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Syntheses and Characterization of Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thioether and Selenoether Ligands. Single-Crystal Structure Analysis of $[(en)_2Co(S(\underline{CHCON(CH_2CH_3)COCH_2})CH_2CH_2NH_2)](ClO_4)_3$[1]

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New synthetic routes to robust metal complexes containing a coordinated thioether ligand are described. These complexes have the general formula $[M(S(R)-X)]^{n+}$ where S–X represents a S,X-chelating moiety and R represents a pendant group bonded to sulfur by a primary, secondary, or tertiary carbon atom. The more general synthetic routes involve reaction of the thiolato complex $[M(S-X)]^{(n-1)+}$ with either alcohols or α,β-unsaturated compounds in acidic aqueous media. By these routes, the series of complexes $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$, with R = CH_3, CH_2CH_3, $C(CH_3)_3$, $(CH_2)_2CN$, $(CH_2)_2COCH_3$, $(CH_2)_2CO_2H$, $(CH_2)_2CHO$, $(CH_2)_2CONH_2$, $CHCHCO_2H$, $\underline{CHCONHCOC}H_2$, $\underline{CHCON(CH_3)COC}H_2$, $\underline{CHCON(CH_2CH_3)COC}H_2$, and $\underline{CHCON(C_6H_5)COC}H_2$, and the series of complexes $[(en)_2Co(S(R)CH_2COO)]^{2+}$, with R = $(CH_2)_2CHO$, $(CH_2)_2CO_2H$, $(CH_2)_2COCH_3$, and $(CH_2)_2CONH_2$, have been prepared. The complex $[(en)_2Co(S(CH(CH_3)CH_2CO_2H)CH_2CH_2NH_2)]^{3+}$ has been prepared by the specific reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with β-butyrolactone in *N,N*-dimethylformamide. The selenoether complexes, $[(en)_2Co(Se(R)CH_2CH_2NH_2)]^{3+}$, with R = CH_3, CH_2CH_3, and $CH_2C_6H_5$, were generated by reaction of alkyl halides with $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ in *N,N*-dimethylformamide, while the complex with R = $CH_2CH_2COCH_3$ was prepared by reaction of the parental selenolato complex with methyl vinyl ketone. All complexes have been characterized by some combination of elemental analysis, ion-exchange behavior, visible–UV and ^1H NMR spectroscopy, and reactivity in alkaline media. In addition, the title complex ((1-ethyl-2,5-dioxo-3-pyrrolidinyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) has been characterized by single-crystal X-ray structural analysis refined to conventional *R* factors of 0.061 and 0.074. Red-orange crystals of the perchlorate salt crystallize in the monoclinic space group $P2_1$ with a = 11.273 (3) Å, b = 12.931 (4) Å, c = 9.880 (3) Å, β = 91.32 (2)°, and Z = 2. In this complex the cobalt(III) center is approximately octahedrally coordinated with five nitrogen atoms at an average distance of 1.969 (16) Å and a thioether sulfur atom at 2.276 (3) Å. As expected, the coordinated thioether sulfur atom does not induce a significant structural trans effect. A preliminary kinetic investigation into the reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $CH_2{=}CH_2COCH_3$ shows the reaction to be first order in each of cobalt complex, olefin, and H^+, consistent with addition of the coordinated thiolate to a protonated olefin. These results are compared to the reaction of noncoordinated thiols with α,β-unsaturated compounds.

Introduction

Our longstanding interest in the chemistry of coordinated chalcogens[4-11] has led us to develop new routes for the syntheses of coordinated thioethers and selenoethers. We have been especially concerned with developing general syntheses of coordinated thioethers containing a pendant group in which a secondary or tertiary carbon atom is bonded to the coordinated sulfur atom. Such complexes are inaccessible by the usual reaction of alkyl halides with the corresponding thiolato complex.[5] Access to a range of thioether complexes of varying physical and chemical properties is important for a variety of mechanistic investigations. For example, recent reports on the base hydrolysis of tripositive cobalt(III) complexes[12-14] have questioned the ubiquity of the S_N1cB mechanism for this reaction. Initial investigations into the base hydrolysis of the tripositive thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ show that this complex undergoes simple Co–S bond cleavage. It would therefore be useful to prepare a series of $[(en)_2Co(X(R)CH_2CH_2NH_2)]^{3+}$ (X = S, Se) complexes in which the R group is systematically varied in a manner designed to explicate kinetic phenomena. This paper describes the synthesis of a variety of such complexes, as well as a single-crystal X-ray structure determination of one of them. Studies on the kinetics and mechanisms of the base hydrolysis reactions of these and related complexes will be detailed in a subsequent publication.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. (2-Mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate, (2-mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate, and (2-mercaptoaniline-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate were prepared via published procedures.[8,15,16] (2-Selenoethylamine-*N,Se*)bis(ethylenediamine)cobalt(III) perchlorate was available from a previous study.[11] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or by Guelph Chemical Laboratories, Ltd., Guelph, Ontario. Total cobalt concentrations for use in determining molar absorptivities were determined by using a modified Kitson procedure.[17,18] Visible–UV spectra were

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Table I. Elemental Analyses for Selected Thioether and Selenoether Complexes

complex		% S	% C	% N	% H	% Co
$[(en)_2Co(S((CH_2)_2COCH_3)(CH_2)_2NH_2)](ClO_4)_3$	calcd	5.13	17.30	11.21	4.03	
	found	5.29	17.28	11.25	4.00	
$[(en)_2Co(S(CHCHCOOH)(CH_2)_2NH_2)](ClO_4)_3$	calcd	5.13	19.23	11.21	4.68	
	found	5.18	19.15	11.41	4.86	
$[(en)_2Co(S((CH_2)_2CONH_2)(CH_2)_2NH_2)](ClO_4)_3$	calcd		17.27	13.43	4.51	
	found		16.97	13.62	4.46	
$[(en)_2Co(Se(CH_2C_6H_5)(CH_2)_2NH_2)](ClO_4)_3$	calcd	11.42[a]	22.58	10.13	4.23	8.52
	found	11.41	22.39	9.97	4.23	8.39
$[(en)_2Co(S(C(CH_3)_3)(CH_2)_2NH_2)](ClO_4)_3$	calcd		19.67	11.47	5.12	9.65
	found		21.47	12.61	6.27	10.68

[a] % Se.

recorded on a Cary 14 or Cary 210 spectrophotometer at ambient temperature. ^{1}H NMR spectra were obtained on a Varian T-60 instrument. IR spectra were recorded on a Perkin-Elmer 590 instrument. Kinetic experiments were monitored on a Cary Model 118B recording spectrophotometer equipped with a thermostated cell compartment 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 thermometer.

Although we have not experienced any explosions, all of the perchlorate salts described in this work are potentially explosive and should be carefully handled in only very small quantities. No attempt was made to resolve any of the optical isomers or diastereomers encountered in this work.

((Alkyl 2-aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(R)CH_2CH_2NH_2)](ClO_4)_3$, and ((Alkyl carboxymethyl thioether)-*O*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(R)CH_2COO)](ClO_4)_2$. Two general methods have been employed to prepare a variety of these complexes.

Method 1. This procedure involves the reaction of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ or $[(en)_2Co(SCH_2COO)](ClO_4)$ in acidic media with compounds containing activated double or triple bonds and has been used to prepare complexes with R = $(CH_2)_2CO_2H$, $(CH_2)_2CONH_2$, $(CH_2)_2COCH_3$, $(CH_2)_2CHO$, $(CH_2)_2CN$, $CHCHCO_2H$, $CH(CO_2H)CH_2CO_2H$, $CHCONHCOCH_2$, $CHCON(CH_3)COCH_2$, $CHCON(CH_2CH_3)COCH_2$, and $CHCON(C_6H_5)COCH_2$. A typical procedure is detailed here for the preparation of the complex $[(en)_2Co(S((CH_2)_2CONH_2)CH_2CH_2NH_2)](ClO_4)_3$. A 9.8-g sample (0.019 mol) of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was dissolved in 50 mL of 6 M $HClO_4$ to give a black solution. To this solution was added 0.26 g (0.0037 mol) of solid acrylamide. Within 20 min the solution turned red-orange. The reaction mixture was then diluted to 3 L with water and absorbed onto an ion-exchange column (Sephadex SP-C25, 3.5 cm i.d. × 20 cm). After the loaded column was washed with 0.01 M $HClO_4$, elution was begun with 0.3 M $NaClO_4$ (pH 2). No starting material was recovered, and the orange product band moved readily down the column, showing no signs of separation. Once it was ascertained that only a single product was present, the complex was then removed from the column as a concentrated band with 0.5 M $Ba(ClO_4)_2$ (pH 2). Addition of K_2SO_4 to the eluate yielded $KClO_4$ and $BaSO_4$, which were removed by filtration. The solution was condensed to 4 mL by rotoevaporation at 30 °C and then filtered again to remove additional $KClO_4$ and $BaSO_4$. To this solution was added 0.5 mL of 72% $HClO_4$, and the resulting solution was refrigerated overnight at 8 °C. The next day the solution was filtered and 0.65 g (54% yield) of the product was recovered. This was then recrystallized by dissolving the complex in a minimum amount of 0.01 M $HClO_4$, adding an equivalent volume of 72% $HClO_4$, and filtering. After the mixture was cooled for 4 h at 8 °C, 0.57 g (48% overall yield) was recovered and dried under vacuum at room temperature.

This general procedure also succeeds with maleic acid and the various maleimide derivatives, but longer reaction times of 1–2 h are required. When methyl vinyl ketone, acrolein, or propiolic acid are used, 1 M $HClO_4$ is sufficient to achieve a rapid reaction.

Method 2. This procedure involves the reaction of the parent thiolate complex with alcohols in acidic media. Complexes with R = methyl, ethyl, or *tert*-butyl were synthesized in this manner. In a typical preparation, 40 g (0.085 mol) of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was added to 50 mL of *tert*-butyl alcohol. The cobalt complex was insoluble in this medium. To this mixture was added 25 mL of concentrated CH_3SO_3H. Immediately the solution became warm (ca. 50 °C), and the cobalt complex dissolved to yield a red solution. The reaction mixture was stirred for 10 min. After an additional 20 min without agitation, the solution separated into an upper, clear, layer and a lower, dark red, layer. The upper layer was removed, and the lower layer was diluted and absorbed onto an ion-exchange column (Sephadex SP-C25, 5 cm i.d. × 20 cm). Elution was begun with 0.2 M $NaClO_4$ (pH 2) to remove a small amount of unreacted starting material. After the starting material was removed, elution was continued with 0.3 M $NaClO_4$ (pH 2), which easily moved the red product band. Once it was ascertained that only a single product was present, the complex was removed from the column with 0.5 M $Ba(ClO_4)_2$. The eluate was treated as before to remove the $Ba(ClO_4)_2$, and the desired product was precipitated by addition of 200 mL of 50/50 *sec*-butyl alcohol/diethyl ether. The resulting red-orange powder was then collected and dried under vacuum at room temperature.

This same general procedure succeeds with methyl alcohol and ethyl alcohol; however, the reaction is much slower. In CH_3OH/CH_3SO_3H, the readction is complete in ca. 1 day while in CH_3CH_2OH/CH_3SO_3H, the reaction is complete in ca. 1 week. These reactions also proceed in the presence of other acids such as $HClO_4$, H_2SO_4, or HCl. When isopropyl alcohol is used, no reaction is observed for at least 3 weeks at ambient temperature.

((2-Carboxy-1-methylethyl 2-aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(CH(CH_3)CH_2CO_2H)CH_2CH_2NH_2)](ClO_4)_3$. This particular complex is prepared from $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ and β-butyrolactone by a specific route involving nucleophilic cleavage of a strained ring system.[19] In a typical preparation, 5.0 g (0.011 mol) of $[(en)_2Co(SCH_2CH_2NH_2](ClO_4)_2$ was dissolved in ca. 40 mL of DMF; 100 mL of β-butyrolactone was added, followed by 4.0 mL of $BF_3{\cdot}OEt_2$. The resulting mixture was stirred in the dark for 4 days, at which time 2 L of diethyl ether and 50 mL of 0.01 M $HClO_4$ were added with vigorous stirring. The resulting orange-brown oil was separated from the ether layer by decantation, diluted to ca. 200 mL with 0.01 M $HClO_4$, and absorbed onto an ion-exchange column (Sephadex SP-C25, 3 cm i.d. × 20 cm). This column was then treated as before to remove excess starting material and isolate the thioether complex.

((Alkyl 2-aminoethyl selenoether)-*N*,*Se*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(Se(R)CH_2CH_2NH_2)](ClO_4)_3$. These complexes were prepared by alkylation of $[(en)_2Co(SeCH_2CH_2NH_2)](ClO_4)_2$. Complexes with R = methyl, ethyl, and benzyl were synthesized by reaction with alkyl halides in a manner analogous to that already described for the alkylation of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$.[5] The complex with R = $CH_2CH_2C(O)CH_3$ was prepared from the parent selenolate complex and methyl vinyl ketone as outlined above for the sulfur analogue.

Data confirming the characterization of these complexes by elemental analyses, visible–UV spectrophotometry, and ^{1}H NMR spectrometry are given in Tables I, II, and III respectively.

Kinetic Measurements and Calculations. Kinetic experiments were conducted in aqueous perchloric acid solutions maintained at a constant ionic strength of 1.20 ± 0.01 M ($LiClO_4$) and with a pseudo-first-order

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Table II. Visible-UV Spectrophotometric Parameters for Selected Bis(ethylenediamine)cobalt(III) Complexes[a]

complex	λ_{max} (ϵ)	λ_{max} (ϵ)
$[(en)_3Co]^{3+}$	465 (87.5)	339 (79)
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$	600 (44), sh 482 (142)	282 (13 800)
$[(en)_2Co(SCH_2COO)]^{1+}$	518 (152)	282 (11 700)
$[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$	490 (170)	297 (18 500)
$[(en)_2Co(SC_6H_4NH_2)]^{2+}$	580 (80), sh 470 (170), sh 400 (240)	350 (300), sh 279 (19 400) 260 (14 600), sh
$[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$		
R = CH_3	487 (180)	282 (8795)
R = CH_2CH_3	487 (186)	282 (8689)
R = $C(CH_3)_3$	499 (359)	299 (12 485)
R = $(CH_2)_2COOH$	489 (179)	282 (8987)
R = $(CH_2)_2CONH_2$	489 (181)	282 (8747)
R = CHCHCOOH	504 (229)	272 (5370), sh 320 (7504)
R = $(CH_2)_2CHO$	488 (153)	283 (9053)
R = $(CH_2)_2COCH_3$	490 (183)	284 (8388)
R = $(CH_2)_2CN$	489 (165)	278 (9180)
R = $(CH_2)_2C_6H_5$	489 (195)	283 (9855)
R = $CH(CH_3)CH_2COOH$	493 (191) 350 (330), sh	288 (7340)
R = $CH(COOH)CH_2COOH$	495 (178)	288 (7130)
R = $CHCONHCOCH_2$	491 (152)	281 (8609)
R = $CHCON(CH_3)COCH_2$	492 (160)	281 (9091)
R = $CHCON(CH_2CH_3)COCH_2$	492 (154)	282 (8860)
R = $CHCON(C_6H_5)COCH_2$		
band 1	495 (200)	281 (9091)
band 2	492 (166)	282 (8860)
$[(en)_2Co(Se(R)CH_2CH_2NH_2)]^{3+}$		
R = CH_3	499 (190)	297 (10 990)
R = CH_2CH_3	499 (200)	297 (11 820)
R = $CH_2C_6H_5$	500 (210)	305 (14 400)
R = $(CH_2)_2COCH_3$	500 (219)	299 (11 034)
$[(en)_2Co(S(R)CH_2COO)]^{2+}$		
R = $(CH_2)_2COCH_3$	500 (164)	280 (7949)
R = $(CH_2)_2CHO$	499 (160)	282 (8689)
R = $(CH_2)_2CONH_2$	500 (167)	280 (7588)
R = $(CH_2)_2COOH$	500 (162)	280 (7609)
$(en)_2Co(S(R)C_6H_4NH_2)^{3+}$		
R = CH_3	487 (150)	253 (7200) 312 (1700), sh

[a] Wavelengths of maxima (λ_{max}) are in nm. Molar absorptivities (ϵ) are in M^{-1} cm^{-1} and represent the average of three determinations. Spectra are recorded in dilute aqueous perchloric acid.

Table III. ^1H NMR Spectral Parameters for Selected Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thioether and Selenoether Ligands[a]

complex	protons[b]	δ	character
$[(en)_2Co(S(R)(CH_2)_2NH_2)]^{3+}$			
R = $(CH_2)_2C_6H_5$	C_6H_5	7.5	singlet
R = $C(CH_3)_3$	$C(CH_3)_3$	1.6	singlet
R = CH_3[c]	CH_3	2.6	singlet
R = $(CH_2)_2COCH_3$	CH_3	2.3	singlet
R = $CHCON(CH_2CH_3)COCH_2$[c]	CH_3 SCH	1.2 4.85	triplet triplet
R = $CHCON(C_6H_5)COCH_2$[c]			
band 1	SCH C_6H_5	4.85 7.5	triplet singlet
band 2	SCH C_6H_5	4.85 7.6	triplet singlet
R = $CHCON(CH_3)COCH_2$[c]	SCH CH_3	4.85 3.0	triplet singlet
R = $CH(CH_3)CH_2COOH$	CH_3	1.5	doublet
R = CHCHCOOH	SCHCH	7.0	multiplet
$[(en)_2Co(Se(R)(CH_2)_2NH_2)]^{3+}$			
R = CH_3	CH_3	2.6	singlet
R = CH_2CH_3	CH_3	1.5	triplet
R = $CH_2C_6H_5$	C_6H_5	7.5	singlet
$[(en)_2Co(S(R)C_6H_4NH_2)]^{3+}$			
R = CH_3[c]	C_6H_4 CH_3	7.3–8.1 2.5	multiplet singlet
$[(en)_2Co(S(R)CH_2COO)]^{2+}$			
R = $(CH_2)_2COCH_3$	CH_3 SCH_2COO	1.8 4.0	singlet singlet

[a] Spectra determined in D_2O/DCl with 3-(trimethylsilyl)-1-propanesulfonic acid as internal standard, unless otherwise noted.
[b] All complexes exhibit broad signals in the ranges δ 4.4–6.0 and 2.4–3.9 arising from the NH_2 groups and the CH_2 linkages of the ethylenediamine ligands, respectively. The broad CH_2 signals often obscure the signals of other CH_2 groups. Only signals characteristic of the pendant moiety are listed.
[c] Spectrum obtained in acetone-d_6 with $(CH_3)_4Si$ as internal standard.

Table IV. Pseudo-First-Order and Derived Third-Order Rate Constants for the Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $CH_2CHCOCH_3$[a]

[Co], M	[H$^+$], M	[olefin], M	k_{obsd}, s^{-1}	k, M^{-2} s^{-1}
0.0075	0.20	0.086	0.00798 ± 0.00009	0.464 ± 0.005
0.0075	0.20	0.172	0.0144 ± 0.0002	0.419 ± 0.006
0.0075	0.20	0.246	0.0173 ± 0.0002	0.352 ± 0.004
0.0075	0.20	0.308	0.0232 ± 0.0002	0.377 ± 0.003
0.0075	0.20	0.369	0.0305 ± 0.0006	0.413 ± 0.008
0.0075	0.20	0.492	0.0399 ± 0.0006	0.405 ± 0.006
0.0075	0.08	0.308	0.00957 ± 0.00003	0.388 ± 0.012
0.0075	0.40	0.308	0.0662 ± 0.0010	0.537 ± 0.008
0.0075	0.60	0.246	0.0532 ± 0.0011	0.360 ± 0.007

[a] Conditions: 25 °C, μ = 1.20 M ($Li/HClO_4$). $k = k_{obsd}/[olefin][H^+]$.

concentration excess of methyl vinyl ketone. Methyl vinyl ketone (Aldrich, stabilized with 1% hydroquinone) was used as supplied without further purification. Absorbance changes were monitored at 600 nm, the characteristic shoulder in the spectrum of the parent thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.[15] Infinite-time absorbance readings were obtained in all experiments. Plots of log ($OD_t - OD_\infty$) vs. time were linear for at least 4 half-lives. Linear least-squares analysis yielded values of k_{obsd} and $\sigma_{k_{obsd}}$. All reported errors are standard deviations.

Collection and Reduction of X-ray Data for $[(en)_2Co(S(CHCON(CH_2CH_3)COCH_2)CH_2CH_2NH_2)](ClO_4)_3$. A crystal of approximate dimensions 0.3 × 0.3 × 0.5 mm was mounted on a glass fiber. Initial centering of reflections, generation of possible unit cell vectors, and assignment of indices were carried out on a Syntex P2$_1$ diffractometer by procedures which have been described.[20] Monoclinic symmetry was suggested by interaxial angles and confirmed by axial-rotation photographs. Refined cell parameters were based on the setting angles of 15 reflections with 30° ≤ 2θ ≤ 35°. The density was measured by flotation in $CCl_4/CHBr_3$. Crystal data are summarized in part A of Table V. Intensity data were collected by the 2θ–θ scan technique in bisecting geometry. Other experimental parameters are listed in part B of Table V. No reflections were strong enough to exceed the valid range of the coincidence correction. No significant change was observed in the intensities of three standard reflections, monitored after every 50 data. Systematic absences in the data set ($0k0$, $k \neq 2n$) indicated space groups $P2_1$ or $P2_1/m$. Data were processed by previously described methods.[21] The p factor in the expression for the standard deviation of the observed intensities[22] was assigned a value of 0.05. No absorption correction was made.

Structure Solution and Refinement. The MULTAN package of direct-method programs[23] was used to solve the structure. Intensity

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Table V. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$CoC_{12}H_{30}Cl_3N_6O_{14}S$	vol, Å^3	1294.1 (7)
fw	679.76	Z	2
a, Å	11.273 (3)	d(obsd), g cm^{-3}	1.76 (2)
b, Å	12.931 (4)	d(calcd), g cm^{-3}	1.74
c, Å	8.880 (3)	space group	$P2_1$
β, deg	91.32 (2)	μ(Mo Kα), cm^{-1}	11.5

B. Experimental Parameters

radiation	Mo Kα; λ(Kα) = 0.71073 Å; graphite monochromator
temp, °C	25
receiving aperture	circular, 4 mm i.d.; 20 cm from crystal
scan rate, deg min^{-1}	variable, 2–12
scan range	$-1.1°$ from Kα_1 to $+1.2°$ from Kα_2
bkgd counting	stationary counts for half of scan time at each end of scan
2θ(max), deg	55
data collected	3130
data with $F_o^2 > 3\sigma(F_o^2)$	2143

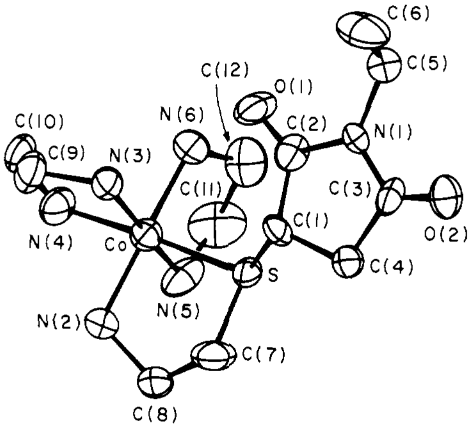

Figure 1. Perspective drawing of the $[(en)_2Co(S(\underline{\text{CHCON}(\text{CH}_2\text{CH}_3)\text{COCH}_2})(CH_2)_2NH_2)]^{3+}$ cation. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

statistics favored the noncentrosymmetric space group $P2_1$, and the structure was solved in this space group. An E map based upon 307 reflections with $E \geq 1.56$ yielded the coordinates of the cobalt atom, all but one nitrogen atom of its inner coordination sphere, and one chlorine atom. Successive difference Fourier maps[24] located the remaining non-hydrogen atoms. Final least-squares refinement with anisotropic thermal parameters was carried out in two blocks, one containing the cation and the other composed of all three anions. The scale factor was refined in each block. Hydrogen atoms were included at fixed, calculated positions (C–H = 0.95 Å, tetrahedral angles), each with a fixed isotropic B value equal to that of the atom to which it was bound. No evidence for methyl hydrogens associated with C(6) was found, so these were not included. Although large thermal parameters were found for some perchlorate oxygen atoms, no simple disorder model for the anions was evident. The conventional R factors converged to $R_1 = 0.061$ and $R_2 = 0.074$.[25] In the final cycle, the maximum parameter shift was 0.7σ for a perchlorate oxygen atom. The highest peak in a final difference map was associated with the cobalt atom and had a electron density of 1.0 e/Å^3, a factor of 3 smaller than that for a typical carbon atom in this structure. Refinement of the enantiomeric configuration produced final R factors within 0.001 of those reported above. Hence, the absolute configuration of the cation in this particular crystal is indeterminate. In all structure factor calculations, neutral-atom scattering factors (including anomalous terms for Co, Cl, and S) were taken from ref 26. The final standard deviation of an observation of unit weight was 1.88. Calculation of structure factors for the data with $F_o^2 < 3\sigma(F_o^2)$ showed 10 reflections with $F_c^2 > 3\sigma(F_o^2)$; of these, only one had $\Delta(F^2)/\sigma > 4$.

Results

Syntheses. The preparative reactions developed in this work are generally more applicable to derivatizing $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ than to derivatizing either of the analogous complexes $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ or $[(en)_2Co(SCH_2COO)]^+$. This situation arises because of the greater instability of the selenolato complex in acidic media[10] and the greater reactivity of the carbon backbone of the $[(en)_2Co(SCH_2COO)]$ complex.[9] Thus, attempts to prepare the 2,5-dioxo-3-pyrrolidinyl derivatives of $[(en)_2Co(SCH_2COO)]^+$ under conditions similar to those used successfully with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ result in a mixture of products, which is separated only with great difficulty. Even in those cases where only the desired $[(en)_2Co(S(R)CH_2COO)]^{2+}$ products are generated and thus can be successfully isolated, the reactions do not proceed to completion as do the analogous reactions of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. However, the new synthetic reactions do successfully yield some derivatives of $[(en)_2Co(SCH_2COO)]^+$ and $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$, and these derivatives are listed in Table II.

The reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with N-phenylmaleimide results in the apparent formation of two thioether products. These product complexes are separable on elution from a Sephadex SP-C25 column with 0.3 M $NaClO_4$ (pH 2). Both complexes appear to be tripositive and have IR and NMR spectra that are indistinguishable. Small differences are observed in the visible–UV spectra of the complexes; e.g., the visible maxima differ by 3 nm. The visible–UV spectral parameters, obtained immediately upon elution of the complexes or after dissolving isolated solid salts of the complexes, are identical. The two products could possibly be diastereomers arising from the chiral cobalt center and the chiral coordinated sulfur atom, but this hypothesis has yet to be proven.

Characterization. In addition to the X-ray structure analysis of $[(en)_2Co(S(\underline{\text{CHCON}(\text{CH}_2\text{CH}_2)\text{COCH}_2})CH_2CH_2NH_2)](ClO_4)_3$, the title complexes were characterized by (1) the synthetic routes employed for their preparation, (2) the elemental analyses listed in Table I, which give empirical compositions in agreement with those predicted, (3) the cation-exchange elution characteristics, which are consistent with the assigned formal charges, (4) the IR spectra, confirming the presence of carbonyl moieties with sharp absorptions at ca. 1690 cm^{-1}, which are not present in the spectra of the parent thiolato complexes, (5) the visible–UV spectral parameters listed in Table II, detailing d–d bands characteristic of cobalt(III) complexes as well as intense ligand-to-metal charge-transfer (LTMCT) bands, which characteristically arise from coordination of sulfur or selenium to a potentially oxidizing center,[27] and (6) the ^{1}H NMR spectral parameters listed in Table III, which confirm the presence and identity of the organic moieties bonded to the chalcogen. In regard to the visible–UV spectra, the data given in Table II are consistent with those reported previously for complexes with simple alkyl R groups.[5] In addition to these general characteristics, the 1-substituted 2,5-dioxo-3-pyrrolidinyl derivatives all undergo a rapid decomposition in alkali media, which proceeds through an intensely colored, violet, intermediate.

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(24) Programs used for difference Fourier syntheses, least-squares refinement, and calculation of derived results have been listed: Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 844.

(25) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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Table VI. Positional Parameters of Non-Hydrogen Atoms[a]

atom	*x*	*y*	*z*
Co	0.21379 (9)	0.37300	0.68934 (13)
S	0.2979 (2)	0.2342 (2)	0.8076 (3)
O(1)	0.4714 (7)	0.4121 (6)	0.9328 (9)
O(2)	0.6134 (6)	0.1322 (6)	1.1865 (9)
N(1)	0.5646 (6)	0.2854 (6)	1.0715 (9)
N(2)	0.0576 (7)	0.3095 (7)	0.7322 (12)
N(3)	0.2037 (7)	0.4632 (6)	0.8643 (9)
N(4)	0.1328 (8)	0.4868 (7)	0.5786 (10)
N(5)	0.2300 (9)	0.2950 (7)	0.5006 (10)
N(6)	0.3675 (7)	0.4334 (7)	0.6399 (9)
C(1)	0.3715 (7)	0.2513 (8)	0.9903 (10)
C(2)	0.4708 (10)	0.3265 (9)	0.9899 (12)
C(3)	0.5451 (9)	0.1846 (8)	1.1144 (12)
C(4)	0.4242 (8)	0.1503 (8)	1.0493 (12)
C(5)	0.6764 (9)	0.3402 (8)	1.1022 (13)
C(6)	0.6746 (11)	0.3945 (12)	1.2548 (15)
C(7)	0.1628 (10)	0.1695 (9)	0.8697 (15)
C(8)	0.0651 (9)	0.1937 (8)	0.7596 (15)
C(9)	0.1149 (10)	0.5476 (9)	0.8376 (14)
C(10)	0.1310 (10)	0.5814 (8)	0.6789 (13)
C(11)	0.3356 (15)	0.3259 (12)	0.4224 (14)
C(12)	0.4309 (10)	0.3676 (14)	0.5316 (13)
Cl(1)	0.0212 (2)	0.3677 (2)	0.1869 (2)
Cl(2)	0.2152 (2)	0.0229 (2)	0.3563 (4)
Cl(3)	0.6722 (4)	0.1283 (4)	0.7316 (5)
O1Cl1	0.1436 (6)	0.3618 (8)	0.1602 (9)
O2Cl1	−0.0024 (8)	0.3243 (9)	0.3310 (12)
O3Cl1	−0.0366 (11)	0.3001 (12)	0.0922 (16)
O4Cl1	−0.0206 (12)	0.4628 (9)	0.1753 (24)
O1Cl2	0.1796 (10)	0.1058 (9)	0.2574 (14)
O2Cl2	0.3213 (9)	−0.0106 (13)	0.3460 (18)
O3Cl2	0.1334 (10)	−0.0517 (13)	0.3856 (22)
O4Cl2	0.2160 (28)	0.0626 (14)	0.4980 (20)
O1Cl3	0.5937 (15)	0.2056 (15)	0.7540 (14)
O2Cl3	0.6254 (23)	0.0448 (19)	0.8166 (27)
O3Cl3	0.6996 (25)	0.1011 (15)	0.6006 (23)
O4Cl3	0.7600 (22)	0.1621 (38)	0.7964 (43)

[a] Numbers in parentheses are estimated standard deviations in the least significant figures.

Table VII. Bond Distances in Cation (Å)

(a) Cobalt Coordination Sphere			
Co–S	2.276 (3)	Co–N(4)	1.981 (8)
Co–N(2)	1.988 (8)	Co–N(5)	1.968 (9)
Co–N(3)	1.948 (8)	Co–N(6)	1.960 (8)
(b) Thioether Ligand			
S–C(1)	1.818 (9)	C(3)–O(2)	1.200 (11)
S–C(7)	1.833 (12)	C(3)–C(4)	1.534 (13)
C(1)–C(2)	1.484 (14)	C(5)–N(1)	1.465 (12)
C(1)–C(4)	1.522 (14)	C(5)–C(6)	1.526 (16)
C(2)–O(1)	1.218 (12)	C(7)–C(8)	1.489 (17)
C(2)–N(1)	1.375 (13)	C(8)–N(2)	1.519 (14)
C(3)–N(1)	1.378 (13)		
(c) Ethylenediamine Rings			
N(3)–C(9)	1.496 (13)	N(5)–C(11)	1.449 (17)
N(4)–C(10)	1.513 (13)	N(6)–C(12)	1.481 (15)
C(9)–C(10)	1.490 (16)	C(11)–C(12)	1.528 (19)

Crystal Structure. Table VI contains the positional parameters of all non-hydrogen atoms. Bond distances and angles within the cation are tabulated in Tables VII and VIII, respectively. Tables of observed and calculated structure factors, atomic thermal parameters, hydrogen atom parameters, and bond lengths and angles within the perchlorate anions are provided as supplementary material (Tables A–D).

Description of the Structure. The crystal structure consists of discrete ((1-ethyl-2,5-dioxo-3-pyrrolidinyl aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) cations and perchlorate anions linked by weak hydrogen bonds. A view of the structure of the cation is shown in Figure 1. The cobalt(III) center is coordinated to five amine nitrogen atoms and the thioether sulfur atom in a slightly distorted octahedral configuration. The largest angular distortion from octahedral symmetry is reflected in the S–Co–N(3) angle of 97.8 (2)°. This angle is a consequence of the bending of N(3) away from S, probably because of steric conflicts between hydrogen atoms on N(3) and C(1). The tris chelate cation has the $\Delta(\lambda\lambda\delta)$ (or the enantiomorphic $\Lambda(\delta\delta\lambda)$) conformation. An intramolecular hydrogen bond links N(6) and O(1), with an N···O distance of 2.841 (11) Å. There is also a probable intermolecular N(3)···O(2) hydrogen bond. Full details of these interactions and of the weak cation–anion hydrogen bonds are given in supplementary Table E.

Table VIII. Bond Angles in Cation (deg)

(a) Cobalt Coordination Sphere			
S–Co–N(2)	87.0 (3)	N(2)–Co–N(6)	177.9 (4)
S–Co–N(3)	97.8 (2)	N(3)–Co–N(4)	85.2 (4)
S–Co–N(4)	175.8 (3)	N(3)–Co–N(5)	173.8 (4)
S–Co–N(5)	86.7 (3)	N(3)–Co–N(6)	90.5 (3)
S–Co–N(6)	93.3 (3)	N(4)–Co–N(5)	90.5 (4)
N(2)–Co–N(3)	91.5 (4)	N(4)–Co–N(6)	89.6 (4)
N(2)–Co–N(4)	90.1 (4)	N(5)–Co–N(6)	85.0 (4)
N(2)–Co–N(5)	92.9 (4)		
(b) Thioether Ligand			
Co–S–C(1)	119.5 (3)	C(2)–N(1)–C(5)	124.0 (8)
Co–S–C(7)	99.1 (4)	C(3)–N(1)–C(5)	123.3 (8)
C(1)–S–C(7)	98.8 (5)	N(1)–C(3)–O(2)	125.3 (10)
S–C(1)–C(2)	114.0 (7)	N(1)–C(3)–C(4)	108.4 (8)
S–C(1)–C(4)	111.6 (7)	O(2)–C(3)–C(4)	126.3 (9)
C(2)–C(1)–C(4)	105.9 (7)	C(3)–C(4)–C(1)	102.6 (7)
C(1)–C(2)–O(1)	127.5 (10)	N(1)–C(5)–C(6)	111.0 (8)
C(1)–C(2)–N(1)	108.5 (8)	S–C(7)–C(8)	108.3 (8)
O(1)–C(2)–N(1)	124.0 (11)	C(7)–C(8)–N(2)	110.5 (9)
C(2)–N(1)–C(3)	112.7 (9)	Co–N(2)–C(8)	113.1 (7)
(c) Ethylenediamine Rings			
Co–N(3)–C(9)	111.2 (7)	Co–N(5)–C(11)	111.1 (8)
N(3)–C(9)–C(10)	105.5 (8)	N(5)–C(11)–C(12)	111.5 (10)
C(9)–C(10)–N(4)	108.9 (8)	C(11)–C(12)–N(6)	105.8 (10)
C(10)–N(4)–Co	108.7 (6)	C(12)–N(6)–Co	111.0 (8)

Kinetics of the Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $CH_2{=}CH_2COCH_3$. When both olefin and acid are present in pseudo-first-order excess, the thiolato complex disappears according to first-order kinetics:

$$-\mathrm{d}(\ln\,[\mathrm{Co}])/\mathrm{d}t = k_{\mathrm{obsd}} \tag{1}$$

At constant [H$^+$] plots of k_{obsd} vs. [olefin] are linear. Plots of k_{obsd}/[olefin] vs. [H$^+$] are also linear. Therefore

$$k = k_{\mathrm{obsd}}/[\mathrm{olefin}][\mathrm{H}^+] \tag{2a}$$

and

$$\mathrm{rate} = k[\mathrm{Co}][\mathrm{olefin}][\mathrm{H}^+] \tag{2b}$$

Thus, over the limited concentration ranges investigated, formation of the thioether complex is first order in each of the thiolato complex concentration, olefin concentration, and acid concentration. Table IV lists values of the observed pseudo-first-order rate constants, k_{obsd}, and the derived third-order rate constants, k. The average value of k is 0.41 ± 0.06 $M^{-2}\,s^{-1}$ at 25 °C, μ = 1.20 M (Li/HClO$_4$).

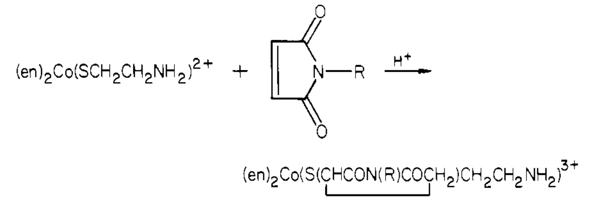
Discussion

Syntheses and Properties. The general procedures outlined herein for the syntheses of coordinated thioethers and selenoethers make available a variety of complexes that are inaccessible by the simple reaction of coordinated thiols with alkyl halides in *N*,*N*-dimethylformamide[5] (DMF).

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + RX \xrightarrow{DMF} (en)_2Co(S(R)CH_2CH_2NH_2)^{3+} + X^- \tag{3}$$

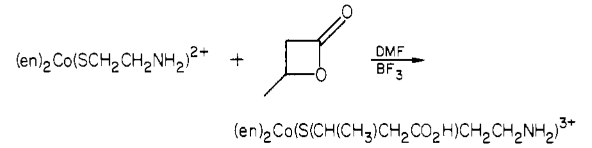
Although this reaction is useful, it suffers a major drawback in that only primary alkyl halides react at a reasonable rate.

The syntheses outlined herein circumvent the steric restrictions imposed by an S_N2 mechanism by utilizing the reactivity of nucleophiles with activated double bonds (eq 4), carbocations (eq 5), and strained molecules (eq 6). In addition to generating thioether complexes in which a secondary or tertiary carbon atom is attached to the sulfur, these syntheses also provide alternate routes to a variety of novel complexes in which a primary carbon atom is bonded to the coordinated chalcogen. All of the reactions involving $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and activated olefins give 100% yields of the desired thioether complex, even when only a slight excess of the olefin is employed. Through appropriate adjustment of the acidity, these reactions can be made to proceed quite rapidly. This is in marked contrast to the reactions of $[(en)_2Co(SCH_2CH_2NH_2]^{2+}$ with alkyl halides in DMF, which may take many hours even in the presence of a large excess of alkyl halide.[5]



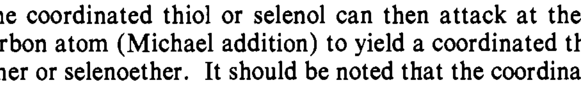
(4)

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + HOC(CH_3)_3 \xrightarrow{H^+} (en)_2Co(S(C(CH_3)_3)CH_2CH_2NH_2)^{3+} \quad (5)$$



(6)

A preliminary kinetic investigation into the reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with methyl vinyl ketone shows this reaction to be first order in cobalt complex, olefin, and H^+. This is in direct contrast to the reaction of noncoordinated thiols with activated olefins, which proceed more rapidly as $[H^+]$ is *decreased*.[28] In the case of noncoordinated thiols, the lower $[H^+]$ is favorable because the reactive species is not RSH but the more nucleophilic RS^-.[28] The coordinated thiolate ligand of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is, however, already deprotonated under the reaction conditions (for $[(en)_2Co(S(H)CH_2CH_2NH_2]^{3+}$, K_a = 6.5 M at μ = 8.0 M (Na/$HClO_4$)),[29] and thus adding base offers no advantage. Increasing acidity favors the addition reaction presumably by enhancing the reactivity of the activated olefin through protonation of the carbonyl group (or possibly the double bond itself). This protonation results in a species with some positive character residing on the α-carbon atom.



$$H_2C{=}CH\overset{\overset{O}{\|}}{C}CH_3 \overset{H^+}{\rightleftharpoons} H_2C{=}CH\overset{\overset{^+OH}{\|}}{C}CH_3 \longleftrightarrow H_2C^+{-}CH{=}\overset{\overset{OH}{|}}{C}CH_3 \quad (7)$$

The coordinated thiol or selenol can then attack at the α-carbon atom (Michael addition) to yield a coordinated thioether or selenoether. It should be noted that the coordinated thiolate ligand of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is about as nucleophilic as a noncoordinated thioether (RSR′) or noncoordinated thiol (RSH).[11]

Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with *tert*-butyl alcohol probably proceeds through an $S_{N}1$ mechanism in which the coordinated thiolate is rapidly attacked by the *tert*-butyl carbocation (eq 5). This is analogous to the smooth reaction of L-cysteine with *tert*-butyl alcohol in 5 M HCl to yield *S*-*tert*-butyl-L-cysteine.[30] The analogous reactions of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with methyl alcohol or ethyl alcohol proceed much more slowly. That the ethyl alcohol reaction occurs more slowly than the methyl alcohol reaction is consistent with an S_N2 mechanism in which the sulfur nucleophile displaces H_2O from the protonated alcohol or displaces $CH_3SO_3^-$ from the sulfonic acid ester produced in situ from CH_3SO_3H and the alcohol. Further evidence in support of the proposed $S_{N}1$ and S_N2 mechanisms is provided by the observations that the *tert*-butyl alcohol reaction proceeds with equal facility in CH_3SO_3H, $HClO_4$, H_2SO_4, or HCl, whereas in HCl, the methyl alcohol reaction goes to completion in ca. 7 days (vs. 1 day in CH_3SO_3H) and the ethanol reaction does not detectably proceed even after 1 week. The lack of reactivity of isopropyl alcohol under these same conditions could be attributed to the decreased stability of the isopropyl carbocation in an $S_{N}1$ process, the increased steric constraints imposed by a secondary carbon atom in an S_N2 process, or competitive dehydration of the alcohol.

Due to its strained cyclic configuration, β-butyrolactone is known to be particularly susceptible to nucleophilic attack.[31] The ring-opening reaction can proceed either by nucleophilic attack at the carbonyl carbon atom or at the secondary carbon atom. Which path is favored depends on the nature of the nucleophile and the particular reaction conditions.[31-33] In DMF, catalyzed by BF_3, the thiolate ligand of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ attacks β-butyrolactone exclusively at the secondary carbon atom to yield a thioether in which a secondary carbon atom is bonded to the coordinated sulfur atom, i.e. $[(en)_2Co(S(CH(CH_3CH_2COOH)CH_2CH_2NH_2)]^{3+}$. This isomer is unambiguously identified by the ^1H NMR data of Table III and is indeed the product expected to result from nucleophilic attack by $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.

Characterization. The changes in the visible spectrum induced upon conversion of the parent thiolate complexes to the corresponding thioether derivatives have been discussed previously.[5] The UV spectra of the coordinated chalcogens are dominated by the intense ligand-to-metal charge-transfer (LTMCT) characteristic of chalcogen–metal complexes (Table II). No discernible pattern is observed in the position of this band relative to the nature of the pendant R group of the thioether ligand. However, the LTMCT transitions in the $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes where R = $C(CH_3)_3$ and CH=CHCOOH occur at much lower energies (299 and 320 nm) than does the same transition in the parent thiolate complex (282 nm). This could arise from the electron-donating properties of these R groups, which would tend to make the coordinated sulfur atom a better reductant.

Structural Analysis. The structure of $[(en)_2Co(S(\underline{CHCON(CH_2CH_3)COCH_2})CH_2CH_2NH_2)]^{3+}$ is as expected from the previously described characterizations and from the known structure of the parent thiolato complex.[34] The primary coordination sphere of cobalt(III) remains intact during the conversion of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to the thioether. The successful refinement of this structure establishes the identity of this complex and demonstrates that a

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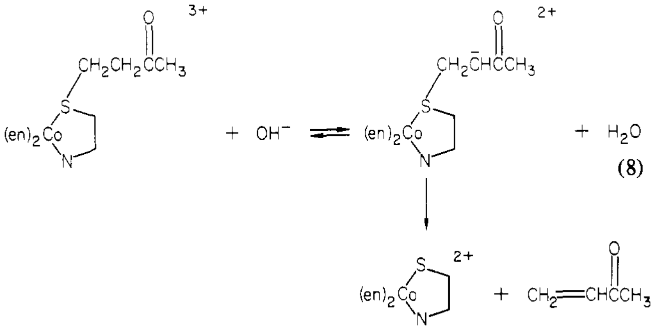
secondary carbon atom is bonded to the thioether sulfur atom. The length of the Co–N bond trans to the sulfur atom (1.981 (8) Å) falls within the range of the other four Co–N bond lengths; thus, as expected,[5] there is no observable structural trans effect induced by the thioether sulfur atom. The cobalt–sulfur bond length (2.276 (3) Å) in this complex is equivalent to the cobalt–sulfur bond length in $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ (2.267 (10) Å), and thus this parameter does not appear to be sensitive to whether the sulfur atom is bonded to a primary or a secondary carbon atom.

Reactivity. All of the complexes prepared in this work are unstable in alkaline solution, decomposing primarily through Co–S or Co–Se bond cleavage. The majority of the complexes are stable in acidic media with only a few exceptions. The *tert*-butyl thioether complex $[(en)_2Co(S(C(CH_3)_3)CH_2CH_2NH_2)]^{3+}$ is unstable over the pH range 0–14, with S–C bond cleavage occurring below ca. pH 8 and Co–S bond cleavage predominating above ca. pH 8. All attempts to crystallize this complex under a variety of pH conditions led to crystals of the parent thiolate complex.

The $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes with R groups $(CH_2)_2COCH_3$ and $(CH_2)_2CHO$ decompose in the pH range 2–6 to yield the parent thiolate complex and the parent olefin. The reaction presumably occurs by a reverse Michael addition:



(8)

This process depends upon the acidity of the protons on the carbon atom adjacent to the carbonyl functionality. Thus, the complex with R = $(CH_2)_2CO_2^-$ does not undergo S–C bond cleavage up to at least pH 14; this is attributed to the decreased acidity of the protons in question due to the formal negative charge on the carboxylate group. Interestingly, these reverse Michael addition reactions involving coordinated thioethers (eq 8) appear to be much more facile than those of noncoordinated thioethers. Thus, the thioether resulting from addition of cysteine to ethyl vinyl sulfone decomposes to the starting materials only in strong alkali (pH 13).[36] It is clear that bonding to a coordinated sulfur atom greatly alters the reactivity of a pendant group, particularly if the pendant group contains potentially acidic protons.

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Registry No. $[(en)_2Co(S((CH_2)_2COCH_3)(CH_2)_2NH_2)](ClO_4)_3$, 85781-94-8; $[(en)_2Co(S(CHCHCOOH)(CH_2)_2NH_2)](ClO_4)_3$, 85781-96-0; $[(en)_2Co(S((CH_2)_2CoNH_2)(CH_2)_2NH_2)](ClO_4)_3$, 85781-98-2; $[(en)_2Co(Se(CH_2C_6H_5)(CH_2)_2NH_2)](ClO_4)_3$, 85782-00-9; $[(en)_2Co(S(C(CH_3)_3)(CH_2)_2NH_2)](ClO_4)_3$, 85782-02-1; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5; $[(en)_2Co(SCH_2COO)](ClO_4)$, 26743-67-9; $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$, 58866-01-6; $[(en)_2Co(SC_6H_4NH_2)]^{2+}$, 72905-16-9; $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, 35594-86-6; $[(en)_2Co(S(CH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 65622-75-5; $[(en)_2Co(S((CH_2)_2COOH)CH_2CH_2NH_2)]^{3+}$, 85782-03-2; $[(en)_2Co(S((CH_2)_2CHO)CH_2CH_2NH_2)]^{3+}$, 85782-04-3; $[(en)_2Co(S((CH_2)_2CN)CH_2CH_2NH_2)]^{3+}$, 85782-05-3; $[(en)_2Co(S((CH_2)_2Ph)CH_2CH_2NH_2)]^{3+}$, 85782-06-5; $[(en)_2Co(S(CH(CH_3)CH_2COOH)CH_2CH_2NH_2)]^{3+}$, 85782-07-6; $[(en)_2Co(S(CH(COOH)CH_2COOH)CH_2CH_2NH_2)]^{3+}$, 85782-08-7; $[(en)_2Co(S(\underline{CHCONHCOC}H_2)CH_2CH_2NH_2)]^{3+}$, 85782-09-8; $[(en)_2Co(S\underline{CHCON(CH_3)COC}H_2)CH_2CH_2NH_2)]^{3+}$, 85782-10-1; $[(en)_2Co(S(\underline{CHCON(CH_2CH_3)COC}H_2)CH_2CH_2NH_2)]^{3+}$, 85782-11-2; $[(en)_2Co(S(\underline{CHCON(C_6H_5)COC}H_2)CH_2CH_2NH_2)]^{3+}$, 85782-12-3; $[(en)_2Co(Se(CH_3)CH_2CH_2NH_2)]^{3+}$, 85848-90-4; $[(en)_2Co(Se(CH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 85782-13-4; $[(en)_2Co(Se((CH_2)_2COCH_3)CH_2CH_2NH_2)]^{3+}$, 85800-03-9; $[(en)_2Co(S((CH_2)_2COCH_3)CH_2COO)]^{2+}$, 85782-14-5; $[(en)_2Co(S((CH_2)_2CHO)CH_2COO)]^{2+}$, 85782-15-6; $[(en)_2Co(S((CH_2)_2CONH_2)CH_2COO)]^{2+}$, 85782-16-7; $[(en)_2Co(S((CH_2)_2COOH)CH_2COO)]^{2+}$, 85800-04-0; $[(en)_2Co(S(CH_3C_6H_4NH_2)]^{3+}$, 85782-17-8; $CH_2CHCOCH_3$, 78-94-4; $HSCH_2CH_2NH_2$, 60-23-1; $HSCH_2CO_2H$, 68-11-1; $HSeCH_2CH_2NH_2$, 21681-94-7; $HSC_6H_4NH_2$, 137-07-5; acrylamide, 79-06-1; maleic acid, 110-16-7; maleimide, 541-59-3; *N*-methylmaleimide, 930-88-1; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; acrolein, 107-02-8; propiolic acid, 471-25-0; 2-propenenitrile, 107-13-1; methanol, 67-56-1; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; β-butyrolactone, 3068-88-0; styrene, 100-42-5; 2-butenoic acid, 3724-65-0.

Supplementary Material Available: Tables A–E, giving $|F_o|$ and F_c, anisotropic thermal parameters, hydrogen positional parameters, bond lengths and bond angles involving the perchlorate anions, and possible hydrogen bonding interactions (19 pages). Ordering information is given on any current masthead page.

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[36] Schoberl, A. *J. Text. Inst., Trans.* **1960**, *51*, T613.