

Reactivity of Coordinated Disulfides. 2.¹ Competitive S-S and Co-S Bond Cleavage in the Base Hydrolysis of the *tert*-Butyl Disulfide-Cobalt(III) Complex [(en)₂Co(S(SC(CH₃)₃)CH₂CH₂NH₂)]³⁺

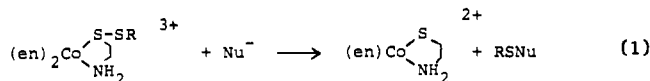
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Base hydrolysis of the *tert*-butyl disulfide-cobalt(III) complex [(en)₂Co(S(SC(CH₃)₃)CH₂CH₂NH₂)]³⁺ in Tris or ammonia buffer yields the thiolato complex [(en)₂Co(SCH₂CH₂NH₂)]²⁺ by S-S bond cleavage and the hydroxo complex [(en)₂Co(OH)-(NH₂CH₂CH₂SSC(CH₃)₃)]²⁺ by Co-S bond cleavage. Both reactions are first order in disulfide complex and first order in hydroxide. In Tris buffer the rate is independent of buffer concentration; at 25 °C and $\mu = 1.00$ M (LiClO₄) the rate of nucleophilic attack of OH⁻ on the S-S bond is 9 ± 2 M⁻¹ s⁻¹ while the rate of S_N1cB Co-S bond fission is 102 ± 2 M⁻¹ s⁻¹. In ammonia buffer, free NH₃ also cleaves the S-S bond to yield the thiolato complex. The ordering of nucleophilicities for attack on the S-S linkage of the title complex is RS⁻ > OH⁻ > NH₃ > RSH. For the series of related complexes [(en)₂Co(S(SR)CH₂CH₂NH₂)]³⁺ the specific rate (M⁻¹ s⁻¹, 25 °C, $\mu = 1.00$ M) of S_N2 attack by OH⁻ on the S-S bond decreases along the series R = CH₃ (1.7×10^6) > CH₂CH₃ (5.6×10^5) > CH(CH₃)₂ (2.0×10^4) \gg C(CH₃)₃ (9). The dramatic drop in reactivity on going from R = isopropyl to R = *tert*-butyl reflects the inability of the *tert*-butyl group to rotate out of the path of the incoming OH⁻ nucleophile and allows S_N1cB Co-S bond cleavage to become competitive with S_N2 S-S bond cleavage in the *tert*-butyl complex.

Introduction

The chemistry of coordinated sulfur and the relevance of this chemistry to biological systems have been recently reviewed in detail.³ Coordinated disulfides are of special concern in this area because of the prevalence and reactivity of sulfur-sulfur bonds in many important biological materials. In a previous paper¹ we reported the kinetics and mechanism of nucleophilic cleavage of the activated sulfur-sulfur bond in the disulfide cobalt(III) complexes [(en)₂Co(S(SR)CH₂CH₂NH₂)]³⁺ where R is methyl, ethyl, isopropyl, or *tert*-butyl and the attacking nucleophiles investigated were OH⁻, thiols, and thiolate anions. In these reactions the rates of S_N2 cleavage of the coordinated disulfide are 10¹⁰-10¹¹ times greater than those of comparable noncoordinated disulfides. For all reactions investigated, except one, heterolytic sulfur-sulfur bond cleavage leads exclusively to the thiolato complex [(en)₂Co(SCH₂CH₂NH₂)]²⁺ (eq 1). The single exception is base hydrolysis



of the *tert*-butyl disulfide complex, which leads to an aquated species as well as the thiolato product. In this paper we report the stoichiometry, kinetics, and mechanism of this unique base hydrolysis reaction.

Experimental Section

Materials. Common laboratory chemicals were of reagent grade unless otherwise noted. Triply distilled water and doubly distilled perchloric acid (70-72%, G. F. Smith) were used in all kinetic experiments. Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate as previously described.⁴ Tris(hydroxymethyl)aminomethane, Tris (Sigma Chemical, Trizma Base), was purified by three crystallizations from 20% aqueous ethanol. A solution of NH₄OH was prepared by dissolving ammonia gas (Matheson) in water at 10 °C and then determined to be 5.81 M by titration with standard 1.00 M HCl (Fisher Standard). Sephadex SP-C25 cation exchanger (sodium form) was generated and stored as recommended by the manufacturer (Pharmacia). Some batches required treatment with excess aqueous bromine (0.0375 M Br₂ in 0.01 M HCl) for 10 h to eliminate a reducing capacity that caused decomposition of coordinated disulfides. This treatment was followed by copious washing with water.

(1-((2-Methyl-2-propyl)dithio)-2-aminoethane-*N*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, [(en)₂Co(S(SC(CH₃)₃)CH₂CH₂NH₂)]-

(ClO₄)₃, was prepared as previously described.^{5,6} A solution of this disulfide complex with the endo sulfur atom labeled with ³⁵S, [(en)₂Co(³⁵S(SC(CH₃)₃)CH₂CH₂NH₂)]³⁺, was prepared as follows. One millicurie of ³⁵S-labeled cystamine dihydrochloride (Amersham) was added to 300 mg of unlabeled cystamine dihydrochloride in 2 mL of water. This solution was deaerated and added to a deaerated mixture of 1 g of Co(ClO₄)₂·6H₂O and 460 mg of ethylenediamine under anaerobic conditions. After 30 min, 2 mL of concentrated HClO₄ was added to the brown solution, which was then refrigerated for 24 h. The resultant black crystals of [(en)₂Co(³⁵SCH₂CH₂NH₂)](ClO₄)₂ were collected by filtration and washed with cold ethanol. To a solution of 454 mg (1 mmol) of this ³⁵S-labeled thiolato complex in 5 mL of dimethylformamide was added 15 mL (ca. 1.7 mmol) of a freshly prepared solution of *tert*-butylsulfenyl iodide⁷ with stirring. After the mixture was stirred for 5 min in the dark, 5 mL of 0.01 M HClO₄ was added, followed by recovery of the aqueous layer, which was then loaded onto a Sephadex ion-exchange column. Unreacted thiolato complex was removed with 0.125 M NaClO₄ (0.01 M HClO₄), and then the desired orange band was eluted with 1 M NaClO₄ (0.01 M HClO₄). A solution of this disulfide complex with the exo sulfur atom labeled with ³⁵S, [(en)₂Co(S(³⁵SC(CH₃)₃)CH₂CH₂NH₂)]³⁺, was similarly prepared from [(en)₂Co(SCH₂CH₂NH₂)](ClO₄)₂ and ³⁵S-labeled *tert*-butylsulfenyl iodide, which was generated from molecular iodine and ³⁵S-labeled *tert*-butyl mercaptan. The latter compound was prepared by modification of a literature procedure⁸ using 14.0 g of *tert*-butyl bromide and 7.6 g of unlabeled thiourea containing 5.6 mCi of ³⁵S-labeled thiourea (New England Nuclear).

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Total cobalt analyses were performed by a modified Kitson procedure.⁹ Formal charges on complexes were inferred from the characteristics of their elution from cation-exchange columns. ³⁵S activity was monitored by liquid scintillation counting techniques using a β -counting cocktail prepared by dissolving 2 g of PPO (2,5-diphenyloxazole) and 40 mg of Me₂POPOP (1,4-bis(4-methyl-5-phenyloxazol-2-yl)benzene) in 52.5 mL of toluene and adding 45 mL of Triton X-100. Seven milliliters of this scintillation cocktail was used for every 5 mL of aqueous sample solution; these aqueous samples were first decolorized by digestion with potassium persulfate.

Equipment. Visible-UV spectra were recorded on a Cary 210 spectrophotometer at ambient temperature. Kinetic data were obtained on a Cary 118B spectrophotometer equipped with a thermostated cell compartment and a Hewlett-Packard 5150A thermal printer. Temperature was monitored with a USC Model 581C digital thermometer that had been calibrated against a NBS Certified thermometer. ¹H NMR spectra were obtained on a Varian T-60 instrument. A Packard Tri-Carb Model 3003 liquid scintillation counter was used to determine ³⁵S activity. pH

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Table I. Yield of Products from the Base Hydrolysis of $[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)]^{3+ a}$

| buffer | % reactn | % yield | |
|---------------|-----------------------------|----------------------------------|---|
| | | $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ | $[(en)_2Co(OH_2)NH_2-CH_2CH_2SSC(CH_3)_3]^{3+}$ |
| 0.5 M Tris | 78 | 7.2 | 93 |
| | 97 | 7.9 | 92 |
| | 100 (14 h ^b) | 7.7 (11) | 92 (89) |
| 0.1 M Tris | 51 | 7.9 | 92 |
| | 100 (16 h ^b) | 6.4 (10) | 94 (91) |
| | 100 (68 h ^b) | 6.4 (12) | 94 (88) |
| 1 M ammonia | 100 | 31 | 69 |
| 0.1 M ammonia | 100 | 8.9 | 91 |
| c | 100 | 5.6 | 94 |

^a pH range 9–10; $t = 25^\circ C$. ^b Time elapsed past completion of the base hydrolysis reaction. ^c 0.2 M NaOH added to maintain pH 9.5.

readings were obtained with a Beckman Research pH meter equipped with a Sorex combination electrode.

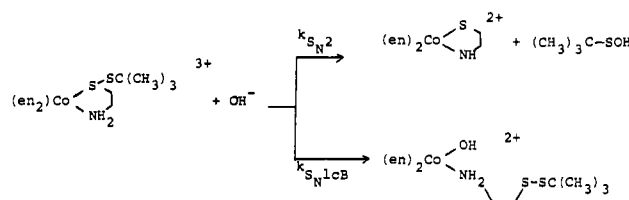
Kinetic Measurements and Calculations. All kinetic experiments were conducted in Tris/HClO₄ or NH₃/HClO₄ buffer systems maintained at constant 1.00 ± 0.01 M ionic strength with LiClO₄. Kinetics were monitored at the characteristic 332-nm peak of the disulfide complex⁵ or the 283-nm ligand-to-metal charge-transfer band characteristic of the Co-S linkage. The initial concentration of the disulfide complex was in the range $(1-4) \times 10^{-4}$ M. Values of the observed pseudo-first-order rate constant, k_{obsd} , and its associated standard deviation, $\sigma_{k_{obsd}}$, were obtained by nonlinear least-squares analysis¹¹ of A_t -time data within the usual first-order rate expression. Values of the second-order rate parameter, k_2 , and its associated standard deviation, σ_{k_2} , were calculated by linear least-squares analysis of the k_{obsd} -[OH⁻] data, each value of k_{obsd} being weighed by $(1/\sigma_{k_{obsd}})^2$. All reported errors are standard deviations.

Results

Product Analysis. As previously reported,¹ base hydrolysis of the disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ with R = CH₃, CH₂CH₃, and CH(CH₃)₂ leads exclusively to the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and organic sulfur compounds via sulfur-sulfur bond cleavage (eq 1). However, with R = *tert*-butyl, base hydrolysis leads to two products that, after quenching the reaction mixture by addition of HClO₄ to bring the pH to 2, can be separated by ion-exchange chromatography. These cobalt-containing products have estimated formal charges of 2+ and 3+ at pH 2. The brown complex of 2+ charge is identified as the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by its characteristic UV-visible spectrum.¹² The formal charge of the second complex (red) changes from 3+ to 2+ when the pH of the eluent is raised to 8, implying that this product contains a coordinated water molecule. The distributions of the thiolato and aquo complexes produced under various reaction conditions are listed in Table I. The ratio of aquo to thiolato complexes decreases in the order unbuffered solution > Tris buffer > ammonia buffer, and in ammonia it increases with the ammonia concentration. On standing, the aquo complex converts slowly into the thiolato complex.

The major point to be decided in the analysis of reaction products is whether the aquo product still contains the intact disulfide moiety or whether S-S bond cleavage has occurred during fission of the Co-S bond. The following lines of evidence establish conclusively that the correct formulation of the aquo complex is $[(en)_2Co(OH_2)(NH_2CH_2CH_2SSC(CH_3)_3)]^{3+}$. (1) The UV-visible spectrum of this product changes reversibly with pH; the absorption maximum is at 490 nm ($\epsilon = 64.4$ M⁻¹ cm⁻¹) for the aquo complex in acidic solution (pH 2) and at 498 nm ($\epsilon = 84.8$ M⁻¹ cm⁻¹) for the hydroxo complex in alkaline solution (pH 10). Spectrophotometric titration of this complex yields a pK_a value of 6.45 at $\mu = 0.25$ M, in good agreement with the value of 6.30 ($\mu = 2.0$ M) for *cis*- $[(en)_2Co(OH_2)(NH_3)]^{3+}$. (2) Titration with molecular bromine shows that 1 mole of the aquo complex reduces

Scheme I



3 mol of bromine, indicating the presence of a disulfide moiety¹³ in the aquo complex. (3) The ¹H NMR spectrum of the aquo complex exhibits a sharp *tert*-butyl resonance at $\delta = 1.38$ (relative to DSS internal standard), again indicating that the disulfide moiety is present in this product. (4) To confirm that neither the exo nor endo sulfur atom of the original disulfide complex is lost during conversion to the aquo product, samples of *exo*-³⁵S- and *endo*-³⁵S-labeled disulfide complex were prepared and subjected to base hydrolysis. The results of this experiment show that the aquo complex contains *both* the original endo and exo sulfur atoms, the thiolato complex contains, as expected, only the original endo sulfur atom, and the sulfur-containing organic products contain only the original exo sulfur atom. (5) A solid sample of the aquo complex was obtained after elution from an ion-exchange column with 0.5 M Ba(ClO₄)₂ and treatment with K₂SO₄ to remove supporting electrolyte. Although this solid material is hygroscopic and contains some salts, elemental analysis shows the C:N:Co:S ratio to be 10:5:1:2, confirming the presence of the intact disulfide ligand in the aquo complex.

Kinetics. In both Tris and ammonia buffers, plots of $\ln(A_t - A_\infty)$ vs. time are linear, indicating that the disulfide complex disappears by first-order kinetics. All applicable plots of k_{obsd} vs. [OH⁻] are linear, and thus the rate law governing base hydrolysis is

$$-d[\text{disulfide complex}]/dt = k_2[\text{OH}^-][\text{disulfide complex}] \quad (2)$$

Table II lists observed pseudo-first-order rate constants and derived second-order rate constants as a function of temperature, buffer, and buffer concentration. For data obtained in 0.5 M Tris buffer, a plot of $\ln(k_2/T)$ vs. $1/T$ is linear. Analysis of this plot yields the following parameters: $k_2(25^\circ C) = 111 \pm 2$ M⁻¹ s⁻¹, $\Delta H^\ddagger = 24.6 \pm 1.1$ kcal mol⁻¹, and $\Delta S^\ddagger = 33 \pm 4$ eu. At a given [OH⁻] the reaction rate is greater in ammonia buffer than in Tris buffer. Also, the reaction rate varies with ammonia concentration but not with Tris concentration.

Discussion

Base hydrolysis of the disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ with R = methyl, ethyl, and isopropyl proceeds exclusively by nucleophilic attack on the S-S bond to yield the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.¹ The rate of this process decreases with increasing steric bulk of the R group, and

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Table II. Observed Pseudo-First-Order and Derived Second-Order Rate Constants for Base Hydrolysis of $[(\text{en})_2\text{Co}(\text{S}(\text{SC}(\text{CH}_3)_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ ^a

| pH | $[\text{OH}^-]$, ^b M | $10^3 k_{\text{obsd}}$, s ⁻¹ | $10^{-2} k_2$, M ⁻¹ s ⁻¹ |
|--------------------------|----------------------------------|--|---|
| $t = 15.0^\circ\text{C}$ | | | |
| 8.300 | 5.13×10^{-6} | 0.0199 ± 0.0002 | } 0.32 ± 0.05 |
| 8.672 | 1.21×10^{-6} | 0.0400 ± 0.0005 | |
| 9.100 | 3.24×10^{-5} | 0.126 ± 0.003 | |
| $t = 25.0^\circ\text{C}$ | | | |
| 8.052 | 2.89×10^{-6} | 0.57 ± 0.02 | } 1.11 ± 0.02 |
| 8.128 | 3.45×10^{-6} | 0.62 ± 0.02 | |
| 8.762 | 1.48×10^{-5} | 1.96 ± 0.01 | |
| 9.213 | 4.20×10^{-5} | 4.93 ± 0.02 | |
| 10.266 | 4.74×10^{-4} | 51.7 ± 0.5 | |
| 7.869 | 1.90×10^{-6} | 0.52 ± 0.01^c | |
| 8.046 | 2.86×10^{-6} | 0.71 ± 0.01^c | 2.50 ^c |
| 9.690 | 1.26×10^{-4} | 13.7 ± 0.1^d | 1.09 ^d |
| 9.076 | 3.11×10^{-5} | 12.9^e | 4.15 ^e |
| 9.117 | 3.42×10^{-5} | 15.0^e | 4.38 ^e |
| 9.080 | 3.14×10^{-5} | 7.26^f | 2.31 ^f |
| $t = 35.0^\circ\text{C}$ | | | |
| 8.055 | 2.92×10^{-6} | 1.44 ± 0.02 | } 3.9 ± 0.1 |
| 8.500 | 8.13×10^{-6} | 3.12 ± 0.05 | |
| 8.800 | 1.62×10^{-5} | 6.74 ± 0.04 | |
| 9.233 | 4.40×10^{-5} | 17.6 ± 0.1 | |
| $t = 45.0^\circ\text{C}$ | | | |
| 8.334 | 5.55×10^{-6} | 9.7 ± 0.1 | } 20.3 ± 1.6 |
| 8.438 | 7.05×10^{-6} | 15.4 ± 0.2 | |
| 8.779 | 1.54×10^{-5} | 31.3 ± 0.2 | |
| 9.200 | 4.07×10^{-5} | 77.5 ± 0.8 | |

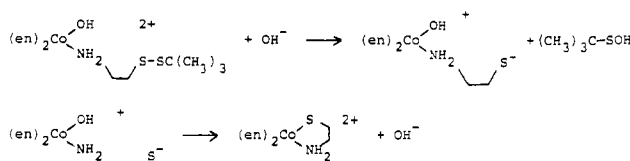
^a Unless otherwise noted, conditions are 0.5 M Tris buffer, $\mu = 1.00 \pm 0.01$ M (LiClO₄), and $\lambda = 332$ nm. ^b $[\text{OH}^-] = 10^{\text{pH}-0.417-14}$. See: Nosco, D. L. Ph.D. Thesis, University of Cincinnati, 1981. The factor 0.417 arises from calibration of the pH electrode in media of unit ionic strength. ^c $\lambda = 283$ nm. ^d 0.1 M Tris buffer. ^e 0.87 M ammonia buffer. ^f 0.2 M ammonia buffer.

when R is *tert*-butyl, the rate of S-S bond cleavage is so slow that S_N1cB Co-S bond fission becomes competitive. The product of Co-S bond breaking in alkaline media is the hydroxo complex $[(\text{en})_2\text{Co}(\text{OH})(\text{NH}_2\text{CH}_2\text{CH}_2\text{SSC}(\text{CH}_3)_3)]^{2+}$. (See Scheme I.) Thus, the rate of disappearance of the disulfide complex $[(\text{en})_2\text{Co}(\text{S}(\text{SC}(\text{CH}_3)_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ is described by

$$-\frac{d \ln [\text{disulfide complex}]}{dt} = k_{\text{obsd}} = k_{\text{S}_{\text{N}2}}[\text{OH}^-] + k_{\text{S}_{\text{N}1\text{cB}}}[\text{OH}^-]$$

and the experimental rate parameter k_2 is equal to the sum of $k_{\text{S}_{\text{N}2}}$ and $k_{\text{S}_{\text{N}1\text{cB}}}$. Since the ratio of $k_{\text{S}_{\text{N}2}}/k_{\text{S}_{\text{N}1\text{cB}}}$ can be obtained from the product distribution data of Table I, values for the individual rate constants of Scheme I can be calculated. Thus, in 0.5 M Tris buffer at 25 °C, $k_{\text{S}_{\text{N}1\text{cB}}} = 102 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{S}_{\text{N}2}} = 9 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$. This calculated value of $k_{\text{S}_{\text{N}1\text{cB}}}$ agrees well with the comparable parameter ($689 \pm 14 \text{ M}^{-1} \text{ s}^{-1}$, 25 °C, $\mu = 0.10$ M) determined¹⁴ for Co-S bond fission in the *tert*-butyl thioether complex $[(\text{en})_2\text{Co}(\text{S}(\text{C}(\text{CH}_3)_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$. Cleavage of the Co-S bond in the thioether complex is somewhat faster presumably because the Co-S-C(CH₃)₃ linkage is somewhat more sterically hindered than the Co-S-S-C(CH₃)₃ linkage, and the rates of S_N1 reactions increase with increasing size of the leaving group. The calculated value of $k_{\text{S}_{\text{N}2}}$ is also reasonable in light of the expected

Scheme II



effect of increased steric hindrance on the rate of nucleophilic attack by OH⁻ on the S-S linkage. Thus, along the series $[(\text{en})_2\text{Co}(\text{S}(\text{SR})\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ with R = methyl, ethyl, isopropyl, and *tert*-butyl, the values of $k_{\text{S}_{\text{N}2}}$ (M⁻¹ s⁻¹, 25 °C, $\mu = 1.00$ M) are 1.7×10^6 , 5.6×10^5 , 2.0×10^4 , and 9, respectively. The dramatic drop in specific rate on going from isopropyl to *tert*-butyl reflects the inability of the *tert*-butyl group to rotate out of the path of the incoming OH⁻ nucleophile.

Since in 0.5 M Tris buffer about 92% of the base hydrolysis reaction proceeds by Co-S bond fission (Table I), the activation parameters measured in this medium describe predominantly the S_N1cB process. In this context the activation parameters measured in this work are comparable to those measured for S_N1cB Co-S bond fission in the thioether complexes $[(\text{en})_2\text{Co}(\text{S}(\text{R})\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ (ΔH^* in the range 25–31 kcal mol⁻¹ and ΔS^* in the range 21–39 eu).¹⁴

Results of both the product analyses (Table I) and the kinetic experiments (Table II) show that in ammonia buffer the free NH₃ participates in the reaction mechanism by cleaving the S-S bond. The more sterically crowded Tris base does not appear to function as a nucleophile in this system. Thus, the yield of the thiolato complex (which results from S-S bond cleavage) is greater in ammonia buffer than in Tris buffer and increases with the concentration of ammonia (Table I). Also, the rate of disappearance of the disulfide complex, corrected for hydroxide concentration, is greater in ammonia buffer than in Tris buffer (Table II). From the very limited data available, the second-order rate parameter governing S_N2 attack by NH₃ on the S-S bond of $[(\text{en})_2\text{Co}(\text{S}(\text{SC}(\text{CH}_3)_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$ can be estimated as $0.02 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 1.00$ M). The ordering of nucleophilicities for attack on this S-S linkage is therefore RS⁻ (4.1×10^4) > OH⁻ (9) > NH₃ (2×10^{-2}) > RSH (2.7×10^{-5}), where the specific rates in M⁻¹ s⁻¹ (25 °C, $\mu = 1.00$ M) are given in parentheses and RSH represents mercaptoethanol.¹

The S_N1cB base hydrolysis path yields a hydroxo complex that contains a dangling disulfide functionality (Scheme I). This dangling, noncoordinated disulfide undergoes S_N2 attack by OH⁻, although the rate of this reaction is much less than that for cleavage of the coordinated disulfide. Cleavage of the dangling disulfide functionality yields a dangling thiolato functionality that can displace the coordinated hydroxo group and form the thiolato complex $[(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)]^{2+}$ (Scheme II). Since absorbance at 283 nm (A_{283}) is characteristic of the Co-S linkage,¹⁰ this slow production of the thiolato complex can be monitored by the increase in A_{283} that occurs after the base hydrolysis reaction is completed. The product analysis data of Table I also show increased yields of thiolato complex at reaction times very much longer than the time required for the base hydrolysis to proceed to completion.

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Registry No. $[(\text{en})_2\text{Co}(\text{S}(\text{SCH}_2)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$, 74037-05-1; $[(\text{en})_2\text{Co}(\text{S}(\text{SCH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$, 74037-02-8; $[(\text{en})_2\text{Co}(\text{S}(\text{SCH}(\text{CH}_3)_2)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$, 74037-00-6; $[(\text{en})_2\text{Co}(\text{S}(\text{SC}(\text{CH}_3)_3)\text{CH}_2\text{CH}_2\text{NH}_2)]^{3+}$, 74036-99-0.

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