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Base Hydrolysis of Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thioether and Selenoether Ligands. Observation of Dramatic Medium Effects[1]

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The kinetics and mechanisms of alkaline hydrolysis of a variety of tripositive (thioether)- and (selenoether)cobalt(III) complexes of the general formula $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ (X = S, Se) are reported. The nature of the reaction is found to strongly depend on R. For instance, if R contains an acidic methylene group such as in $-CH_2COO^-$, $-CH_2C_6H_5$, or $-CH_2C(O)CH_3$, reaction in base leads to a variety of products. However, for many complexes (e.g., those with R = $-CH_3$, $-CH_2CH_3$, $-CH_2C_6H_{11}$, $-(CH_2)_2COO^-$, $-(CH_2)_2C_6H_5$, etc.) reaction in base leads to simple Co–S or Co–Se bond cleavage. The kinetics of these hydrolysis reactions depend markedly on the nature and concentration of the supporting electrolyte. In perchlorate media significant deviation from a linear dependence of k_{obsd} on $[OH^-]$ is observed at $\mu = 1.0$ and 2.0 M. No such marked deviation is observed in chloride media. At $\mu = 0.1$ M, no medium effects are observed and $k_{obsd} = k_{OH}[OH^-]$ regardless of the nature of the supporting electrolyte. At $\mu = 0.1$ M a marked steric acceleration is observed as R is changed from $-CH_3$ to $-C(CH_3)_3$. For the complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, $k_{OH} = 0.163 \pm 0.013$ M^{-1} s^{-1} (25 °C), while for the complex $[(en)_2Co(S(C(CH_3)_3)CH_2CH_2NH_2)]^{3+}$, $k_{OH} = 686 \pm 14$ M^{-1} s^{-1} (25 °C). For the CH_3 complex, $\Delta H^* = 29.0 \pm 0.4$ kcal/mol and $\Delta S^* = 33.1 \pm 1.4$ eu. In all instances of simple Co–S or Co–Se bond cleavage, added azide ion is trapped and incorporated into the final product. These results are consistent with an S_N1CB mechanism for base hydrolysis. Consistent with their lower positive charge, the parental thiolate and selenolate complexes $[(en)_2Co(XCH_2CH_2NH_2)]^{2+}$ (X = S, Se) are resistant to base hydrolysis under conditions where the $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ complexes hydrolyze rapidly.

Introduction

In the course of our studies into the chemistry of coordinated sulfur and selenium we have investigated the alkaline hydrolysis of a variety of tripositive (thioether)- and (selenoether)cobalt(III) complexes of the general formula $[(en)_2Co(X(R)CH_2CH_2NH_2\text{-}N,X)]^{3+}$ (X = S, Se). The reaction originally attracted our attention because it proceeds much more rapidly than does alkaline hydrolysis of the parental thiolato and selenolato complexes, $[(en)_2Co(XCH_2CH_2NH_2\text{-}N,X)]^{2+}$ (X = S, Se), thus allowing a facile determination of the effect of R and X on the rate of Co–X bond cleavage and thereby hopefully some understanding as to the intimate nature of this process. This reaction is also of mechanistic interest since the thioether and selenoether functionalities are neutral leaving groups. Recent studies on alkaline hydrolysis of other tripositive cobalt(III) complexes with neutral leaving groups have cast doubts on the often assumed ubiquity of the S_N1CB methanism in cobalt(III) chemistry.[2,3] For example, plots of k_{obsd} vs. $[OH^-]$ for $[(tren)Co(NH_3)_2]^{3+}$ and s-$[(Me(tren)Co(NH_3)_2]^{3+}$ (tren = 2,2′,2″-triaminotriethylamine; Me(tren) = 2-(methylamino)-2′,2″-diaminotriethylamine) all deviate markedly from linearity and approach a limiting rate of hydrolysis at base concentrations that are too low to be consistent with deprotonation of a coordinated ammine.[4] In addition, competition studies conducted with $[(en)_2Co(NH_3)X]^{3+}$ complexes, where X is the neutral leaving ligand dimethyl sulfoxide or trimethyl phosphate, have shown that the ratio of azido and hydroxo products are dependent on the identify of the leaving group; no such dependence would be observed if a strict S_N1CB mechanism were operative.[5] These phenomena have been interpreted in terms of an ion-pairing mechanism for alkaline hydrolysis.[4-6] However, a more recent report[7] on the hydrolysis of tripositive complexes of the type $[(NH_3)_5CoL]^{3+}$ where L = dimethyl sulfoxide or trimethyl phosphate has shown that for these complexes k_{obsd} depends linearly on $[OH^-]$. This evidence has been used to vigorously defend the S_N1CB mechanism,[7] but clearly the experimental distinction between the S_N1CB and ion-pairing mechanisms is difficult and subject to considerable controversy.[8-10]

In this paper we report on the detailed kinetics of alkaline hydrolysis of 11 thioether and selenoether complexes. Departures from a linear dependence of k_{obsd} on $[OH^-]$ are observed if perchlorate salts are used to maintain the ionic strength, but no such departures are observed if chloride salts are used. The rates of these reactions are discussed in terms of medium effects and the S_N1CB and ion-pairing mechanisms for base hydrolysis of cobalt(III) complexes. Additionally, the effects of varying X and R on the rate and mechanism of the hydrolysis reaction are discussed.

Experimental Section

General Data. Triply distilled, charcoal-filtered water was used in all kinetic experiments. Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate and doubly distilled perchloric acid (70–72%, G. F. Smith) as previously described.[11] Lithium hydroxide and sodium chloride were recrystallized once from triply distilled water and dried under vacuum at 80 °C for 5 h. Sodium azide was recrystallized once from triply distilled water. The hydroxide concentrations of the reaction solutions were determined by triplicate titrations to a phenolphthalein end point with standard solutions of hydrochloric acid (Fisher). Sephadex SP-C25 cation-exchange resin (Pharmacia) was converted to the lithium form and stored under triply distilled water at ca. 5 °C.

Elemental analyses on isolated aqueous solutions were performed by Galbraith Laboratories, Inc., Knoxville, TN. Total cobalt concentrations for use in establishing molar asorptivities were determined by using a modified Kitson procedure.[12,13]

All of the complexes used in this work were available from previous studies.[14,16] The purity of each thioether complex was confirmed by

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dissolving a small amount of the solid salt in water, loading an aliquot onto an ion-exchange column (Sephadex SP C-25, 7-mm i.d. × 100-mm length), and slowly eluting with $NaClO_4$ solutions. The solid salts were found to be sufficiently pure for kinetic experiments as the complexes exhibited only a single band, the visible–UV spectrophotometric parameters of which were in agreement with literature values. The solid selenoether salts were always purified by ion-exchange chromatography before use.

Equipment. All kinetic experiments were monitored on a Cary Model 118B recording spectrophotometer equipped with a thermostated cell compartment, maintained at temperature by a Haake FK2 constant-termperature bath, and a Hewlett-Packard 5105A thermal printer. Temperature was maintained to ±0.1 °C and was monitored with a USC Model 581C digital thermometer that had been calibrated against an NBS certified mercury thermometer. All computer calculations were performed on the AMDAHL 470/V6-11 system located at the University of Cincinnati.

Product Analysis. In each case a procedure similar to that outlined below for $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)](ClO_4)_3$ was followed. A 0.1-g sample of the complex was dissolved in 5 mL of 1.0 M NaOH. The solution rapidly changed color from orange to red. After 2 min the reaction was quenched by diluting the solution with water to ca. pH 7. This diluted solution was adsorbed onto an ion-exchange column (Sephadex SP C-25, 10-mm i.d. × 100-mm length). The solution loads as an orange band preceded by a red-pink band. After washing with water, elution was begun with 0.1 M $NaClO_4$ (pH ca. 7) and the bands did not move. Elution with 0.2 M $NaClO_4$ (pH ca. 7) easily removed the red-pink band. The orange band was then removed with 0.3 M $NaClO_4$ and shown by visible–UV analysis to be the original thioether complex. All of the complexes studied in which Co–S or Co–Se bond cleavage occurred were treated in a similar manner, with reaction times varying from 1 to 100 half-lives and base concentrations ranging from 0.025 to 2.00 M. In all instances only the original complexes and red-pink products were detected. To ensure that chloride would not promote aquation, 0.1 g of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)](ClO_4)_3$ was dissolved in 10 mL of 2.0 M NaCl. After 24 h, no noticeable color change had occurred and elution from an ion-exchange column showed that only the original thioether complex was present.

Competition Experiments. A 0.3-g sample of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)](ClO_4)_3$ was dissolved in 10 mL of 1.0 M NaN_3, and to this solution was added 1 mL of 1.0 M LiOH. The color of the solution changed rapidly from orange to dark red. After 3 min the reaction was quenched with 250 mL of 0.01 M $HClO_4$. This dilute solution was adsorbed onto an ion-exchange column (Sephadex SP C-25, 5-mm i.d. × 80-mm length). Upon loading, the column exhibits an orange band preceded by a purple band. The purple band was removed with 0.2 M $NaClO_4$. The spectrum of the purple band shows a visible peak at 512 nm ($\epsilon = 313\ M^{-1}\ cm^{-1}$), consistent with the spectra of other azidopentamminecobalt(III) complexes.[17] The isolated purple band was then loaded onto another ion-exchange column (Dowex (H^+) 50W-X2, 200–400 mesh, 10-mm i.d. × 150-mm length) and the column eluted with 1.0 M $NaClO_4$. The purple band did not separate into components, and the visible–UV spectra of the front and trailing edges of the band showed no detectable differences. Other attempts to isolate cis and trans isomers of the azido complex were also unsuccessful.

To ensure that azide did not directly replace the thioether function, the above experiment was repeated without the addition of base. After 10 min the solution was diluted and loaded onto an ion-exchange column. No azido complexes were detected upon elution with 0.2 M $NaClO_4$. To ensure that the azido species was not formed after hydrolysis, a solution of $[(en)_2Co(OH)(NH_2CH_2CH_2SCH_3)]^{2+}$ (pH 12), isolated from the base hydrolysis reaction of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ by ion-exchange chromatography, was added to a solution of 1.0 M NaN_3 (pH 12). After 10 min the solution was diluted and loaded onto an ion-exchange column. No azido complexes were detected upon elution. Repeating the competition experiments with $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ also resulted in no azido complexes being detected.

Kinetic Measurements and Calculations. Kinetic experiments were conducted in aqueous $LiOH/LiClO_4$, LiOH/LiCl, $NaOH/NaClO_4$, or NaOH/NaCl solutions maintained at a constant ionic strength of 2.0, 1.0, or 0.1 M. Kinetics were monitored spectrophotometrically for at least 4 half-lives either at the UV LTMCT (ligand-to-metal charge-transfer) transition characteristic of the cobalt–sulfur bond or at the visible band resulting from a cobalt(III) d–d transition.[14-16] The observed first-order rate constants were independent of the monitoring wavelength. For each experiment an infinite time measurement, OD_∞, could be determined experimentally. Plots of log $(OD_\infty - OD_t)$ vs. time gave straight lines for at least 4 half-lives of the reaction. Linear least-squares analysis yielded values of k_{obsd} and $\sigma_{k_{obsd}}$. In those cases where k_{obsd} is linearly dependent on $[OH^-]$, values of the corresponding second-order rate parameter k_{OH} were obtained by linear least-squares analysis. In those cases where k_{obsd} is not linearly dependent on $[OH^-]$, a nonlinear least-squares analysis[18] was used to fit the dependence of k_{obsd} on $[OH^-]$ to two different expressions:

$$k_{obsd} = k_{OH}'K[OH^-]/(1 + K[OH^-]) \qquad (1)$$

$$k_{obsd} = k_{OH}''[OH^-]e^{-\alpha[OH^-]} \qquad (2)$$

Activation parameters were calculated by using standard linear techniques, the limited range of available data barring the use of a nonlinear analysis. All reported errors are standard deviations.

Results

Product Analysis for Base Hydrolysis Reactions of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ Complexes (X(R) = $-SCH_3$, $-SCH_2CH_3$, $-SCH_2C_6H_{11}$, $-S(CH_2)_2COO^-$, $-S(CH_2)_3COO^-$, $-SCH(CH_3)CH_2COO^-$, $-S(CH_2)_2C_6H_5$, $-SC(CH_3)_3$, $-SeCH_2CH_3$, $-SeCH_2C_6H_5$). In each case the product of the base hydrolysis reaction is identified as $[(en)_2Co(OH)(NH_2CH_2CH_2XR)]^{2+}$ on the basis of several observations. Duplicate elemental analyses of isolated solutions of the aquated product (X = S; R = $-CH_3$) show one cobalt atom per sulfur atom, but the UV spectrum shows no LTMCT band at 282 nm, which would be expected to be present if the sulfur atom were still coordinated.[14] Upon acidification of the product solutions, the sulfur (or selenium) atom rechelates, the LTMCT band reappears, and the original starting material is recovered. In all cases rechelation is negligible at the reaction pH. At 52 °C, pH 2, and $\mu = 1.0$ M, the rechelation rate for the complex with X = S and R = $-CH_3$ is $4.5 \times 10^{-5}\ s^{-1}$. At pH 2 rechelation does not proceed to completion even after 4 weeks (i.e., after the rechelation reaction has ceased, some of the material remains in the unchelated form). The complex with X = Se and R = $-CH_3$ rechelates much more rapidly: $k_{obsd} = 5.7 \times 10^{-4}\ s^{-1}$ at 25 °C, pH 2, and $\mu = 1.0$ M. At ca. pH 7 or greater, the hydrolysis product is red-pink and elutes easily as a 2+ species, whereas at lower pH values the product is orange and elutes as a mixture of the 3+ species $[(en)_2Co(H_2O)(NH_2CH_2CH_2XR)]^{3+}$ and $[(en)_2Co(X(R)CH_2CH_2NH_2\text{-}N,X)]^{3+}$, which are inseparable on Sephadex SP C-25.

The visible–UV spectra of the various red-pink products are identical, all having a peak at ca. 500 nm ($\epsilon = 75\ M^{-1}\ cm^{-1}$, pH 10) and at ca. 350 nm ($\epsilon = 70\ M^{-1}\ cm^{-1}$, pH 10). The intensities and positions of these peaks are dependent on the pH of the solution. The 350-nm absorption varies from a definite peak at pH 10 to a shoulder at pH 7. When a solution of the hydrolysis product is acidified with a drop of concentrated $HClO_4$, the spectrum behaves as depicted in Figure 1. The 500-nm peak becomes less intense and shifts to 480 nm; the peak at 350 nm disappears due to the appearance of the intense UV LTMCT absorption. In the UV region the LTMCT band can be observed to reappear upon acidification. As Figure 1 also shows, the visible–UV spectrum of $[(NH_3)_5Co(OH)]^{2+}$ does not have a similar acid–base dependence. In base, the spectrum is very similar to the spectrum of the hydrolysis product. In acid, however, the 350-nm peak is retained with a somewhat decreased intensity. Thus, the disappearance of the 350-nm peak in reacidified solutions of the hydrolysis product undoubtedly results from the reappearance of the intense LTMCT band upon rechelation of the thioether or selenoether functionality.

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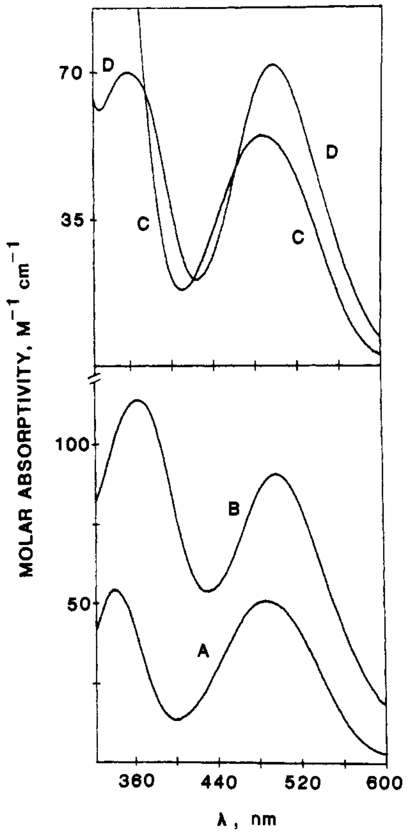


Figure 1. Comparative acid–base dependence of the visible–UV spectra of $[(NH_3)_5CoOH_2]^{3+}$ and the product resulting from base hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$: (A) $[(NH_3)_5CoOH_2]^{3+}$ at pH 2; (B) $[(NH_3)_5CoOH]^{2+}$ at pH 10; (C) hydrolysis product after standing at pH 2; (D) hydrolysis product at pH 10.

Base Hydrolysis. $[(en)_2Co(S(O)_nCH_2CH_2NH_2)](ClO_4)_2$ (n = 0–2) and $[(en)_2Co(SeCH_2CH_2NH_2)](ClO_4)_2$. The bipositive thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is stable in 1.0 M LiOH at 45 °C for at least 2 days. The selenolato complex $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ decomposes slowly in 1.0 M LiOH at 25 °C with $k_{obsd} = 1.6 \times 10^{-5}$ s^{-1}; at pH 2 k_{obsd} is equivalent at 1.4×10^{-5} s^{-1}. The sulfenato and sulfinato complexes $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ are stable in 1.0 M LiOH at 25 °C for at least 2 h.

$[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ Complexes (R = $-CH_2CO_2H$, $-CH(CO_2H)CH_2CO_2H$, $-CH_2COCH_3$, $-(CH_2)_2COCH_3$, $-(CH_2)_2CHO$, $-(CH_2)_2CN$, $-(CH_2)_2CONH_2$). In each of these complexes simple Co/S cleavage is not observed. Multiple products result from base hydrolysis of the complexes with R = $-CH_2CO_2H$ and $-CH(CO_2H)CH_2CO_2H$ under conditions that yield a single product when R = $-(CH_2)_2CO_2H$. These more complicated reactions were not characterized further.

The complex with R = $-CH_2COCH_3$ undergoes what appears to be a rapid intramolecular condensation to form a coordinated imine.[16] This yellow product ($\epsilon_{474} = 240$, $\epsilon_{336} = 226$, $\epsilon_{271} = 6480$ M^{-1} cm^{-1}) of 3+ charge is formed quantitatively from the thioether complex via a violet intermediate. A brief kinetic investigation of this intramolecular condensation reaction shows linear log ($A_t - A_\infty$) vs. time plots for over 4 half-lives; $k_{obsd} = 0.0044$ s^{-1} at 25 °C, pH 4.67 in 0.1 M succinic acid buffer. When R = $-(CH_2)_2COCH_3$ or $-(CH_2)_2CHO$, the complexes decompose ca. pH 6 to yield the original thiolato complex, $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and the corresponding alkene. The brown, 2+ thiolato complex is characterized by its ion-exchange elution characteristics and visible–UV spectrophotometric parameters that are in agreement with literature values. The alkenes are identified by their characteristic foul odor and by the fact that upon reacidification of sealed reaction solutions the original thioether complex is quentiatively regenerated from the product mixture.[15] Above ca. pH 6 a yellow 3+ product is also formed that has visible–UV spectral characteristics similar to those of the just described imine complex. For the product from R = $-(CH_2)_2COCH_3$, $\epsilon_{476} = 176$, $\epsilon_{348} = 254$, $\epsilon_{278} = 8328$, and $\epsilon_{218} = 22\,900$ M^{-1} cm^{-1}, and for that from R = $-(CH_2)_2CHO$, $\epsilon_{474} = 202$, $\epsilon_{348(sh)} = 180$, and $\epsilon_{278} = 9500$ M^{-1} cm^{-1}. No violet intermediate is observed in the formation of these products.

When R = $-(CH_2)_2CN$ or $-(CH_2)_2CONH_2$, hydrolysis proceeds predominantly by carbon–sulfur bond cleavage in 0.1 M NaOH. In each case a small amount of the product resulting from cobalt–sulfur bond cleavage is also obtained. This product is identified from the acid–base dependence of its visible–UV spectrum, which is similar to the dependence illustrated in Figure 1. Additionally, when R = $-(CH_2)_2CONH_2$, a red 2+ product is also formed; this material has visible–UV spectrophotometric characteristics similar to those of the thioether complexes $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ ($\epsilon_{282}/\epsilon_{490} = 50$). Further characterization of this minor product was not attempted.

$[(en)_2Co(S(\overline{CHC(O)N(R')C(O)CH_2})CH_2CH_2NH_2)]^{3+}$ Complexes (R′ = $-H$, $-CH_3$, $-CH_2CH_3$, $-C_6H_5$). In 0.1 M NaOH the base hydrolysis of these N-substituted succinimidyl thioether complexes proceeds through a violet intermediate to the formation of five products. Only a very minor fraction of the product mixture is identified as the complex resulting from cobalt–sulfur bond cleavage. Further characterization of these products was not pursued. At neutral pH the complexes decompose in ca. 2 h to yield a yellow-brown solution. When this solution is subjected to cation-exchange chromatography, two bipositive cobalt-containing species are isolated and identified. On the basis of their elution characteristics and visible–UV spectrophotometric parameters, these are the parental thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and the sulfenato complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

$[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ Complexes (R = $-CH_2C_6H_5$ (Benzyl), $-CH_2C_6H_4CH_3$ (*p*-Methylbenzyl), $-CH_2C_6H_4F$ (*p*-Fluorobenzyl), and $-CH_2C_{10}H_7$ (Naphthylmethyl)). The base hydrolysis reactions of these complexes are also complicated by the formation of multiple products. A minor component (<10%) of the mixture is identified as that resulting from cobalt–sulfur bond cleavage. The predominate product (>50%) is a brown dipositive species that is neither $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ nor $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. Preliminary investigations into this reaction at lower base concentrations (≤0.006 M) show isosbestic behavior, with the above-mentioned brown complex being produced in >95% yield. Two other minor products are also detected at this low [OH$^-$], one being that resulting from cobalt–sulfur bond fission. Whether or not these two minor components result from decomposition of the as yet unidentified brown complex, or from direct reaction of the parental thioether complex, has not been determined.

Attempted Base Hydrolysis of $[(en)_2Co(S(CH_3)C_6H_4NH_2)]^{3+}$. Addition of base to solutions of this aryl thioether complex result in the formation of an intensely colored, dark violet solution ($\epsilon_{584} = 647$, $\epsilon_{408(sh)} = 476$, $\epsilon_{350} = 3805$, $\epsilon_{250} = 26\,200$ M^{-1} cm^{-1}). Reacidification of this solution results in regeneration of the original spectrum ($\epsilon_{487} = 206$, $\epsilon_{306(sh)} = 2140$, $\epsilon_{253} = 975$ M^{-1}cm^{-1}). Solutions of the violet complex are stable for ca. 15 min before eventually decomposing to an uncharacterized black oil.

Kinetics of Base Hydrolysis. Kinetic data are summarized in Tables I–VI. Alkaline hydrolysis of the tripositive thioether and selenoether cobalt(III) complexes listed in Tables I and IV obeys first-order kinetics for at least 4 half-lives throughout the range [OH$^-$] = 0.004–2.00 M. As Figures 2 and 3 show, plots of k_{obsd} vs. [OH$^-$] deviate markedly from linearity depending on the medium and ionic strength. Table V summarizes the calculated values of k_{OH}' and K, obtained by weighted nonlinear least-squares

Table I. Derived Second-Order Rate Constants for the Base Hydrolysis of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ Complexes (X = S, Se) at 25 °C (μ = 0.10 M)[a]

X	R	λ,[b] nm	medium	k_{OH}, M^{-1} s^{-1}	n[c]
S	$-CH_3$	282	$LiOH/LiClO_4$	0.163 ± 0.013	6
			LiOH/LiCl	0.159 ± 0.005	4
			$NaOH/NaClO_4$	0.181 ± 0.006	15
			NaOH/NaCl	0.181 ± 0.002	4
S	$-CH_2CH_3$	282	$LiOH/LiClO_4$	0.193 ± 0.007	5
S	$-CH_2C_6H_{11}$	286	$LiOH/LiClO_4$	0.160 ± 0.016	5
S	$-(CH_2)_2COO^-$	282	$LiOH/LiClO_4$	0.216 ± 0.016	5
S	$-(CH_2)_3COO^-$	282	$LiOH/LiClO_4$	0.194 ± 0.006	5
S	$-CH(CH_3)CH_2CO^-$	288	NaOH/NaCl	2.89 ± 0.06	7
S	$-(CH_2)_2C_6H_5$	283	NaOH/NaCl	0.589 ± 0.010	5
S	$-C(CH_3)_3$	299	0.050 M Tris buffer/$LiClO_4$	689 ± 14	9
			0.10 M Tris buffer/NaCl	627 ± 15	2
			0.10 M NH_4OH buffer/NaCl	428 ± 12	1
Se	$-CH_3$	297	NaOH/NaCl	0.238 ± 0.010	4
Se	$-CH_2C_6H_5$	305	NaOH/NaCl	2.43 ± 0.08	7

[a] k_{OH} values derived from observed first-order rate parameters, k_{obsd}. A complete listing of k_{obsd} vs. $[OH^-]$ data is given in Table A.[40] [b] Wavelength at which reaction is monitored. [c] Number of independent k_{obsd}-$[OH^-]$ determinations used to calculate k_{OH}.

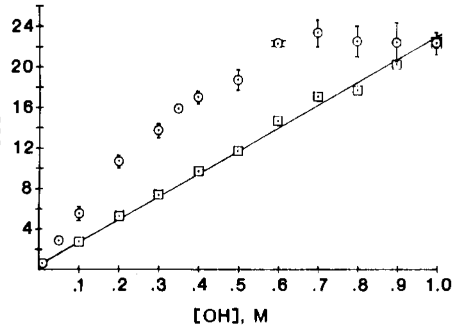


Figure 2. Plot of 10^3k_{obsd} (s^{-1}) vs. $[OH^-]$ (M) for the base hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ at μ = 1.00 M and 25 °C. The squares represent experiments conducted in LiOH/LiCl media, while the circles represent experiments conducted in $LiOH/LiClO_4$ media.

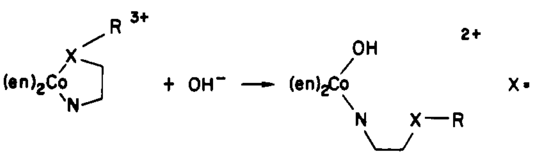
analysis, which describe the $[OH^-]$ dependence of k_{obsd} within the rate law (1). The average deviation between the observed values of k_{obsd} and the values of k_{obsd} calculated from the optimized k_{OH}' and K parameters analyses is 6.1%, with the maximum deviation being 8.3%.

Table V also summarizes the values of k'' and α, again obtained from weighted nonlinear least-squares analyses, which best fit the rate law (2). The average deviation between the observed values of k_{obsd} and those calculated from the optimized k_{OH}'' and α parameters within the above rate law is 4.6% with a maximum deviation of 5.8%.

Summarized in Table VI are activation parameters resulting from the temperature dependence of k_{obsd} at μ = 1.0 M ($LiOH/LiClO_4$).

Discussion

Reactions Proceeding through Cobalt-Sulfur or Cobalt-Selenium Bond Cleavage. The complexes listed in Tables I and IV all decompose in alkali through cobalt-sulfur or cobalt-selenium bond cleavage.



X = S, Se (3)

The kinetic results obtained at μ = 0.1 M (Table I) are independent of the nature of the supporting electrolyte and are also consistent with a dissociative process. Examination of the values of the second-order rate parameter k_{OH} reveals two trends. First, the reaction rate is insensitive to the steric bulk of the alkyl chain as long as the carbon atom attached to the sulfur atom is primary.

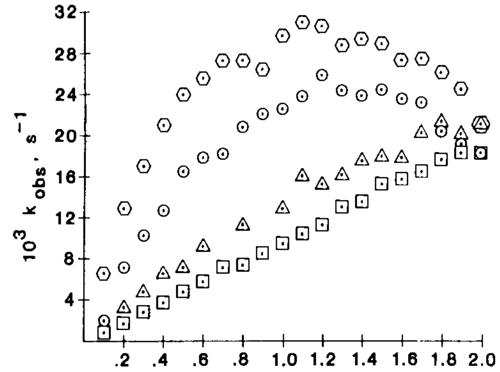


Figure 3. Plot of 10^3k_{obsd} (s^{-1}) vs. $[OH^-]$ (M) for the base hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ at μ = 2.00 M and 25 °C. Experiments conducted in LiOH/LiCl media are represented by squares, those in NaOH/NaCl media by triangles, those in $LiOH/LiClO_4$ media by circles, and those in $NaOH/NaClO_4$ media by hexagons.

This is consistent with the findings of Hay and Cropp[19] who observed that, in complexes of the type $[(en)_2Co(RNH_2)Cl]^{2+}$, k_{OH} is independent of R over the series methyl to n-butyl. Second, the rate of reaction increases markedly as the nature of the carbon atom bonded to the sulfur atom is changed from primary to secondary to tertiary. When R = $-C(CH_3)_3$ the complex undergoes base hydrolysis ca. 4.5 × 10^4 times faster than when R = $-CH_3$. The large magnitude of this steric effect, induced by changing only one R group, is noteworthy for the reaction of a coordination complex; effects of this size are more usually observed in purely organic systems. In coordination complexes, the largest steric acceleration known to us involves changing five R groups; when $(A)_5$ in $[(A)_5CoCl]^{2+}$ is changed from $(NH_3)_5$ to (i-$C_4H_9NH_2)_5$,k_{OH} increases by a factor of over 10^5.[20] Changing the nature of the carbon atom bonded to the sulfur atom from primary to secondary (i.e., from R = $-CH_2CH_2COOH$ to R = $-CH(CH_3)CH_2COOH$) increases k_{OH} by a factor of 12. This is significantly larger than the factor of 4 increase in k_{OH} observed on varying R in $[(en)_2Co(RNH_2)Cl]^{2+}$ from n-propyl to isopropyl.

The rate enhancement induced upon increasing steric bulk conclusively demonstrates the dissociative nature of the hydrolysis reaction.[20] As expected for a dissociative process, increasing the steric bulk of the leaving group (i.e., $-SR$) is more effective in accerating the rate than is increasing the steric bulk of the ancillary

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Table II. Observed Pseudo-First-Order Rate Constants for the Base Hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ ($\mu = 1.0$ M, temp 25.0 °C, $\lambda = 282$ nm)[a]

medium	[OH], M	10^3k_{obsd}, s^{-1}	medium	[OH], M	10^3k_{obsd}, s^{-1}
$NaOH/NaClO_4$	0.05	5.06 ± 0.05	NaOH/NaCl	0.30	9.25 ± 0.03
	0.05	4.49 ± 0.05		0.30	9.47 ± 0.07
	0.10	8.10 ± 0.03		*0.40	11.5 ± 0.2
	0.10	8.19 ± 0.03		0.40	11.6 ± 0.1
	0.10	8.23 ± 0.05		0.50	15.6 ± 0.1
	0.15	13.5 ± 0.1		0.50	14.7 ± 0.1
	0.15	13.1 ± 0.1		*0.50	15.1 ± 0.1
	0.20	15.8 ± 0.1		0.60	16.5 ± 0.1
	0.20	15.0 ± 0.1		0.60	16.2 ± 0.1
	0.25	18.1 ± 0.1		0.70	19.1 ± 0.3
	0.25	16.8 ± 0.1		*0.70	19.3 ± 0.1
	0.30	19.2 ± 0.1		0.80	20.1 ± 0.2
	0.30	19.1 ± 0.1		0.80	20.0 ± 0.1
	0.40	22.0 ± 0.1		*0.90	21.8 ± 0.1
	0.40	22.0 ± 0.1		0.01	0.629 ± 0.003
	0.40	22.8 ± 0.1	$LiOH/LiClO_4$	0.05	2.87 ± 0.02
	0.50	22.4 ± 0.1		0.10	5.04 ± 0.02
	0.50	24.1 ± 0.1		0.17	8.94 ± 0.03
	0.50	25.0 ± 0.1		0.24	13.2 ± 0.1
	0.60	25.4 ± 0.1		0.35	15.9 ± 0.1
	0.60	25.9 ± 0.1		0.40	16.7 ± 0.1
	0.60	26.1 ± 0.1		0.50	20.9 ± 0.1
	0.70	26.0 ± 0.1		0.66	20.8 ± 0.1
	0.70	24.8 ± 0.1		0.80	21.9 ± 0.1
	0.70	27.0 ± 0.1		1.00	20.9 ± 0.1
	0.80	27.8 ± 0.1		1.00	22.2 ± 0.1
	0.80	24.4 ± 0.1		1.00	23.5 ± 0.1
	0.80	27.5 ± 0.1	LiOH/LiCl	0.10	2.67 ± 0.02
	0.90	24.4 ± 0.1		0.20	5.24 ± 0.04
	0.90	25.9 ± 0.1		0.30	7.37 ± 0.04
	0.90	27.7 ± 0.1		0.40	9.73 ± 0.06
	1.00	24.1 ± 0.1		0.50	11.7 ± 0.1
	1.00	24.6 ± 0.1		0.60	14.6 ± 0.1
	1.00	23.4 ± 0.1		0.60	14.6 ± 0.1
NaOH/NaCl	*0.10	3.15 ± 0.07		0.70	17.0 ± 0.1
	*0.10	3.27 ± 0.02		0.80	17.6 ± 0.1
	*0.10	6.07 ± 0.03		0.90	20.2 ± 0.1

[a] In the experiments marked by an asterisk the cobalt complex was eluted from Sephadex SP C-25 with 1.0 M NaCl.

ligands. These observations, coupled with the fact that added azide ligand is trapped during hydrolysis,[21] exclude an associative mechanism (in which hydroxide directly displaces the thioether or selenoether moiety) and are consistent with an S_N1CB mechanism. The positive ΔS^* values listed in Table VI are also consistent with a dissociative process.

When analogous thioether and selenoether complexes are compared (Table V), it is seen that the Co–Se bond cleaves about two or three times faster than does the Co–S bond. While this effect is in the direction expected for a dissociative process, it is surprisingly small. For the two complexes with R = $-CH_3$, essentially no differences are observed in the activation parameters for the S and Se species (Table VI). These results imply that, surprisingly, the Co–S and Co–Se bond strengths in these complexes are approximately equal. Much more dramatic effects induced by changing S to Se are observed in other aspects of this system (vide infra).

The values of k_{OH} observed for the complexes investigated in this work are much smaller than values observed for other tripositive bis(ethylenediamine)cobalt(III) complexes with neutral leaving groups. For example, in $[(en)_2Co(NH_3)X]^{3+}$, $k_{OH} = 235$ M^{-1} s^{-1} for X = dimethyl sulfoxide and $k_{OH} = 2500$ M^{-1} s^{-1} for X = dimethyl methylphosphonate (data[5] at 25 °C). In contrast, under the same conditions $k_{OH} = 0.0223$ M^{-1} s^{-1} for the least sterically hindered complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$. Thus, a neutral leaving group does not necessarily imply a large value of k_{OH}. The slower reactions of $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes undoubtedly result in part from a chelate effect, ring opening being known to proceed much less rapidly than monodentate ligand loss.[22]

Medium Effects. The major issue concerning the mechanism of alkaline hydrolysis of the complexes investigated in this work is the nature of the process or processes governing the curvature depicted in Figures 2 and 3. At $\mu = 2.0$ M (Figure 3), k_{obsd} first increases with $[OH^-]$ and then at high base concentrations actually decreases with increasing $[OH^-]$. At $\mu = 1.0$ M (Figure 2), the maximum achievable $[OH^-]$ is not quite sufficient to manifest the rate retardation observed at $\mu = 2.0$ M, but the deviation from linearity is dramatic. There are four possible explanations for the deviation from linearity, two of which can be readily discounted. Only one explanation (medium effects) can account for the rate retardation, but by itself this explanation does not provide a completely satisfactory description of the observed phenomena.

(1) A nonlinear k_{obsd}–$[OH^-]$ relationship could occur if the ammine protons were sufficiently acidic. For example, in the alkaline hydrolysis of the aniline complex $[(en)_2Co(NH_2C_6H_5)Cl]^{2+}$, a nonlinear dependence is observed because the acidity of the coordinated aniline protons ($K_a = 10^{-10}$ M)[23,24] is considerably greater than the acidity of the coordinated ammine protons ($K_a = 10^{-15}$–10^{-16} M).[25] Likewise, in the complexes $[(en)_2Co(NH_2(CH_2)_nSO_3)Cl]^+$ (n = 1, 2) the $NH_2CH_2SO_3^-$ complex is 200 times as reactive toward alkaline hydrolysis as are the analogous complexes containing unsubstituted alkylamine or amino carboxylic ligands.[26] This increased reactivity is attributed to

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Table III. Observed Pseudo-First-Order Rate Constants for the Base Hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ (μ = 2.0 M, temp 25.0 °C, λ = 282 nm)

medium	[OH], M	10^3k_{obsd}, s^{-1}	medium	[OH], M	10^3k_{obsd}, s^{-1}
$NaOH/NaClO_4$	0.10	6.82 ± 0.05	NaOH/NaCl	1.1	16.1 ± 0.1
	0.10	6.43 ± 0.02		1.2	15.3 ± 0.1
	0.20	13.8 ± 0.1		1.3	16.2 ± 0.1
	0.20	12.0 ± 0.1		1.4	17.6 ± 0.2
	0.30	17.4 ± 0.1		1.5	18.0 ± 0.1
	0.30	16.5 ± 0.1		1.6	17.9 ± 0.1
	0.40	21.0 ± 0.1		1.7	20.3 ± 0.1
	0.40	21.0 ± 0.1		1.8	22.2 ± 0.2
	0.50	24.3 ± 0.2		1.8	20.7 ± 0.1
	0.50	23.7 ± 0.2		1.9	20.2 ± 0.2
	0.50	23.7 ± 0.2	$LiOH/LiClO_4$	0.10	3.98 ± 0.05
	0.60	25.6 ± 0.1		0.20	7.09 ± 0.05
	0.70	27.4 ± 0.1		0.30	10.2 ± 0.1
	0.70	27.2 ± 0.2		0.40	12.7 ± 0.1
	0.80	26.9 ± 0.1		0.50	16.5 ± 0.1
	0.80	27.7 ± 0.1		0.60	17.9 ± 0.1
	0.90	26.5 ± 0.2		0.70	18.2 ± 0.1
	0.90	26.5 ± 0.2		0.80	20.8 ± 0.2
	1.00	29.8 ± 0.2		0.90	22.1 ± 0.2
	1.00	29.7 ± 0.2		1.00	22.6 ± 0.1
	1.10	31.1 ± 0.2		1.20	25.9 ± 0.1
	1.10	31.0 ± 0.2		1.30	24.4 ± 0.1
	1.20	30.5 ± 0.2		1.40	23.9 ± 0.2
	1.30	29.4 ± 0.3		1.50	24.5 ± 0.1
	1.30	28.1 ± 0.2		1.60	23.6 ± 0.2
	1.40	30.6 ± 0.1		1.70	23.2 ± 0.1
	1.40	28.2 ± 0.1		1.80	20.4 ± 0.1
	1.50	29.0 ± 0.1		1.90	19.2 ± 0.1
	1.50	29.0 ± 0.1		2.00	18.0 ± 0.1
	1.60	27.6 ± 0.1		2.00	18.5 ± 0.1
	1.60	26.7 ± 0.1	LiOH/LiCl	0.10	0.853 ± 0.004
	1.70	27.4 ± 0.1		0.20	1.75 ± 0.02
	1.70	27.7 ± 0.1		1.30	2.81 ± 0.02
	1.80	27.0 ± 0.1		0.40	3.76 ± 0.02
	1.80	25.2 ± 0.1		0.50	4.76 ± 0.02
	1.90	24.4 ± 0.1		0.60	5.77 ± 0.03
	1.90	24.6 ± 0.1		0.70	7.08 ± 0.04
	2.00	21.8 ± 0.1		0.80	7.34 ± 0.03
	2.00	21.0 ± 0.1		0.90	8.1 ± 0.05
	2.00	20.7 ± 0.1		1.00	9.43 ± 0.09
NaOH/NaCl	0.10	1.81 ± 0.03		1.10	10.4 ± 0.1
	0.20	3.27 ± 0.03		1.20	11.3 ± 0.1
	0.30	4.75 ± 0.04		1.30	13.1 ± 0.1
	0.40	6.91 ± 0.07		1.40	13.6 ± 0.1
	0.40	6.48 ± 0.11		1.50	15.3 ± 0.1
	0.50	7.14 ± 0.02		1.60	15.8 ± 0.1
	0.60	9.22 ± 0.07		1.70	16.5 ± 0.1
	0.80	12.4 ± 0.1		1.80	17.7 ± 0.1
	0.80	10.2 ± 0.1		1.90	18.3 ± 0.2
	1.00	12.9 ± 0.1			

the increased acidity of the ammine protons in coordinated $NH_2CH_2SO_3^-$. However, the $NH_2CH_2CH_2SO_3^-$ complex exhibits no special reactivity, and thus it is very unlikely that the thioether functionality of the $RSCH_2CH_2NH_2$ ligand could sufficiently enhance the acidity of the ammine protons to cause the curvature depicted in Figures 2 and 3. This explanation is thus eliminated from further discussion.

(2) Given the potential for rechelation of the aquated product, the nonlinearity could arise from an approach to equilibrium. However, if this were the case, the observed absorbance changes would be a function of [OH$^-$] and they are not. Also, ion-exchange analysis detects no rechelation products in the pH range utilized in this work. This explanation is thus also eliminated from further discussion.

(3) The observed nonlinearity could also be explained by the ion-pairing mechanism for base hydrolysis proposed by Buckingham et al.[4] Analysis of k_{obsd}–[OH$^-$] data within this mechanism (rate law expressed by eq 1) leads to derived values of K (the ion-pairing constant) similar to those obtained by Buckingham et al.[4] However, true values of K are expected to depend on the charge of the complex, those for 3+ complexes being greater than those for 2+ complexes; in this work derived K values are the same for complexes of net 2+ charge (i.e., R = $-(CH_2)_2COO^-$, $-(CH_2)_3COO^-$) and of net 3+ charge (e.g., R = $-CH_2CH_3$). Thus, the simple ion-pairing mechanism does not satisfactorily account for the nonlinearity observed at μ = 1.0 M and cannot cope at all with the rate retardation observed for high [OH$^-$] at μ = 2.0 M.

(4) The rate retardation at high base concentrations can be qualitatively accounted for by a medium effect. Medium effects in acidic media are well established, and it is known that replacement of H^+ by Li^+ at constant ionic strength can generate different rates and proposed mechanisms than those obtained if H^+ is replaced by Na^+ at the same constant ionic strength.[27-30]

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Table IV. Derived Second-Order Rate Constants for the Base Hydrolysis of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ Complexes (X = S, Se) at μ = 1.00 M ($LiOH/LiClO_4$)[a]

X	R	λ,[b] nm	temp, °C	k_{OH}, $M^{-1}\ s^{-1}$	n[c]
S	$-CH_2CH_3$	282	25.0	0.065 ± 0.001	5
S	$-CH_2C_6H_{11}$	286	17.1	0.0096 ± 0.0013	3
			25.0	0.0496 ± 0.0003	5
			35.1	0.255 ± 0.008	5
			45.0	1.40 ± 0.03	3
S	$-(CH_2)_2COO^-$	282	17.5	0.0228 ± 0.0009	3
			25.0	0.087 ± 0.004	4
			35.1	0.379 ± 0.012	4
			45.0	1.19 ± 0.02	3
S	$-(CH_2)_3COO^-$	282	17.4	0.024 ± 0.001	3
			25.0	0.089 ± 0.001	4
			35.1	0.402 ± 0.004	4
			45.0	1.36 ± 0.14	3
S	$-CH_3$	282	17.4	0.0124 ± 0.0005	3
			35.1	0.242 ± 0.007	4
			45.2	1.15 ± 0.02	4
Se	$-CH_3$	297	13.9	0.0088 ± 0.0003	3
			25.0	0.079 ± 0.002	4
			36.2	0.443 ± 0.008	3
Se	$-CH_2CH_3$	297	25.0	0.093 ± 0.002	4
Se	$-CH_2C_6H_5$	305	14.3	0.122 ± 0.007	4
			25.0	0.808 ± 0.011	3
			35.5	4.07 ± 0.12	3

[a] k_{OH} values calculated from linear portions of k_{obsd} vs. $[OH^-]$ plots only. A complete listing of k_{obsd} vs. $[OH^-]$ data is given in Table B.[40] [b] Wavelength at which reaction is monitored. [c] Number of independent k_{obsd}-$[OH^-]$ determinations used to calculate k_{OH}.

In base hydrolysis reactions $NaClO_4$ is generally used to maintain the ionic strength of NaOH solutions, and thus in these systems OH^- is replaced by ClO_4^- as $[OH^-]$ is varied at constant ionic strength. The functional form used to describe a medium effect resulting from this type of replacement is given in (2), and depending on the value of α, k_{obsd} can first increase and then decrease with increasing $[OH^-]$. Figure 3 shows that this behavior is qualitatively observed at μ = 2.0 M, with the effect of ClO_4^-/OH^- exchange being much larger than that for Cl^-/OH^- exchange. However, this functional form, which is derived from Harned's Rule for activity coefficient ratios,[31] must only provide an approximate description of the system since Figure 3 also shows that the magnitude of the effect is dependent on the *cation* used; i.e., the medium effects observed for NaX/NaOH exchange are significantly larger than those observed for LiX/LiOH exchange (X = Cl, ClO_4). That this functional form is not sufficient to provide a total description of the system can also be appreciated by comparing the values of k_{OH}'' obtained for hydrolysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ at 25 °C and μ = 1.00 M, in LiCl/LiOH and $LiClO_4$/LiOH media. If the Harned Rule were obeyed, the k_{OH}'' values would be identical, but in reality they are 0.022 ± 0.001 and 0.061 ± 0.002 $M^{-1}\ s^{-1}$ for the Cl^- and ClO_4^- media, respectively. This difference in calculated k_{OH}'' values can be qualitatively reconciled by considering ion pairing within the medium effect framework. I.e., the first step in the formation of a reactive ion pair with OH^- is the displacement of Cl^- or ClO_4^- from an existing ion pair. Since ClO_4^- has a lower charge density than Cl^-, it is more readily displaced by OH^- and thus the observed value of k_{OH}'' is greater. The available data are not sufficient to allow a quantitative development of this combined ion-pairing/medium effect treatment.

It is noteworthy that other studies of cobalt(III) base hydrolysis reactions have not reported medium effects of the magnitude seen in this work. This is largely due to the fact that most studies are conducted at μ = 0.10 M, and even in studies where μ = 1.0 M the concentration of base is generally held less than 0.10 M. Under these conditions of low $[OH^-]$, even in our study, k_{obsd} is linearly dependent on $[OH^-]$. Detectable medium effects are only observed at high $[OH^-]$, which requires the use of high ionic strengths.

In summary, at μ = 1.0 M the nonlinear dependence of k_{obsd} on $[OH^-]$ (Figure 2) is adequately accounted for by a medium effect, but not by the ion-pairing mechanism. At μ = 2.0 M, neither the ion-pairing mechanism alone nor the medium effect formalism alone can adequately describe the data, but a combination of the two may suffice. These results cast doubt on the generality of the ion-pairing mechanism, but more importantly they conclusively demonstrate the importance of medium effects in base hydrolysis reactions.

Rechelation of the Aquation Product. In alkaline media no rechelation of the pendant thioether or selenoether moieties is observed. However, in acidic media rechelation occurs slowly. Recoordination of a thioether functionality in acid has also been qualitatively observed[32] for the complex $[Co(tren)(OH_2)(NH_2CH_2CH_2SCH_3)]^{3+}$ to yield $[Co(tren)(S(CH_3)CH_2CH_2NH_2\text{-}N,S)]^{3+}$. For $[(en)_2Co(OH_2)(NH_2CH_2CH_2SCH_3)]^{3+}$ the rechelation rate is 4.5 × $10^{-5}\ s^{-1}$ (52 °C, μ = 1.0 M, pH 2.0), in good agreement with the value of 2.3 × $10^{-5}\ s^{-1}$ (55 °C, μ = 0.01 M, pH 2.0) reported for the same reaction of the photochemically generated complex.[33] Rechelation of the thermal aquation product is not quantitative, implying that a significant fraction of this species has a trans configuration. Rechelation of the selenoether analogue $[(en)_2Co(OH_2)(NH_2CH_2CH_2SeCH_3)]^{3+}$ is much faster, with k_{obsd} being 10 times greater at a much lower temperature (k_{obsd} = 5.7 × $10^{-4}\ s^{-1}$ at 25 °C, μ = 1.0 M, pH 2.0). Assuming a reasonable activation energy, this comparison shows that a pendant selenoether functionality is 10^2–10^3 more efficient is an entering group than is a pendant thioether functionality. This is not surprising in light of the fact that selenium species are better nucleophiles than their sulfur analogues. But more surprisingly, this large dependence of rate on the nature of the entering group strongly implies that the rechelation step has associative character.

Attempted Hydrolysis of $[(en)_2Co(S(CH_3)C_6H_4NH_2)]^{3+}$. This complex was studied in hopes of observing a nonlinear dependence of k_{obsd} on $[OH^-]$ which could be attributed to a large deprotonation equilibrium. The ammine protons of the *o*-mercaptoaniline ligand are known to be of enhanced acidity, being easily lost from complexes where the metal is in a high oxidation state.[34] However, no cobalt–sulfur bond cleavage is observed for this complex presumably because the formal negative charge induced by proton loss is delocalized over the *o*-mercaptoaniline ligand.

Base Hydrolysis of $[(en)_2Co(S(O)_nCH_2CH_2NH_2)]^{2+}$ (n = 0–2). In an effort to define the effect of charge on the base hydrolysis reaction, the stabilities in alkaline media of the dipositive thiolato, sulfenato, and sulfinato complexes $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, and $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ were investigated. However, while the tripositive (thioether)cobalt(III) complexes readily undergo alkaline hydrolysis, the three dipositive complexes do not undergo detectable reaction in base. Decreasing reactivity with increasing negative charge of the leaving group is a well-established kinetic phenomenon in cobalt(III) chemistry. For example, in the series of complexes $[(NH_3)_5CoX]^{n+}$, the rate of base hydrolysis decreases from 2.9 × $10^4\ M^{-1}\ s^{-1}$ for X = ReO_4^- to 4.9 × $10^{-2}\ M^{-1}\ s^{-1}$ for X = SO_4^{2-} and to 5.0 × $10^{-7}\ M^{-1}\ s^{-1}$ for X = PO_4^{3-}. Coupled to this kinetic phenomenon is the ground-state phenomenon that the negative RS^-, $RS(O)^-$, and $RS(O)_2^-$ ligands form stronger

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Table V. Derived First- and Second-Order Rate Constants for the Base Hydrolysis of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ Complexes (X = S, Se) Obtained from Nonlinear Least-Squares Fit to the Equations $k_{obsd} = k_{OH}'K[OH^-]/(1 + K[OH^-])$ and $k_{obsd} = k_{OH}''[OH^-]e^{-\alpha[OH^-]}$ at 25 °C[a]

X	R	medium	μ, M	K, M^{-1}	k_{OH}', s^{-1}	$k_{OH}'K$, M^{-1} s^{-1}	k_{OH}'', M^{-1} s^{-1}	α
S	$-CH_3$	$LiOH/LiClO_4$	2.0	1.99 ± 0.54	0.030 ± 0.003	0.060 ± 0.017	0.046 ± 0.002	0.74 ± 0.03
		LiOH/LiCl	2.0			0.00972 ± 0.00008*		
		NaOH/NaCl	2.0			0.0106 ± 0.0003*		
		$LiOH/LiClO_4$	1.0	1.61 ± 0.21	0.040 ± 0.004	0.064 ± 0.011	0.061 ± 0.002	0.99 ± 0.06
		LiOH/LiCl	1.0			0.0223 ± 0.0005*		
		NaOH/NaCl	1.0			0.0239 ± 0.0007*		
S	$-CH_2CH_3$	$LiOH/LiClO_4$	1.0	1.13 ± 0.23	0.067 ± 0.011	0.076 ± 0.020	0.074 ± 0.002	0.84 ± 0.01
S	$-(CH_2)_2C_6H_5$	$LiOH/LiClO_4$	1.0	1.36 ± 0.19	0.143 ± 0.015	0.194 ± 0.034	0.188 ± 0.005	0.92 ± 0.06
S	$-CH_2C_6H_{11}$	$LiOH/LiClO_4$	1.0	1.33 ± 0.23	0.048 ± 0.006	0.064 ± 0.014	0.059 ± 0.002	0.83 ± 0.07
S	$-(CH_2)_2CO_2^-$	$LiOH/LiClO_4$	1.0	1.24 ± 0.14	0.086 ± 0.008	0.107 ± 0.016	0.104 ± 0.001	0.88 ± 0.04
S	$-(CH_2)_3CO_2^-$	$LiOH/LiClO_4$	1.0	1.31 ± 0.25	0.082 ± 0.011	0.107 ± 0.025	0.103 ± 0.004	0.94 ± 0.09
Se	$-CH_3$	$LiOH/LiClO_4$	1.0	1.13 ± 0.17	0.075 ± 0.010	0.085 ± 0.017	0.083 ± 0.002	0.86 ± 0.08
Se	$-CH_2CH_3$	$LiOH/LiClO_4$	1.0	1.03 ± 0.24	0.104 ± 0.020	0.107 ± 0.032	0.106 ± 0.004	0.80 ± 0.10
Se	$-CH_2C_6H_5$	$LiOH/LiClO_4$	1.0	1.19 ± 0.63	0.70 ± 0.35	0.833 ± 0.606	0.830 ± 0.023	1.15 ± 0.55

[a] The values indicated by an asterisk were obtained from linear least-squares analysis of the k_{obsd}-$[OH^-]$ data.

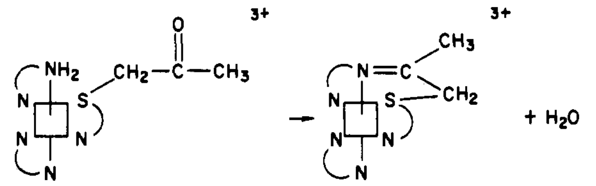
Table VI. Activation Parameters for the Base Hydrolysis of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ Complexes (X = S, Se) at μ = 1.00 M ($LiOH/LiClO_4$)

X	R	ΔH^*, kcal/mol	ΔS^*, eu
S	$-CH_3$	29.0 ± 0.4	33.1 ± 1.4
S	$-CH_2C_6H_{11}$	30.8 ± 0.5	38.6 ± 1.6
S	$-(CH_2)_2COO^-$	25.2 ± 1.1	21 ± 4
S	$-(CH_2)_3COO^-$	26.7 ± 0.4	26.3 ± 1.4
Se	$-CH_3$	29.7 ± 1.8	36 ± 6
Se	$-CH_2C_6H_5$	27.9 ± 1.0	35 ± 3

Co–S bonds than does the neutral RSR ligand, thus making it easier to break the Co–thioether bond in either a dissociative or associative process. These relative Co–S bond strengths of complexes derived from $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ are reflected in the corresponding Co–S bond lengths determined by X-ray crystallography: the longest, weakest bond is in the thioether complex, i.e. 2.276 (3) Å,[15] while the thiolato, sulfenato, and sulfinato complexes have shorter, stronger bonds at 2.226 (3),[35] 2.253 (1),[36] and 2.191 (2) Å,[37] respectively.

Reactions That Do Not Proceed via Simple Cobalt–Sulfur Bond Cleavage. In alkaline media those complexes containing acidic C–H bonds in the pendant thioether moiety undergo a variety of reactions in addition to, or instead of, Co–S bond cleavage. For instance, while the $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complex with R = $-CH_2CH_2COOH$ undergoes simple Co–S bond fission, the analogous complex with R = $-CH_2COOH$ yields several different products because of the acidic methylene group in the pendant moiety. Likewise, when R = $-CH_2C_6H_5$ (benzyl), five products are generated upon reaction in base, but when R = $-CH_2CH_2C_6H_5$, the reduced acidity of the methylene groups permits the reaction to proceed solely by Co–S bond fission even in 1.0 M OH^-. Interestingly, the benzyl selenoether analogue $[(en)_2Co(Se(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$ reacts solely by Co–Se bond fission even though Co–S bond fission is only a minor reaction path for $[(en)_2Co(S(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$. Given the similarity in rates of Co–S and Co–Se bond fission in these systems (vide supra), the observation that side reactions stemming from the acidic $-SeCH_2C_6H_5$ moiety do not effectively compete with Co–Se fission implies that the $-SeCH_2C_6H_5$ moiety is less acidic than the $-SCH_2C_6H_5$ moiety.

Most of the products arising from reactions of acidic C–H bonds in the pendant thioether moieties have not been identified. However, reaction of the complex with R = $-CH_2C(O)CH_3$ proceeds cleanly through a violet intermediate to give 100% yield of the product containing a coordinated imine:[16]



This is a remarkably facile cyclization reaction, the estimated second-order rate constant (assuming that the reaction is first order in $[OH^-]$) being 10^7 M^{-1} s^{-1} at 25 °C. This facility is undoubtedly due to the coordinated sulfur atom enhancing the acidity of the pendant moiety since similar cyclization reactions of complexes without a coordinated sulfur atom proceed much more slowly.[38,39] The violet intermediate observed in this reaction is presumed to be one of the tautomeric forms resulting from deprotonation of the thioether complex. Similarly, the violet intermediates observed in the alkaline reactions of the N-substituted succinimidyl thioethers are presumed to be deprotonated forms of the original complexes. The thioether complexes with R = $-CH_2CH_2C(O)CH_3$ and $-CH_2CH_2CHO$ also yield coordinated imines upon reaction at pH >7, but at pH <6 they decompose to the respective alkenes and the parental thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ presumably via a reverse Michael addition reaction.[15] As noted above, the complex with R = $-CH_2CH_2COO^-$ undergoes simple Co–S bond fission because of the reduced acidity of the CH_2 groups engendered by the negative carboxylate functionality.

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Registry No. $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, 35594-86-6; $[(en)_2Co(S(CH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 65622-75-5; $[(en)_2Co(S(CH_2C_6H_{11})CH_2CH_2NH_2)]^{3+}$, 65622-89-1; $[(en)_2Co(S((CH_2)_2COO^-)CH_2CH_2NH_2)]^{3+}$, 65622-83-5; $[(en)_2Co(S((CH_2)_3COO^-)CH_2CH_2NH_2)]^{3+}$, 65622-81-3; $[(en)_2Co(S((CH(CH_3)CH_2COO^-)CH_2CH_2NH_2)]^{3+}$, 94090-12-7; $[(en)_2Co(S((CH_2)_2C_6H_5)CH_2CH_2NH_2)]^{3+}$, 85782-06-5; $[(en)_2Co(S(C(CH_3)_3)CH_2CH_2NH_2)]^{3+}$, 85782-01-0; $[(en)_2Co(Se(CH_3)CH_2CH_2NH_2)]^{3+}$, 85848-90-4; $[(en)_2Co(Se(CH_2C_6H_5)CH_2CH_2NH_2)]^{3+}$, 85781-99-3; $[(en)_2Co(Se(CH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 85782-13-4; $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$,

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(40) Supplementary material. This includes all tables designated by alphabetic characters.

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Supplementary Material Available: Tables A and B, giving observed pseudo-first-order and derived second-order rate constants (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Binary Metal Sulfides. Structural Characterization of the $[(S_4)_2Zn]^{2-}$, $[(S_4)_2Ni]^{2-}$, $[(S_5)Mn(S_6)]^{2-}$, and $[(CS_4)_2Ni]^{2-}$ Anions

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A general procedure for the synthesis of the polysulfido, $[M(S_x)_2]^{2-}$, complexes (M = Zn, x = 4–6; M = Cd, x = 5; M = Ni, x = 4; M = Mn, x = 5, 6) is described. These complexes and the mixed thiophenolate polysulfido complexes, $[M(SPh)_2(S_x)_2]^{2-}$ (M = Zn, x = 4, 5; M = Cd, x = 5), are obtained by the oxidation of all or two of the thiophenolate ligands in the $[M(SPh)_4]^{2-}$ complexes by dibenzyl trisulfide with the concomitant generation of the polysulfide dianions. The diamagnetic $[Ni(S_4)_2]^{2-}$ and high-spin $[Mn(S_x)_2]^{2-}$ complexes react readily with CS_2 to give the corresponding perthiocarbonate complexes $[Ni(CS_4)_2]^{2-}$, $[Mn(CS_4)_2]^{2-}$, and $[Mn(S_6)(CS_4)]^{2-}$. The structures of the tetraethylammonium salts of $[Zn(S_4)_2]^{2-}$ (I) and $[Ni(S_4)_2]^{2-}$ (II) and of the tetraphenylphosphonium salts of $[Ni(CS_4)_2]^{2-}$ (III) and $[MnS_{11}]^{2-}$ (IV) have been determined by X-ray crystallography. Lattice parameters and space group information are as follows: for I, a = 12.410 (3) Å, b = 16.350 (1) Å, c = 13.906 (2) Å, α = 90.00°, β = 95.73 (1)°, γ = 90.00°, monoclinic, $P2_1/c$ (Z = 4); for II, a = 10.475 (2) Å, b = 10.452 (2) Å, c = 12.738 (2) Å, $\alpha = \beta = \gamma$ = 90.00°, orthorhombic, $Pnn2$ (Z = 2); for III, a = 9.231 (3) Å, b = 10.156 (3) Å, c = 13.694 (4) Å, α = 82.48 (1)°, β = 72.12 (1)°, γ = 85.51 (1)°, triclinic, $P\bar{1}$ (Z = 1); for IV, a = 23.266 (5) Å, b = 20.390 (3) Å, c = 23.894 (5) Å, α = 90.00°, β = 118.03 (1)°, γ = 90.00°, monoclinic, $P2_1/n$ (Z = 8). Diffraction data (Mo Kα radiation, $2\theta_{max}$ = 50, 45, 40, 45, respectively, for I–IV) were collected by either a Picker FACS-I (I) or a Nicolet P3F automatic diffractometer (II–IV). The structures were solved and refined by direct methods and full-matrix least-squares procedures to R values of 0.062, 0.041, 0.030, and 0.121, respectively, for I–IV from 2481, 831, 1971, and 6495 reflections on 244, 149, 280 and 277 variables, respectively, for I–IV. The anion in I contains the Zn tetrahedrally coordinated by two bidentate S_4^{2-} chelates, $\overline{Zn{-}S}$ = 2.351 Å. In II the coordination of the two S_4^{2-} chelates around the Ni(II) ion gives a square-planar complex, Ni–S = 2.179 Å. The anion in III is planar, and in the two bidentate CS_4^{2-} chelates the C=S groups are located trans to each other, $\overline{Ni{-}S}$ = 2.170 Å. The $[(S_5)Mn(S_6)]^{2-}$ and $[(S_5)Mn(S_5)]^{2-}$ anions both occupy the anion sites in IV where the Mn(II) is tetrahedrally coordinated by the S_x^{2-} chelates $\overline{Mn{-}S}$ = 2.425 Å. A discussion of S–S bonding in the S_4^{2-} and CS_4^{2-} chelates is presented.

Introduction

An ever-increasing interest in the synthesis and reactivity of polysulfido–metal complexes and derivatives has been stimulated by the recognized importance of metal–sulfide complexes in both industrial and enzymatic catalysis. The catalytic hydrodesulfurization (HDS) of fossil fuels,[1] biological nitrogen fixation,[2] and biological electron transfer[3] are among processes that are facilitated by metal–sulfide compounds.

Numerous metal–sulfide complexes are known to contain $(S_x)^{2-}$ chelating ligands (x = 4–9). In these complexes the MS_x metallocycles have been characterized by X-ray crystallography in the structures of $(C_5H_5)_2MS_5$ (M = Ti,[4,5] V[5]), $[(S_5)Fe_2S_2(S_5)]^{2-}$,[6] $[(S_5)FeMS_4]^{2-}$ (M = Mo, W),[7] $[(S_6)FeMoS_4]^{2-}$,[7] $(C_5H_5)Co(S_5)PMe_3$,[8] $Os_2(Et_2Dtc)(Et_2DtcS)(\mu\text{-}S_5)$,[9] $[PdS_{11}]^{2-}$,[10] $[PtS_{15}]^{2-}$,[11] NH_4CuS_4,[12] $Pt(S_4)(PPh_3)_2$,[13] $(C_5H_5)_2MS_4$ (M = Mo,[14] W[15]), $[Cu_3(S_6)_3]^{3-}$,[16] $[MoS_9]^{2-}$,[17] $[Mo_2S_{10}]^{2-}$,[17,18] $[(Mo)_2(NO)_2(S_2)_3(S_5)OH]^{3-}$,[19] $[Hg(S_6)_2]^{2-}$,[20] $[Cu_6S_{17}]^{2-}$,[21] and $[AuS_9]^-$.[22]

The unusual reactivity characteristics of the coordinated polysulfido ligands in either binary or organometallic polysulfido complexes have become apparent in recent years. Examples of this reactivity include the addition of disubstituted acetylenes, RC≡CR (R = COOCH$_3$), to MoS_9^{2-},[23] $[Fe_2S_{12}]^{2-}$,[24] $(Cp)_2M(S_5)$

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