt	
n	pK_a[a]	obsd	calcd
1	2.10 ± 0.03	645 ± 8	649[b]
2	3.17 ± 0.01	621 ± 1	627
3	3.98 ± 0.01	679 ± 5	677[b]

[a] Estimated as the pH at half the equivalence point. [b] Formulated as the dihydrate (quantitatively confirmed by elemental analyses for n = 3; qualitatively confirmed by IR analysis for n = 1; see ref 12).

Analyses. Elemental analyses of solid samples, and analyses of aqueous solutions for total organic carbon (TOC) and total sulfur, were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Total chromium analyses were performed by a standard procedure.[24]

Kinetic Measurements and Calculations. Unless otherwise noted, kinetic experiments were conducted (1) in aqueous perchloric acid solutions maintained at a constant ionic strength of 1.00 ± 0.01 M with $LiClO_4$, (2) under a nitrogen or argon atmosphere using syringe techniques that have been previously described,[25] and (3) with a pseudo-first-order concentration excess of chromium(II) over cobalt(III) complex. Kinetics were monitored for at least 4 half-lives either at the UV LTMCT band characteristic of the cobalt–sulfur bond[29] or at a visible band characteristic of a cobalt(III) d–d transition; observed pseudo-first-order rate constants, k_{obsd}, were independent of the monitoring wavelength. Three methods were used to calculate k_{obsd} and its associated standard deviation $\sigma_{k_{obsd}}$. (1) For many experiments an infinite time measurement, OD_∞, could be determined experimentally and plots of log ($OD_t - OD_\infty$) vs. time gave straight lines for more than 95% reaction (linear least-squares analysis yielded values of k_{obsd} and $\sigma_{k_{obsd}}$). This observation justifies the use of the following two methods which are based upon the assumption of first-order kinetic behavior. (2) For most experiments, and all those conducted on the stopped-flow apparatus, the previously described[33] LASL nonlinear least-squares program was employed to determine the values of k_{obsd}, OD_0 and OD_∞ which best fit the OD_t–t data within the first-order rate expression

$$OD_t = OD_\infty - (OD_\infty - OD_0)e^{-k_{obsd}t} \tag{1}$$

(3) The previously described[29] Kezdy procedure (an exponential form of the Guggenheim treatment) was also used when OD_∞ was not accessible experimentally; in many calculations the time interval chosen was varied over a wide range (1–3 half-lives) resulting in no significant variation in the calculated value of k_{obsd}. For a given set of OD_t–t data, any of the three methods yielded a value of k_{obsd} within 2% of that obtained by one of the other methods. Therefore, methods 2 and 3 were used interchangeably, with the restriction that comparable data sets were treated by the same method. The second-order rate constant, k_2, and its standard deviation, σ_{k_2}, were calculated by the expressions

$$[Cr^{II}]_{av} = [Cr^{II}]_0 - [Co^{III}]_0/2 \tag{2a}$$

$$k_2 = k_{obsd}/[Cr^{II}]_{av} \tag{2b}$$

$$\sigma_{k_2} = \sigma_{k_{obsd}}/[Cr^{II}]_{av} \tag{2c}$$

In the nonlinear least-squares calculation[33] of activation parameters, each individual value of k_2 was weighted by $(1/\sigma_{k_2})^2$. Unless otherwise noted, all reported errors are standard deviations.

Procedures. Table I lists the equivalent weights and pK_a values of $[(en)_2Co(S((CH_2)_nCOOH)CH_2CH_2NH_2)]^{3+}$ complexes obtained at μ = 1.00 M ($LiClO_4$) by potentiometric titration of four independently weighed samples of each complex with standardized LiOH–$LiClO_4$ solutions.[25] The formal charges on complex cations were inferred from the characteristics of their elution from Dowex 50W-X2 (200–400 mesh, H^+ or Li^+ form) ion-exchange columns which had been calibrated with the following ions of known formal charge: $[(NH_3)_4Co(C_2O_4)]^+$, $[(H_2O)_4CrCl_2]^+$, $[C_6H_5CH_2SCH_2CH_2NH_3]^+$, $[(H_2O)_5CrCl]^{2+}$, $[(H_2O)_5CrOOCCH_3]^{2+}$, $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, $[(H_2O)_6Cr]^{3+}$, and several $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes.

Table II. Visible–UV Spectrophotometric Parameters for Selected Aquochromium(III) Complexes[a]

complex	λ_{max} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	ϵ_{250}	ϵ_{240}
$(H_2O)_6Cr^{3+}$ [b]	575 (13.2)	410 (15.5)	480 (3.1)	3.3	1.7
$(H_2O)_5CrOOCCH_3{}^{2+}$ [b]	571 (24.1)	412 (22.2)	480 (5.0)	29	40
$(H_2O)_5CrOOCCH_2SCH_2CH_2NH_3{}^{3+}$ [c,d]	573 (24.5)	411 (24.1)	485 (6.8)	520	740

[a] Wavelengths, λ, of maxima (max) and minima (min) are in nm. Molar extinction coefficients, ϵ, given in parentheses for λ_{max} and λ_{min}, are in $M^{-1}\ cm^{-1}$. Subscripts on ϵ values indicate wavelength. [b] Data taken from ref 25 and 36. [c] Visible spectrum taken in 2 M $NaClO_4$ (pH 1–2); UV spectrum taken after dilution. Equivalent spectra were obtained in 2 M NaCl and 1 M Na_2SO_4. [d] This formulation is only an approximation; there is presumably an equilibrium amount of the chelated, tetraaquo complex (see text).

Many experiments, employing a variety of conditions, were conducted in order to characterize the products of the title reactions. Following are some selected, optimized procedures.

Product Analysis of the $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ + $[Cr(aq)]^{2+}$ Reaction. A solution of chromium(II) (1.00 mL, 1.000 mmol of Cr(II), 1.20 mmol of $HClO_4$) was injected into a solution of the cobalt(III) complex (10.00 mL, 0.100 mmol of Co(III), 0.100 mmol of $HClO_4$) and the ensuing reaction allowed to proceed anaerobically for 25 min at ambient temperature (ca. 4.7 half-lives). Excess chromium(II) was then quenched by injecting the reaction solution into a deaerated solution of $[(NH_3)_4Co(C_2O_4)]^+$ (100.0 mL, 1.004 mmol of Co(III), 4.02 mmol of $HClO_4$). This solution was then immediately diluted to 250 mL with water precooled to 4 °C and charged onto a calibrated Dowex column maintained at 4 °C. The results of the column separation are described in the next section. In order to obtain higher yields of high-charged species, this experiment was also conducted using 0.500 mmol of cobalt(III) complex, 5.00 mmol of chromium(II), and 4.67 mmol of quenching agent (with appropriate increases in amounts of $HClO_4$) for the same reaction time. This product mixture was charged onto a short (2-cm diameter, 2-cm height), cooled Dowex column so that low-charged species would not be retained on the column. Elutions with $HClO_4$, $NaClO_4$, HNO_3, $NaNO_3$, HCl, NaCl, or Na_2SO_4 solutions were carried out by standard techniques.[25,34]

Product Analysis of the $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ + $[Cr(aq)]^{2+}$ Reaction. A solution of chromium(II) (0.75 mL, 0.075 mmol of Cr(II), 0.090 mmol of $HClO_4$) was injected into a solution of the cobalt(III) complex (9.00 mL, 0.100 mmol of Co(III), 0.804 mmol of $HClO_4$). After 10 s (over 99.9% reaction), the reaction solution was diluted to ca. 30 mL with 4 °C water and charged onto a calibrated Dowex column maintained at 4 °C. Elution was conducted with $NaClO_4$, NaCl, or Na_2SO_4 solutions that had been adjusted to pH 2.0 with the appropriate acid.

Results

Product Analysis of the $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ + $[Cr(aq)]^{2+}$ Reaction. The products of this reaction, and its quenching by $[(NH_3)_4Co(C_2O_4)]^+$ (see previous section), are separated by ion-exchange chromatography and identified by elution characteristics, visible–UV spectra, and, where appropriate, chemical and TLC analyses. The color, identity, origin, and in some cases the spectrophotometrically determined quantity of reaction products are given in their order of elution: (1) violet, $[(H_2O)_4Cr(C_2O_4)]^+$, from quenching of excess chromium(II); (2) carmine, $[(NH_3)_4Co(C_2O_4)]^+$, excess quenching agent; (3) pink, $[Co(aq)]^{2+}$, product of both the quenching and title reactions; (4) blue, $[(H_2O)_6Cr]^{3+}$, from decay of the initial chromium(III) reaction product (vide infra) and possibly a product of the title reaction, comprising 80–88% of the amount of the original thioether–cobalt(III) complex; (5) colorless, $[C_6H_5CH_2SCH_2CH_2NH_3]^+$, from decay of the initial chromium(III) reaction product (vide infra) and possibly a product of the title reaction, comprising up to 85% of the amount of the original thioether–cobalt(III) complex; (6) forest green, $[(H_2O)_5CrS(CH_2C_6H_5)CH_2CH_2NH_3]^{4+}$, initial unstable chromium(III) reaction product, the quantity of this product increasing with decreased column loading time and increasing absolute quantity of starting thioether–cobalt(III) complex (relative reactant concentrations and reaction time being held constant); (7) orange, $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$, unreacted starting material. The forest green product (sixth band) is unstable on the ion-exchange column, splitting into two bands upon elution with HNO_3, $NaNO_3$, NaCl, HCl, and Na_2SO_4 (pH 7 and pH 1); the chloride eluents generate bright green $[(H_2O)_5CrCl]^{2+}$ which "fronts" the forest green band, while the nitrate and sulfate eluents generate blue "fronting" species which have column characteristics that would be expected for $[(H_2O)_5CrONO_2]^{2+}$ and $[(H_2O)_5CrOSO_3]^+$. Upon elution with $HClO_4$, the forest green band gradually generates a "fronting" edge of blue $[(H_2O)_6Cr]^{3+}$. All isolated samples of the forest green band exhibit a UV spectrum of steadily increasing (from 260 to 200 nm) absorbance, devoid of diagnostic peaks. This material is further characterized by the following two ion-exchange experiments. (1) All low-charged species, especially free $[C_6H_5CH_2SCH_2CH_2NH_3]^+$, are eluted from the column. The forest green band is collected with 6 M $HClO_4$ eluent and then decomposed by the addition of concentrated HCl. This decomposed product mixture is adjusted to pH 12, extracted into diethyl ether, and back-extracted into 1 M HCl. Spectrophotometric and TLC analyses of this HCl extract show that it contains $[C_6H_5CH_2SCH_2CH_2NH_3]^+$. (2) All low-charged species, especially free $[C_6H_2CH_2SCH_2CH_2NH_3]^+$, are eluted from the column and then the forest green band is collected with 0.75 M Na_2SO_4 (pH 1) eluent. Total organic carbon (TOC) analysis of the eluate immediately preceding the forest green band yields <1 mg/L TOC while analysis of the band itself yields 15 mg/L TOC and 1.16 mM total chromium, corresponding to ca. 1.1 C/Cr. This result confirms that the forest green product contains an organic moiety; the low observed C/Cr ratio is understood on the basis that Na_2SO_4 promotes dissociation of this product during elution.[34,35]

Product Analysis of the $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ + $[Cr(aq)]^{2+}$ Reaction. The products of this reaction, conducted with excess thioether–cobalt(III) complex (see previous section), are separated, identified, and quantified as above. Only three bands are observed in the ion-exchange separation. The first and third bands are $[Co(aq)]^{2+}$ and $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ respectively. The second band is comprised of a blue chromium(III) species eluting as a 3+ ion and containing 100% of the injected chromium. This blue species may be approximately formulated (vide infra) as $[(H_2O)_5CrOOCCH_2SCH_2CH_2NH_3]^{3+}$. The visible spectrum of this blue product is almost identical with that of $[(H_2O)_5CrOOCCH_3]^{2+}$[25,36] and is certainly *not* that of $[(H_2O)_6Cr]^{3+}$[25,36] (see Table II). The UV spectrum (Table II), however, contains a broad band ranging from ca. 250 to 240 nm which is not present in the spectrum of $[(H_2O)_5CrOOCCH_3]^{2+}$. TOC and total chromium analyses of three independently collected (0.75 M Na_2SO_4, 1.0 M Na_2SO_4, and 1.0 M NaCl eluents) samples of this species show a C/Cr ratio of 4.0 ± 0.6. Total sulfur analyses of these samples qualitatively confirm that sulfur is present.[37]

Characterization of $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)](ClO_4)_3$. When the orange oil resulting from the original nonaqueous preparation[12] (*N*,*N*-dimethylformamide solvent) is dissolved in dilute $HClO_4$ and quickly loaded onto a small ion-exchange column, a single orange band of 3+ charge is eluted with 4 M $HClO_4$. The visible–UV spectrum of this

Table III. Observed First-Order and Derived Second-Order Rate Constants for the Chromium(II) Reduction of $[(en)_2Co(S(CH_2COOCH_3)CH_2CH_2NH_2)]^{3+}$ as a Function of Acid Concentration[a]

$10^4 \times [Co^{III}]_0$, M	$[Cr^{II}]_0$, M	$[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	k_2, $M^{-1}\ s^{-1}$
2.83	0.0882	0.609	16.6 ± 0.1	0.189 ± 0.001
2.83	0.0882	0.609	17.3 ± 0.2	0.196 ± 0.002
2.83	0.0882	0.609	17.8 ± 0.2	0.202 ± 0.002
2.96	0.0088	0.070	2.057 ± 0.008	0.237 ± 0.001
2.96	0.0088	0.070	1.978 ± 0.008	0.228 ± 0.001
2.96	0.0088	0.070	1.987 ± 0.009	0.229 ± 0.001
2.86	0.0176	0.024	4.34 ± 0.02	0.248 ± 0.001
2.86	0.0176	0.024	4.27 ± 0.02	0.244 ± 0.001
2.86	0.0176	0.024	4.29 ± 0.06	0.245 ± 0.004
2.86	0.0176	0.024	4.33 ± 0.02	0.247 ± 0.002

[a] Conditions: 24.5 ± 0.3 °C, $\mu = 1.00 \pm 0.01$ M ($LiClO_4$), λ 490 nm.

material exhibits peaks at 482 and 323 nm (ε's of 88 and 240 $M^{-1}\ cm^{-1}$, respectively) and a shoulder at 250 nm (ε 2600 $M^{-1}\ cm^{-1}$) which is assigned as arising from the LTMCT characteristic of Cr–S bonds.[29] The shoulder at 250 nm disappears as a function of time ($t_{1/2}$ = 2.3 h, 22 °C, 0.100 M $HClO_4$) indicating aquation of the Cr–S bond. Ion-exchange separation of partially aquated solutions yields two orange bands of 3+ charge, the first band being the chelated species and the second band being the aquated species. Attempts at recrystallization of $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)](ClO_4)_3$ from aqueous solution lead only to mixtures of the chelated and aquated species. When either species is decomposed with base and then the solution extracted with diethyl ether, spectrophotometric and TLC analyses identify $C_6H_5CH_2SCH_2CH_2NH_2$ in the extract.

Kinetics of the $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ + $[Cr(aq)]^{2+}$ Reaction. Reduction of all 12 complexes studied is first order in cobalt(III) complex and first order in chromium(II):

$$-d[Co^{III}]/dt = k_2[Cr^{II}][Co^{III}] \tag{3}$$

Using pseudo-first-order concentration excesses of chromium(II) over cobalt(III), this rate law is confirmed for selected complexes for over a 10^3-fold range of $[Co^{III}]_0$ and over a tenfold range of $[Cr^{II}]_0$. For complexes with R = methyl, ethyl, cyclohexylmethyl, benzyl, 4-fluorobenzyl, 4-methylbenzyl, 1-naphthylbenzyl, and 2-naphthylbenzyl, k_2 exhibits no acid dependence and Tables A–F[38] give values of k_{obsd} and k_2 for individual concentration and temperature conditions. For the complex with R = methylcarboxymethyl, k_2 exhibits a slight acid dependence and the relevant data are given in Table III. Table IV summarizes the values of k_2 for these nine complexes which do not contain a free carboxyl group and also lists activation parameters (calculated within the Eyring formalism by weighted nonlinear least-squares techniques[33]) for four of the complexes. The values of k_2, ΔH^*, and ΔS^* listed for the complex with R = methyl are in good agreement with those values reported previously.[11] The ionic strength dependence of k_2 when R = benzyl is given in Table V.

For the complexes with R = $(CH_2)_nCOOH$ (n = 1, 2, 3) k_2 exhibits a generally inverse dependence on $[H^+]$. Table VI gives the relevant data for the complex with n = 1. For these data a plot of k_2 vs. $[H^+]^{-1}$ is *not* linear, whereas a plot of k_2^{-1} vs. $[H^+]$ is linear. Weighted nonlinear least-squares analysis[33] within the rate law

$$k_2 = a/(1 + b[H^+]) \tag{4}$$

yields $a = 19 \pm 5\ M^{-1}\ s^{-1}$ and $b = (4.92 \pm 0.84) \times 10^3\ M^{-1}$; the average deviation between observed values of k_2 and values calculated from these optimized a and b parameters is 5.3%, and the maximum deviation is 17%. Tables VII and VIII give the relevant data for the complexes with n = 2 and 3, respectively. For these data plots of k_2 vs. $[H^+]^{-1}$ are linear, whereas plots of k_2^{-1} vs. $[H^+]$ are not linear. Results of weighted linear least-squares analyses within the rate law

$$k_2 = c + d/[H^+] \tag{5}$$

are given in Table IX as a function of temperature. Also listed in Table IX are activation parameters resulting from weighted nonlinear least-squares analyses[33] within the Eyring formalism of the raw data of Tables VII and VIII.

Discussion

Thioether Sulfur as an Electron-Transfer Bridge. Bennett's conclusion[11,20] that the chromium(II) reduction of $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ proceeds via an outer-sphere mechanism is based on the *lack* of observation of a thioether–chromium(III) product; this erroneous conclusion can now be corrected on the basis of positive evidence. By using improved techniques and by choosing systems advantageously, we have directly observed inner-sphere thioether–chromium(III) products. Specifically, we have (a) quenched excess chromium(II) with $[(NH_3)_4Co(C_2O_4)]^+$ in order to eliminate the high-charged, green chromium(III) species resulting from the molecular oxygen quenching used by Bennett[20] (these species have the same ion-exchange characteristics and color as would be expected for the thioether–chromium(III) product and, therefore, obviate ion-exchange detection of this product), (b) used low temperatures in order to inhibit aquation of the thioether–chromium(III) product, (c) chosen to work with the benzyl thioether complex, rather than the methyl thioether complex used by Bennett,[20] since the benzyl functionality is

Table IV. Derived Second-Order Rate Constants and Available Activation Parameters for the Chromium(II) Reduction of $[(en)_3Co]^{3+}$, $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, and $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ Complexes[a]

complex	k_2, $M^{-1}\ s^{-1}$	ΔH^*, kcal/mol	ΔS^*, eu	ref
$(en)_3Co^{3+}$	0.00034			*i*
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	33 000	7.3 ± 0.3	−13.5 ± 1.0	11
$(en)_2Co(S(R)CH_2CH_2NH_2)^{3+}$				
R = CH_3	0.381 ± 0.012	5.5 ± 0.2	−42.1 ± 0.6	11
R = CH_3	0.337 ± 0.004	4.9 ± 0.2	−44.2 ± 0.6	*b*
R = CH_2COOCH_3[c]	0.193 ± 0.001			*b*
R = CH_2CH_3	0.0270 ± 0.0002	6.5 ± 0.2	−43.9 ± 0.6	*b*
R = $CH_2C_6H_{11}$[d]	0.0126 ± 0.0003	7.6 ± 0.2	−41.6 ± 0.6	*b*
R = $CH_2C_6H_5$	0.0345 ± 0.0006	7.4 ± 0.2	−40.3 ± 0.5	*b*
R = $CH_2C_6H_4F$[e]	0.0356 ± 0.0008			*b*
R = $CH_2C_6H_4CH_3$[f]	0.033 ± 0.001			*b*
R = $CH_2C_{10}H_7$[g]	0.044 ± 0.002			*b*
R = $CH_2C_{10}H_7$[h]	0.033 ± 0.002			*b*

[a] Conditions: $\mu = 1.00 \pm 0.01$ M ($LiClO_4$); k_2 reported at 25 °C. [b] This work. [c] Methylcarboxymethyl; entry is for $[H^+] = 0.609$ M; k_2 has a slight acid dependence—see Table III and text. [d] Cyclohexylmethyl. [e] 4-Fluorobenzyl. [f] 4-Methylbenzyl. [g] 1-Naphthylmethyl. [h] 2-Naphthylmethyl. [i] T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, 95, 5545 (1973).

Table V. Observed First-Order and Derived Second-Order Rate Constants for the Chromium(II) Reduction of $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ as a Function of Ionic Strength[a]

μ, M	$10^4 \times [Co^{III}]_0$, M	$[Cr^{II}]_0$, M	10^3k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
0.100	0.87	0.0121	1.521 ± 0.007	0.0126 ± 0.0001
0.100	0.87	0.0121	1.581 ± 0.005	0.0131 ± 0.0001
0.100	0.87	0.0121	1.671 ± 0.007	0.0139 ± 0.0001
0.500	0.90	0.0091	2.156 ± 0.004	0.0240 ± 0.0001
0.500	0.90	0.0091	2.195 ± 0.004	0.0244 ± 0.0001
0.500	0.90	0.0091	2.246 ± 0.005	0.0249 ± 0.0001
0.500	0.90	0.0091	2.199 ± 0.006	0.0244 ± 0.0001
2.002	0.88	0.0060	2.790 ± 0.008	0.0468 ± 0.0002
2.002	0.88	0.0060	2.850 ± 0.010	0.0478 ± 0.0002
2.002	0.88	0.0060	2.792 ± 0.011	0.0468 ± 0.0002

[a] Conditions: 24.2 ± 0.3 °C, $[H^+] = 0.100$ M, μ maintained with $LiClO_4$, λ 291 nm.

Table VI. Observed First-Order and Derived Second-Order Rate Constants for the Chromium(II) Reduction of $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ as a Function of Acid and Chromium(II) Concentration[a]

no. of experiments[b]	$[Cr^{II}]_0$, M	$[H^+]$, M	$\bar{k}_{obsd}$,[c] s^{-1}	k_2, M^{-1} s^{-1}
17	0.0010	0.1002	1.574 ± 0.002	1574 ± 2
18	0.0030	0.1002	5.159 ± 0.001	1720 ± 1
19	0.0050	0.1001	8.133 ± 0.003	1627 ± 1
20	0.0070	0.1001	12.05 ± 0.03	1721 ± 4
21	0.0100	0.1002	18.5 ± 0.1	1845 ± 10
6	0.0150	0.0996	29.7 ± 0.2	1979 ± 12
14	0.0100	0.0502	30.1 ± 0.7	3010 ± 70
9	0.0100	0.0504	28.0 ± 0.4	2800 ± 30
17	0.0100	0.0673	25.1 ± 0.4	2510 ± 40
14	0.0100	0.1252	14.90 ± 0.04	1490 ± 4
14	0.0100	0.1260	15.4 ± 0.1	1542 ± 12
21	0.0100	0.200	10.78 ± 0.03	1078 ± 3
10	0.0100	0.201	10.4 ± 0.1	1037 ± 11
11	0.0100	0.275	8.2 ± 0.9	822 ± 9
10	0.0100	0.338	6.71 ± 0.04	671 ± 4
10	0.0100	0.351	6.34 ± 0.06	634 ± 6
11	0.0100	0.412	5.52 ± 0.03	552 ± 3
14	0.0100	0.480	4.74 ± 0.14	474 ± 14
6	0.0100	0.525	4.36 ± 0.04	436 ± 4
11	0.0100	0.555	4.13 ± 0.07	413 ± 7
10	0.0100	0.562	4.18 ± 0.04	418 ± 4
10	0.0100	0.600	3.90 ± 0.02	390 ± 2
14	0.0100	0.750	3.1 ± 0.2	309 ± 20
10	0.0100	0.767	3.11 ± 0.03	311 ± 3
18	0.0100	0.955	2.24 ± 0.02	224 ± 2
11	0.0100	0.955	2.46 ± 0.02	246 ± 2

[a] Conditions: 25.3 ± 0.5 °C, $\mu = 1.00 \pm 0.01$ M ($LiClO_4$), λ 282 nm, $[Co^{III}]_0 = 3.5 \times 10^{-5}$ M. [b] Number of experiments refers to the number of individually collected OD_t–t data sets treated to obtain k_{obsd} values. [c] $\bar{k}_{obsd}$ is the average of individually determined k_{obsd} values for a given set of conditions.

Table VII. Observed First-Order and Derived Second-Order Rate Constants for the Chromium(II) Reduction of $[(en)_2Co(S(CH_2CH_2COOH)CH_2CH_2NH_2)]^{3+}$ as a Function of Temperature and Acid Concentration[a]

T, °C	$[Cr^{II}]_0$, M	$[H^+]$, M	10^3k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
15.4	0.0100	0.9497	0.946 ± 0.006	0.0946 ± 0.0006
15.4	0.0100	0.2000	3.66 ± 0.03	0.366 ± 0.003
15.4	0.0100	0.0995	7.71 ± 0.07	0.771 ± 0.007
15.4	0.0100	0.0660	11.55 ± 0.06	1.155 ± 0.006
15.4	0.0100	0.0660	11.3 ± 0.1	1.134 ± 0.010
15.4	0.0100	0.0493	11.7 ± 0.2	1.70 ± 0.02
15.4	0.0100	0.0258	30.5 ± 0.4	3.05 ± 0.04
25.0	0.0100	0.0256	41.1 ± 0.3	4.11 ± 0.03
25.0	0.0100	0.0501	22.5 ± 0.1	2.25 ± 0.01
25.0	0.0100	0.0501	22.1 ± 0.2	2.21 ± 0.02
25.0	0.0100	0.0685	17.45 ± 0.07	1.745 ± 0.007
25.0	0.0100	0.0685	17.59 ± 0.08	1.759 ± 0.008
25.0	0.0100	0.1006	12.05 ± 0.07	1.205 ± 0.007
25.0	0.0100	0.1006	12.40 ± 0.06	1.240 ± 0.006
25.0	0.0100	0.2506	4.74 ± 0.02	0.474 ± 0.002
25.0	0.0100	0.2506	4.92 ± 0.02	0.492 ± 0.002
25.0	0.0100	0.9647	1.46 ± 0.02	0.146 ± 0.002
25.0	0.0100	0.9647	1.61 ± 0.02	0.161 ± 0.002
35.0	0.0050	0.0668	15.0 ± 0.2	2.99 ± 0.03
35.0	0.0050	0.0936	10.90 ± 0.06	2.18 ± 0.01
35.0	0.0050	0.2509	4.24 ± 0.06	0.85 ± 0.01
35.0	0.0050	0.9974	1.268 ± 0.006	0.254 ± 0.001
44.9	0.0048	0.0549	28.2 ± 0.1	5.87 ± 0.03
44.9	0.0048	0.0679	24.4 ± 0.2	5.09 ± 0.04
44.9	0.0048	0.0970	16.6 ± 0.2	3.45 ± 0.05
44.9	0.0048	0.9522	2.40 ± 0.02	0.500 ± 0.005

[a] Conditions: $\mu = 1.00 \pm 0.01$ M ($LiClO_4$), λ 282 nm, $[Co^{III}]_0 = 8.5 \times 10^{-5}$ M.

Table VIII. Observed First-Order and Derived Second-Order Rate Constants for the Chromium(II) Reduction of $[(en)_2Co(S(CH_2CH_2CH_2COOH)CH_2CH_2NH_2)]^{3+}$ as a Function of Temperature and Acid Concentration[a]

T, °C	$[Cr^{II}]_0$, M	$[H^+]$, M	10^4k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
15.4	0.0100	0.0493	2.872 ± 0.008	$(2.872 \pm 0.008) \times 10^{-2}$
15.4	0.0100	0.0660	2.81 ± 0.02	$(2.81 \pm 0.02) \times 10^{-2}$
15.4	0.0100	0.2013	2.39 ± 0.02	$(2.39 \pm 0.02) \times 10^{-2}$
15.4	0.0100	0.9497	2.06 ± 0.02	$(2.06 \pm 0.02) \times 10^{-2}$
25.0	0.0100	0.0256	6.81 ± 0.02	$(6.81 \pm 0.02) \times 10^{-2}$
25.0	0.0100	0.0501	4.93 ± 0.03	$(4.93 \pm 0.03) \times 10^{-2}$
25.0	0.0100	0.0685	5.22 ± 0.04	$(5.22 \pm 0.05) \times 10^{-2}$
25.0	0.0100	0.1006	5.32 ± 0.04	$(5.32 \pm 0.04) \times 10^{-2}$
25.0	0.0100	0.2506	3.92 ± 0.02	$(3.92 \pm 0.02) \times 10^{-2}$
25.0	0.0100	0.9497	4.38 ± 0.02	$(4.38 \pm 0.02) \times 10^{-2}$
44.9	0.0048	0.0549	7.99 ± 0.06	$(1.664 \pm 0.014) \times 10^{-1}$
44.9	0.0048	0.0679	6.31 ± 0.08	$(1.314 \pm 0.016) \times 10^{-1}$
44.9	0.0048	0.0970	5.69 ± 0.08	$(1.185 \pm 0.016) \times 10^{-1}$
44.9	0.0048	0.2461	4.71 ± 0.06	$(9.81 \pm 0.13) \times 10^{-2}$
44.9	0.0048	0.9522	4.69 ± 0.03	$(9.77 \pm 0.06) \times 10^{-2}$

[a] Conditions: $\mu = 1.00 \pm 0.01$ M ($LiClO_4$), λ 282 nm, $[Co^{III}]_0 = 8.5 \times 10^{-5}$ M.

readily detected by both TLC and UV spectrophotometry, and (d) in an alternative system used a chelating functionality in order to afford greater stability to the thioether–chromium(III) product. Our evidence for the participation of thioether sulfur as an electron-transfer bridge may be summarized as follows:

(1) Chromium(II) reduction of $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ yields *at least* 15% of a forest green chromium(III) species which is identified as $[(H_2O)_5CrS(CH_2C_6H_5)CH_2CH_2NH_3]^{4+}$ on the basis of its ion-exchange behavior (consistent with a 4+ formal charge) and its aquation to $[(H_2O)_6Cr]^{3+}$ and $[C_6H_5CH_2SCH_2CH_2NH_3]^+$ (the latter being positively identified by TLC and UV spectrophotometry). Rapid aquation of $[(H_2O)_5CrS(CH_2C_6H_5)CH_2CH_2NH_3]^{4+}$ is expected from our knowledge of thiolato–chromium(III) species[21–24,29] and accounts for the low percent recovery of this product. From the observed aquation rate of $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ ($t_{1/2}$ = 2.3 h at 22 °C), and previous studies on the aquation of $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$ [29] and $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$,[23] we can estimate the half-life for aquation of $[(H_2O)_5CrS(CH_2C_6H_5)CH_2CH_2NH_3]^{4+}$ to be about 14 min at 22 °C.

Also, the catalysis of aquation of $[(H_2O)_5CrS(CH_2C_6H_5)CH_2CH_2NH_3]^{4+}$ by chloride, nitrate, and sulfate is consistent with previous observations[21] on the effect of added ligands on the rate of chromium–sulfur bond fission in $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$.

(2) Our synthesis of $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ confirms that thioether–chromium(III) complexes are viable entities and that the chromium–sulfur

Table IX. Derived Rate and Activation Parameters Describing the Dependence of k_2 for the Chromium(II) Reduction of $[(en)_2Co(S((CH_2)_nCOOH)CH_2CH_2NH_2)]^{3+}$ ($n = 2, 3$) on Acid Concentration According to the Rate Law $k_2 = c + d/[H^+]$[a]

	$n = 2$		$n = 3$	
	c, $M^{-1}\ s^{-1}$	d, s^{-1}	c, $M^{-1}\ s^{-1}$	d, s^{-1}
$T = 15.4$ °C	−0.077 ± 0.0005	0.083 ± 0.0002	0.0212 ± 0.0001	0.00038 ± 0.00005
$T = 25.0$ °C	0.03 ± 0.01	0.114 ± 0.002	0.040 ± 0.003	0.0007 ± 0.0001
$T = 35.0$ °C	0.055 ± 0.002	0.198 ± 0.001		
$T = 44.9$ °C	0.17 ± 0.03	0.318 ± 0.007	0.092 ± 0.005	0.0034 ± 0.0006
ΔH^*, kcal/mol	13.0 ± 0.3	8.5 ± 0.3	8.3 ± 0.7	13.9 ± 0.3
ΔS^*, eu	−22 ± 10	−34 ± 1	−37 ± 3	−26 ± 9
av devn[b]	4.9%		7.3%	
max devn[b]	14.8%		15.4%	

[a] Conditions: $\mu = 1.00 \pm 0.01$ M ($LiClO_4$). [b] Average and maximum percent deviation of experimental k_2 values from those calculated using the optimized activation parameters listed above.

bond of these complexes is relatively labile.

(3) The data of Table IV show that the rate of chromium(II) reduction of $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes increases as the size of the R group decreases, k_2 for the smallest group (R = methyl) being 27 times larger than k_2 for the largest group (R = cyclohexylmethyl). This observation is readily understood in terms of an inner-sphere mechanism (since steric crowding at sulfur will hinder its attaining four-coordination in the redox transition state) but is difficult to rationalize within an outer-sphere mechanism. On this basis the complex with R = methyl, i.e., the complex studied by Bennett,[11,20] should be the most likely to proceed exclusively by bridged electron transfer.

(4) The chromium(II) reduction of $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ gives an inner-sphere thioether–chromium(III) product in 100% yield. Since the visible spectrum of this product is almost identical with that of $[(H_2O)_5CrOOCCH_3]^{2+}$, it is formulated as existing predominantly in the monodentate form $[(H_2O)_5CrOOCCH_2SCH_2CH_2NH_3]^{3+}$. However, since the UV spectrum exhibits a definite absorbance in the region characteristic of the LTMCT of Cr–S bonds,[29] it is likely that the monodentate form exists in equilibrium with the O,S-chelated form $[(H_2O)_4Cr(OOCCH_2S(CH_2CH_2NH_3))]^{3+}$.[39] On the basis of extinction coefficients of related species, we estimate the ratio of monodentate to chelate forms to be about 10:1; attainment of this equilibrium will be relatively rapid since the Cr–S bond of thioether complexes is reasonably labile (vide supra). Regardless of the form of this product, the quantitative recovery of a carboxylato–chromium(III) species demonstrates that the initial chromium(II)–cobalt(III) electron transfer proceeded 100% by a sulfur-bridged, inner-sphere mechanism. Presumably the pendant carboxylate function of $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ coordinates to chromium(II) before electron transfer to generate an O,S-chelated precursor complex and transition state; this added chelate stability promotes inner-sphere electron transfer through sulfur. Enhancement of chromium(II)–cobalt(III) inner-sphere electron-transfer rates by pendant chelating groups (especially carboxylate[13,40–42]) is a well-established phenomenon.[40]

(5) The rates of chromium(II) reduction of $[(en)_2Co(S((CH_2)_nCOOH)CH_2CH_2NH_2)]^{3+}$ complexes increase markedly with decreasing $[H^+]$ (Tables VI–VIII). While the detailed functional dependencies of k_2 on $[H^+]$, and especially the fact that these dependencies are a function of n, are readily understood within an inner-sphere mechanism (the deprotonated carboxylate forms a more stable chelated precursor complex, and the stability of this complex is a function of n; vide infra), they are difficult to rationalize within an outer-sphere mechanism.

Thus, thioether sulfur does function as an electron-transfer bridge in the chromium(II) reduction of $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes. For the carboxymethyl R group, and probably for all the less sterically hindered alkyl R groups, reaction proceeds 100% by the inner-sphere path. Within the inner-sphere redox transition state, bridging thioether sulfur must be four-coordinate with two of the groups bonded to sulfur being octahedral metal complexes. That sulfur is indeed large enough to attain this configuration is supported by two recent reports of metal complexes containing four-coordinate sulfur in the ground state: Stein and Taube[43] have synthesized $[(NH_2)_5Ru^{II}S(CH_3)_3]^{3+}$, while Lane et al.[44] have described the crystal structure of the $[(en)_2Co(SCH_2CH_2NH_2)Cu(CH_3CN)_2]_2^{6+}$ cation in which each sulfur is bonded to one carbon atom, one octahedral cobalt(III) atom, and two tetrahedral Cu(I) atoms.

Complexes without a Pendant Carboxylate Group. With one exception, the specific rates (k_2) for chromium(II) reduction of $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes in which R does not contain a free carboxylate group (a) are independent of acid concentration and (b) depend primarily on the size of the R group (see Table IV). The sole exception occurs when R = CH_2COOCH_3 (methylcarboxymethyl); k_2 for this complex is about 10 times larger than k_2 for the equivalently hindered complex with R = CH_2CH_3, and k_2 for this complex also shows a very slight inverse acid dependence (see Table III). These results presumably arise from chelation of chromium(II) by the pendant CH_2COOCH_3 ester group in the redox transition state. As noted above, pendant chelating functionalities are well-known to enhance the rates of chromium(II)–cobalt(III) inner-sphere electron transfer,[13,40–42] and rate enhancement by a pendant ester group has previously been reported[45] for the chromium(II) reduction of (methylmalonato)pentaamminecobalt(III). The slight inverse acid dependence of k_2 (Table III) may be due to a medium effect,[18,46,47] but since none of the other R groups listed in Table IV engender such a dependence, it is more likely the result of a real but minor kinetic path. A possible path could involve addition of OH^- to the carbonyl carbon atom of the coordinating ester which would improve the ligating ability of the carbonyl oxygen atom and thus stabilize the chelated transition state.

The steric retardation of k_2 is manifested primarily in the enthalpy of activation—Table IV shows that complexes with smaller R groups have significantly smaller values of ΔH^* but only marginally more negative values of ΔS^*. This observation is consistent with previously observed steric effects in Cr(II)–Co(III) inner-sphere reactions: e.g., Barrett et al.[48] report that for the chromium(II) reduction of $[(NH_3)_5CoOOCR]^{2+}$ complexes, when R is changed from CH_3 to $C(CH_3)_3$, ΔH^* increases from 8.2 to 11.1 kcal/mol but ΔS^* varies only from −33 to −31 eu. The $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ system seems to be more sensitive to the size of R than does the $[(NH_3)_5CoOOCR]^{2+}$ system, presumably because in the thioether system the R group is directly attached to the atom that is bridging electron transfer whereas in the carboxylate system the R group is remote from the actual site of electron transfer.

The thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is related to the thioether complexes $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ in that it may be viewed as having the minimun steric hindrance about sulfur, and indeed k_2 for the thiolato complex is ca. 10^5 times greater than the largest k_2 observed for a thioether complex (Table IV). However, this rate enhancement arises *solely* because of a more positive ΔS^* and is, therefore, more likely to be due to the lower formal charge of the thiolato complex than to reduced steric requirements which are generally reflected in ΔH^* (see above). The effect of formal charge on the entropy of activation of redox reactions is well established in both theory and experiment. Even when the source of varying formal charge is *remote* from the actual site of electron transfer, the ensuing effect on ΔS^* is significant. E.g., Holwerda et al.[49] report that for the chromium(II) reduction of $[(NH_3)_5CoOOCR]^{n+}$, when R is changed from neutral CH_3 to charged $[CH_2N(CH_3)_3]^+$, the concomitant 20-fold reduction in k_2 results solely from ΔS^* becoming more negative by 8 eu (μ = 1.00 M). When the source of varying charge is the oxidation state of one of the redox partners, the effect is larger still. Extensive compilations by Newton[50] indicate that at μ = 1.00 M changing the reaction type from 2+/2+ to 2+/3+ should make ΔS^* more negative by ca. 20 eu. In the $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ comparison, the source of increasing formal charge is the bridging atom itself and this should lead to at least a 20-eu decrease in ΔS^*. In addition, the presence of an R group at the site of electron transfer should require significant alteration of solvent structure as sulfur goes from three-coordinate to four-coordinate in the transition state. This should further decrease ΔS^* for the thioether complex, and, thus, the observed 30-eu difference in ΔS^* values for the thiolato and thioether complexes is not unreasonable. It should be noted that the ionic strength dependence of the $[Cr(aq)]^{2+}$–$[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ reaction (Table V) is normal[51] for a 2+/3+ reaction and, therefore, it is not necessary to invoke any special effects in connection with the ΔS^* values of these reactions.

The last five entries of Table IV show that variations in the electronic properties of R groups related to the benzyl moiety do *not* lead to significant rate variations even though such variations do lead to changes in the LTMCT band arising from the Co–S bond.[12] This again indicates that steric effects are predominant in determining the rate of electron transfer from chromium(II) to various $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes. Of the five benzyl complexes listed, the 1-naphthylmethyl derivative is the only one which contains a functionality ortho to the methylene carbon, and it is this particular derivative which enjoys a modest rate advantage over the other four. This effect may arise from the detailed interactions of these hydrophobic R groups with the solvent and the ethylenediamine ligands.

Complexes Containing a Pendant Carboxylate Group. The specific rates, k_2, for chromium(II) reduction of the complexes $[(en)_2CoS((CH_2)_nCOOH)CH_2CH_2NH_2)]^{3+}$ (n = 1, 2, 3) increase with decreasing $[H^+]$. Haim[52,53] has commented at length on the mechanistic ambiguities arising from inverse acid pathways, pointing out that the proton may be lost before, during, or after formation of the precursor complex. These ambiguities are still sources of active discussion with regard to chelated precursor complexes.[40] For simplicity, we will present the most straightforward interpretation of our acid-dependent data that is consistent with all of the information available on these systems—we fully recognize that other plausible interpretations are also possible.

When n = 2 or 3, $k_2 = c + d/[H^+]$, suggesting that the protonated (AH) and deprotonated (A) forms of the thioether complex react with chromium(II) by parallel paths:

$$AH \overset{K_a}{=} A + H^+ \tag{6}$$

$$Cr(II) + AH \xrightarrow{k_0} products \tag{7}$$

$$Cr(II) + A \xrightarrow{k_{-1}} products \tag{8}$$

$$k_2 = k_0 + \frac{K_a k_{-1}}{[H^+]} \tag{9}$$

Therefore, $c = k_0$ and represents unassisted electron transfer to the protonated form; from the data of Table IX, k_0 = 0.03 ± 0.01 and 0.040 ± 0.003 $M^{-1}\ s^{-1}$ (25 °C) for n = 2 and 3, respectively. These k_0 values are very reasonable, being just about that observed for the complex with R = CH_2CH_3 (Table IV) which should have equivalent steric requirements. Also, $d = K_a k_{-1}$, and from the data of Tables I and IX values of k_{-1} may be calculated to be 168 ± 3 and 6.6 ± 1.0 $M^{-1}\ s^{-1}$ (25 °C) for n = 2 and 3, respectively. Thus, reduction of the deprotonated form, presumably via a chelated transition state, is favored with respect to the protonated form by factors of 5600 and 16 for n = 2 and 3, respectively. These relative rate enhancements are consistent with known chelate stabilities[54] since in the transition state the complex with n = 2 will form a six-membered ring while the complex with n = 3 must form a relatively unfavorable seven-membered ring.

When n = 1, $k_2 = a/(1 + b[H^+])$, suggesting a steady-state mechanism involving a deprotonated binuclear intermediate (I):

$$Cr(II) + AH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} I + H^+ \tag{10}$$

$$I \xrightarrow{k_1} products \tag{11}$$

$$k_2 = k_f/(1 + \frac{k_r}{k_1}[H^+]) \tag{12}$$

Thus $a = k_f$ = 19 ± 5 $M^{-1}\ s^{-1}$ and $b = k_r/k_1$ = (4.92 ± 0.84) × $10^3\ M^{-1}$ (25 °C). A reasonable estimate for k_0 (25 °C) in this system (i.e., the path corresponding to reduction of the protonated form AH; eq 7) is 0.19 $M^{-1}\ s^{-1}$ (the specific rate of the $[Cr(aq)]^{2+}$–$[(en)_2Co(S(CH_2COOCH_3)CH_2CH_2NH_2)]^{3+}$ reaction from Table IV) which is too small to be detected experimentally. It should be noted that the mechanisms proposed for n = 1 and for n = 2 or 3 are not unrelated, differing primarily in the stability assigned to the deprotonated, chelated precursor complex. When n = 1, this chelated complex is stable enough to enter the kinetic scheme as a steady-state intermediate; when n = 2 or 3 the complex is not as stable and appears in the kinetic scheme only as an activated complex. This conclusion is demanded by the change in observed rate law as n goes from 1 to 2 or 3 and is not a result of the specific mechanistic interpretation we have chosen. Thus, the overall stability of the chelate ring in the deprotonated precursor complex and concomitant overall rate of electron transfer decrease in the order 1 > 2 > 3 for n, which corresponds to the ordering of ring sizes 5 > 6 > 7.

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Registry No. $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$, 56522-86-8; $[(en)_2Co(S((CH_2)_2COOH)CH_2CH_2NH_2)]^{3+}$, 65622-84-6; $[(en)_2Co(S((CH_2)_3COOH)CH_2CH_2NH_2)]^{3+}$, 65622-82-4; $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, 35594-86-6; $[(en)_2Co(S$-

$(CH_2COOCH_3)CH_2CH_2NH_2)]^{3+}$, 65622-88-0; $[(en)_2Co(S(CH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 65622-76-6; $[(en)_2Co(S(CH_2C_6H_{11})CH_2CH_2NH_2)]^{3+}$, 65622-90-4; $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$, 65622-68-6; $[(en)_2Co(S(CH_2C_6H_4F)CH_2CH_2NH_2)]^{3+}$, 65622-80-2; $[(en)_2Co(S(CH_2C_6H_4CH_3)CH_2CH_2NH_2)]^{3+}$, 65622-78-8; $[(en)_2Co(S(1\text{-naphthylmethyl})CH_2CH_2NH_2)]^{3+}$, 65651-35-6; $[(en)_2Co(S(2\text{-naphthylmethyl})CH_2CH_2NH_2)]^{3+}$, 65622-92-6; Cr(II), 22541-79-3; $[(NH_3)_4Co(C_2O_4)]ClO_4$, 15293-32-0; $C_6H_5CH_2SCH_2CH_2NH_2\cdot HCl$, 22572-33-4; $[(en)_2Cr(S(CH_2C_6H_5)CH_2CH_2NH_2)](ClO_4)_3$, 66719-25-3; $(H_2O)_5CrOOCCH_2SCH_2CH_2NH_3^{3+}$, 66719-26-4.

Supplementary Material Available: Tables A–F giving observed first-order and derived second-order rate constants for the chromium(II) reductions of $[(en)_2CO(S(R)CH_2CH_2NH_2)]^{3+}$ complexes where R = methyl, benzyl, ethyl, cyclohexylmethyl, 4-fluorobenzyl, 4-methylbenzyl, 1-naphthylmethyl, and 2-naphthylmethyl (6 pages). Ordering information is given on any current masthead page.

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