Synthesis and Characterization of Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thioether Ligands. Crystal Structures of [(en)₂Co(S(CH₃)CH₂CH₂NH₂)][Fe(CN)₆] and [(en)₂Co(S(CH₂C₆H₅)CH₂COO)](SCN)₂

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A general synthesis of coordinated thioethers via alkylation of coordinated thiols in *N,N*-dimethylformamide is described. The series of complexes [(en)₂Co(S(R)CH₂CH₂NH₂)]³⁺, with R = methyl, ethyl, cyclohexylmethyl, benzyl, 4-fluorobenzyl, 4-methylbenzyl, 1-naphthylmethyl, 2-naphthylmethyl, carboxymethyl, methylcarboxymethyl, carboxyethyl, and carboxypropyl, and the complex [(en)₂Co(S(CH₂C₆H₅)CH₂COO)]²⁺ are characterized. Single-crystal x-ray structure analyses of ((methyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) hexacyanoferrate(III) tetrahydrate and ((benzyl 2-carboxymethyl thioether)-*O,S*)bis(ethylenediamine)cobalt(III) thiocyanate, refined to conventional *R* factors of 0.042 and 0.037, respectively, are reported. Both cobalt(III) centers are approximately octahedrally coordinated with one coordination site occupied by a thioether sulfur atom. The salient structural feature of both complexes is that the coordinated thioether sulfur does *not* induce a significant structural trans effect (STE). This result is ascribed to the lack of a formal negative charge on the thioether sulfur atom inasmuch as other sulfur atoms which do carry a formal charge also exert significant STE's. The visible–UV spectra of the thioether complexes are discussed in relation to the spectra of the analogous thiolato complexes.

Introduction

Our long-standing interest in the chemistry of coordinated sulfur[1-14] has led us to a consideration of coordinated thioethers, a divers class of ligands which may readily be prepared via alkylation of coordinated thiols.[15-17] Recent reports have indicated that when coordinated to cobalt(III), thioether sulfur induces remarkable effects upon the kinetics of electron transfer to cobalt[17-21] and on the kinetics of ligand substitution trans to sulfur.[22] In this context, complexes of the type [(en)₂Co(S(R)CH₂CH₂NH₂)]³⁺ and [(en)₂Co(S(R)-CH₂COO)]²⁺ are of special interest since we have previously studied the parent thiolato complexes,[23] as well as the analogous sulfenic[24] and sulfinic[3] acid complexes [(en)₂Co(S-(O)CH₂CH₂NH₂)]²⁺ and [(en)₂Co(S(O)₂CH₂CH₂NH₂)]²⁺. The sulfur atoms of all of these complexes are known to induce structural trans effects (i.e., the Co–N bond that is trans to the coordinated sulfur is significantly longer than the average of the Co–N bonds that are cis to sulfur). It has been suggested[2,8,17] that this structural trans effect may be correlated with many of the kinetic phenomena associated with coordinated sulfur. We therefore desired to determine whether or not thioether sulfur exerts a structural trans effect when coordinated to cobalt(III), and also to prepare a series of [(en)₂Co(S(R)CH₂CH₂NH₂)]³⁺ complexes in which the R group is systematically varied in a manner designed to explicate kinetic phenomena. This paper describes the preparation and characterization of this series of complexes, as well as single-crystal x-ray determinations of the structure of two specific thioether complexes. Our studies[25] on the kinetics and mechanism of electron transfer to the title complexes will be detailed in subsequent papers.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. (2-Mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate and (mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) chloride were available from previous studies.[12,23,25] Dowex 50W-X2 (200–400 mesh) cation-exchange resin was cleaned by a previously detailed procedure.[26] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Visible–UV spectra were recorded on a Cary 14 spectrophotometer at ambient temperature. ¹H NMR spectra were obtained on Varian T-60 and A-60 instruments.

((Alkyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) Salts, [(en)₂Co(S(R)CH₂CH₂NH₂)]X₃, X = ClO₄⁻, I⁻, ¹/₃[Fe(CN)₆]³⁻, ¹/₃[Co(CN)₆)]³⁻. These compounds are readily prepared via the alkylation of [(en)₂Co(SCH₂CH₂NH₂)](ClO₄)₂.[12,25] We have synthesized complexes with R = methyl, ethyl, cyclohexylmethyl, benzyl, 4-fluorobenzyl, 4-methylbenzyl, 1-naphthylmethyl, 2-

naphthylmethyl, carboxymethyl, methylcarboxymethyl, carboxyethyl, and carboxypropyl. Our general procedure, using alkyl halides as alkylating agents and *N,N*-dimethylformamide (DMF) as reaction solvent, is detailed here for the preparation of the complex with R = benzyl. Twenty-two millimoles of [(en)₂Co(SCH₂CH₂NH₂)]-(ClO₄)₂ was dissolved in 50 mL of DMF to give a black solution. Benzyl chloride (12 mL, ca. 100 mmol, Aldrich) was added. Within 12 h (reaction time depends on the specific alkyl halide used) the solution turned deep red-orange and the product complex precipitated. The DMF and excess benzyl chloride were extracted into diethyl ether leaving a red-black oil which was dissolved in a minimum amount of warm (30 °C) water. After filtration, this solution was treated with an equal volume of 72% HClO₄ and then slowly cooled to give an essentially quantitative yield of [(en)₂Co(S(CH₂C₆H₅)-CH₂CH₂NH₂)](ClO₄)₃.

The general procedure succeeds when cyclohexylmethyl bromide is used as alkylating agent, but the reaction time is excessively long (50% completion in ca. 90 days). Therefore the complex with R = cyclohexylmethyl was prepared using the more reactive alkylating agent cyclohexylmethyl trifluoromethanesulfonate. Over a period of 1 h, with cooling, a solution of trifluoromethanesulfonic anhydride (177 mmol, Cationics Chemicals) in 50 mL of dry dichloromethane was added dropwise to a solution of (hydroxymethyl)cyclohexane (150 mmol, Aldrich) and *N,N*-diisopropylethylamine (200 mmol, Aldrich, dried over CaH₂) in 200 mL of dry CH₂Cl₂. The resulting solution of ester was added to 22 mmol of [(en)₂Co(SCH₂CH₂NH₂)](ClO₄)₂ dissolved in 300 mL of DMF and this mixture was stirred overnight at ambient temperature. After removal of volatile components by rotary evaporation, the resulting orange-red oil was dissolved in water and absorbed on a Dowex 50W-X2 cation-exchange column. The desired 3+ product band was eluted with 50% (v/v) ethanol–water which was 6 M in HClO₄; the central 80% of this band yielded 4.0 g of red-orange solid after treatment with large volumes of 2-butanol and diethyl ether. Recrystallization from water–NaClO₄ yielded 1.1 g of the desired [(en)₂Co(S(CH₂C₆H₁₁)CH₂CH₂NH₂)](ClO₄)₃ complex.

All perchlorate salts, with the exception of the naphthylmethyl complexes, were recrystallized three times from water–HClO₄ or water–NaClO₄ solutions; the naphthylmethyl complexes were recrystallized three times from 50% (v/v) ethanol–water and HClO₄. It should be noted that it is very difficult to remove bromide and iodide ions (resulting from alkylation with alkyl bromides and iodides) by successive recrystallizations of the perchlorate salts. This problem may be circumvented by the use of alkyl chlorides in the original reaction (however, alkyl chlorides react more slowly than do the corresponding bromides and iodides) or by treatment of the thioether complex with excess AgClO₄ solution. After removal of the silver halide, excess silver ion is readily removed by recrystallization of the thioether complex from water–HClO₄.

Iodide salts of the thioether complexes may be prepared either by using a saturated aqueous solution of NaI rather than 72% HClO₄

Table I. Elemental Analyses for Thioether Complexes

Complex		% C[a]	% H	% N	% Co	% S	% Cl
$[Co(en)_2(S(CH_3)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	14.78	4.43	12.32	10.36	5.64	18.70
	Found	14.55	4.59	11.86	9.85	5.43	18.03
$[Co(en)_2(S(CH_3)(CH_2)_2NH_2)]I_3$	Calcd	12.92	3.87	10.76		4.93	58.48[b]
	Found	12.79	4.16	10.46		4.94	58.26
$[Co(en)_2(S(CH_3)(CH_2)_2NH_2)][Co(CN_6)]\cdot$	Calcd	28.01	5.97	27.64	21.14	5.75	
$4H_2O^c$	Found	28.20	5.87	27.81	20.71	5.67	
$[Co(en)_2(S(CH_2C_6H_5)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	24.22	4.53	10.86	9.14	4.97	
	Found	22.50	4.74	11.09	9.42	4.90	
$[Co(en)_2(S(CH_2C_6H_5)(CH_2)_2NH_2)]I_3\cdot2H_2O^d$	Calcd	20.46	4.35	9.17	7.72	4.20	
	Found	20.66	4.30	9.17	7.69	3.84	
$[Co(en)_2(S(CH_2C_{10}H_7)(CH_2)_2NH_2)](ClO_4)_3\cdot$	Calcd	28.72	5.09	9.30	7.83	4.26	
$2H_2O\cdot^1/_2CH_3CH_2OH^e$	Found	28.51	4.88	9.33	7.44	4.18	
$[Co(en)_2(S(CH_2C_{10}H_7)(CH_2)_2NH_2)](ClO_4)_3\cdot$	Calcd	30.07	5.18	9.23	7.77	4.22	
$H_2O\cdot CH_3CH_2OH^f$	Found	30.33	5.12	9.90	7.69	4.23	
$[Co(en)_2(S(CH_2C_6H_{11})(CH_2)_2NH_2)](ClO_4)_3$	Calcd	23.99	5.42	10.76	9.06	4.93	
	Found	24.49	5.58	11.20	9.14	5.19	
$[Co(en)_2(S(CH_2CO_2CH_3)(CH_2)_2NH_2)](ClO_4)_3\cdot$	Calcd	16.99	4.34	10.86	9.14	4.97	
H_2O	Found	16.76	4.30	10.82	9.19	4.94	
$[Co(en)_2(S(CH_2CO_2H)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	15.68	4.11	11.43	9.62	5.23	17.36
	Found	15.56	4.33	11.56	9.74	5.20	17.54
$[Co(en)_2(S((CH_2)_2CO_2H)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	17.24	4.34	11.18	9.40	5.12	16.97
	Found	17.24	4.42	11.17	9.31	5.05	17.16
$[Co(en)_2(S((CH_2)_3CO_2H)(CH_2)_2NH_2)](ClO_4)_3\cdot$	Calcd	17.75	4.91	10.34	8.71	4.74	
$2H_2O$	Found	17.28	4.88	9.90	8.77	4.03	
$[Co(en)_2(S(CH_2C_6H_4F)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	23.56	4.26	10.57	8.89	4.84	
	Found	22.13	4.83	10.85	8.50	4.54	
$[Co(en)_2(S(CH_2C_6H_4CH_3)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	25.52	4.74	10.63	8.95	4.87	
	Found	24.81	4.77	10.59	8.92	4.59	
$[Co(en)_2(S(CH_2CH_3)(CH_2)_2NH_2)](ClO_4)_3$	Calcd	16.49	4.67	12.02	10.11	5.50	
	Found	16.37	5.00	12.16	9.77	5.19	
$[Co(en)_2(S(CH_2C_6H_5)CH_2COO)](SCN)_2$	Calcd	37.81	5.29	17.64	12.37	20.19	
	Found	37.83	5.61	17.71	12.17	19.95	

[a] % C analyses of perchlorate salts are often low due to the explosive nature of these compounds. [b] % I. [c] See results of crystal structure on $Fe(CN)_6^{3-}$ salt. [d] Iodide salt prepared by metathesis from perchlorate salt. [e] 1-Naphthylmethyl derivative. [f] 2-Naphthylmethyl derivative; molecules of solvation confirmed by ^{1}H NMR.

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

Complex	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)
$[(en)_3Co]^{3+}$	465 (87.5)	387 (9.2)	339 (79)	
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$	482 (142)	423 (95)	282 (13 800)	250 (1550)
	600 (44) sh			
$[(en)_2Co(SCH_2COO)]^+$	518 (152)	430 (73)	282 (11 700)	255 (4270)
$[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$				
R = CH_3[b]	487 (177)	405 (18)	282 (8380)	257 (4140)
R = CH_2CH_3	487 (182)	405 (20)	283 (9040)	258 (4640)
R = CH_2COOCH_3	490 (153)	405 (19)	280 (8060)	258 (4720)
R = CH_2COOH	489 (170)	405 (19)	282 (8410)	258 (4760)
R = CH_2CH_2COOH	489 (186)	405 (19)	282 (8920)	258 (4890)
R = $CH_2CH_2CH_2COOH$	488 (175)	406 (19)	282 (8930)	258 (4460)
R = $CH_2C_6H_{11}$	489 (194)	410 (35)	286 (9480)	261 (5330)
R = $CH_2C_6H_5$	487 (182)	405 (20)	291 (9920)	255 (5100)
R = p-$CH_2C_6H_4F$	486 (196)	409 (25)	290 (10 300)	256 (5500)
			274 (8220) sh	
R = p-$CH_2C_6H_4CH_3$[c]	488 (212)	421 (51)	285 (9390)	257 (5440)
			278 (9230)	276 (9150)
R = 1-$CH_2C_{10}H_7$	480 (222)	460 (213)	288 (18 100)	256 (7490)
R = 2-$CH_2C_{10}H_7$	484 (238)	446 (178)	283 (17 300)	254 (9490)
$[(en)_2Co(S(R)CH_2COO)]^{2+}$				
R = CH_3[d]	499 (168)		280 (7300)	
R = $CH_2C_6H_5$	504 (175)	420 (36)	293 (10 200)	225 (8600)

[a] Wavelengths, λ, of maxima (max), minima (min), and shoulders (sh) are in nm. Molar extinction coefficients, ϵ, given in parentheses, are in M^{-1} cm^{-1}. Spectra are recorded in dilute aqueous perchloric acid. [b] Average of determinations on three independently prepared samples. [c] The charge-transfer band is split into two components separated by a shallow minimum. See Figure 2. [d] Data from ref 17.

in the above general procedure or by simple metathesis from perchlorate salts. Crystals of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]$-$[Fe(CN)_6]\cdot4H_2O$ and $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)][Co(CN)_6]\cdot4H_2O$ were grown by allowing layers of 0.01 M $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]I_3$ and 0.02 M $K_3M(CN)_6$ (M = Fe, Co) to slowly diffuse together; these crystals, which are isomorphous, form as hollow needles. They were cleaved to yield pieces suitable for x-ray diffraction experiment.

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.

((Benzyl 2-carboxymethyl thioether)-O,S)bis(ethylenediamine)-cobalt(III) Salts. $[(en)_2Co(S(CH_2C_6H_5)CH_2COO)]X_2$, X = Cl⁻, SCN⁻. The chloride salt was prepared from $[(en)_2Co(SCH_2COO)]Cl^{23}$ and benzyl chloride in DMF according to the general procedure outlined above and then recrystallized from water–isopropyl alcohol mixtures containing LiCl. Crystals of the thiocyanate salt suitable for x-ray diffraction measurements were grown by allowing to slowly diffuse together layers of (a) a saturated aqueous solution of the chloride salt that had been diluted 1:6 with 50% (v/v) ethanol–water and (b)

Table III. ^{1}H NMR Spectral Parameters for
$[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ Thioether Complexes^a

-R	Protons^b	δ	Character	Integral
-CH$_2$CH$_3$	A	4.4-5.4	Broad	10
	B	2.4-3.1	Broad	14
	SCH$_2$-	Under H$_B$		
	-CH$_3$	1.45	Triplet	3
-CH$_2$C$_6$H$_{11}$	A	4.1-5.2	Broad	10
	B	2.2-3.1	Broad	14
	SCH$_2$-	Under H$_B$		
	-C$_6$H$_{11}$	0.8-2.2	Multiplet	11
-CH$_2$C$_6$H$_5$	A	4.4-5.5	Broad	10
	B	2.4-2.9	Broad	12
	SCH$_2$-	2.0	Singlet	2
	-C$_6$H$_5$	7.5	Singlet	5
-CH$_2$C$_6$H$_4$F	A	4.4-5.4	Broad	10
	B	2.4-3.0	Broad	12
	SCH$_2$-	4.0	Doublet	2
	-C$_6$H$_4$-	7.2-7.8	Multiplet	4
-CH$_2$C$_6$H$_4$CH$_3$	A	4.4-5.4	Broad	10
	B	2.4-3.0	Broad	12
	SCH$_2$-	4.0	Doublet	2
	-C$_6$H$_4$-	7.4	Singlet	5
	-CH$_3$	2.4	Singlet	3
-CH$_2$C$_{10}$H$_7$	A	4.7-5.8	Broad	10
(1-Naphthylmethyl)	B	2.4-3.1	Broad	14
	SCH$_2$-	Under H$_B$		
	-C$_{10}$H$_7$	7.6-8.6	Multiplet	7
-CH$_2$C$_{10}$H$_7$	A	4.6-5.8	Broad	10
(2-Naphthylmethyl)^c	B	2.6-3.1	Broad	14
	SCH$_2$-	Under H$_B$		
	-C$_{10}$H$_7$	7.6-8.5	Multiplet	7
	-CH$_2$OH	3.62	Quartet	2
	-CH$_3$	1.12	Triplet	3
-CH$_2$CO$_2$CH$_3$	A	4.4-5.4	Broad	10
	B	2.4-3.2	Broad	12
	SCH$_2$-	3.95	Singlet	2
	-CO$_2$CH$_3$	3.82	Singlet	3
-CH$_2$CO$_2$H	A	4.6-5.6	Broad	10
	B	2.4-3.2	Broad	12
	SCH$_2$-	3.88	Singlet	2
-(CH$_2$)$_2$CO$_2$H	A	4.4-5.4	Broad	10
	B	2.4-2.8	Broad	14
	SCH$_2$-	2.95	Triplet	2
	-CH$_2$CO$_2$	Under H$_B$		
-(CH$_2$)$_3$CO$_2$H	A	4.4-5.4	Broad	10
	B	2.0-3.2	Broad	18
	S(CH$_2$)$_3$	Under H$_B$		

^{a} Spectra determined in Me$_2$SO-d_6 with Me$_4$Si as internal standard. Values of δ are in ppm and values of the integral are based on relative peak areas. ^{b} Protons designated "A" are those of the five NH$_2$ groups. Protons designated "B" are those of the CH$_2$ linkages. ^{c} This complex crystallizes with one ethanol of solvation (see Table I).

a 1 M aqueous solution of KSCN. Characterization data for these complexes are also given in Tables I and II.

X-Ray Characterization, $[(en)_2Co(S(CH_3)CH_3CH_2NH_2)][Fe(CN)_6] \cdot 4H_2O$. A red-orange, plate-shaped crystal of approximate dimensions $0.10 \times 0.16 \times 0.26$ mm was mounted parallel to its longest dimension on a glass fiber. Preliminary precession photographs exhibited systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, consistent with the space groups[27] Cc (No. 9) and $C2/c$ (No. 15). This same crystal was centered on a Syntex $P\bar{1}$ diffractometer equipped with a molybdenum target tube and graphite monochromator (Mo Kα, λ 0.710 69 Å) and operated at ambient temperature (22 ± 2 °C). Our usual procedures[23] were employed to check the crystal quality (three axial rotation photographs and mosaic scan measurements), determine unit cell constants (15 reflections), and measure intensities. The crystal is of the monoclinic class with $a = 13.756$ (2) Å, $b = 10.570$ (1) Å, $c = 17.704$ (2) Å, and $\beta = 111.22$ (1)°. With $Z = 4$, $d_{calcd} = 1.53$, $d_{measd} = 1.51$ (3) g cm^{-3}. The rate for the $\theta/2\theta$ scan varied between 1 and 12°/min depending on the intensity of the reflection being measured. The scan ranged from 1.0° in 2θ below the calculated Kα_1 peak position to 1.0° above that calculated for Kα_2. Four standard reflections were

monitored to check crystal stability and to account for long-term drift. The drift correction varied from 0.994 to 1.038 and was random in behavior. Absorption corrections were not applied since $\mu = 14.5$ cm^{-1} and the maximum relative error in the measured intensities was estimated to be less than 4%. Within the sphere $2\theta < 55°$, 2892 reflections were measured in the forms hkl and $h\bar{k}l$; 2760 unique reflections were obtained by averaging.[28] Of these, 2025 had $I > 2\sigma(I)$, where p the ignorance factor used to calculate[23,29] $\sigma(I)$ was set equal to 0.02.

X-Ray Characterization, $[(en)_2Co(SCH_2C_6H_5)CH_2COO)](SCN)_2$. A deep red, plate-shaped crystal of approximate dimensions $0.25 \times 0.18 \times 0.12$ mm was generally characterized as above, with the following differences in procedures and data. Preliminary precession photographs indicated a crystal of the triclinc class. Cell constants (13 reflections) are $a = 6.976$ (1) Å, $b = 7.884$ (1) Å, $c = 20.358$ (2) Å, $\alpha = 99.48$ (1)°, $\beta = 90.94$ (1)°, and $\gamma = 107.91$ (1)°, these parameters corresponding to the reduced primitive cell obtained by the method of Buerger.[30,31] With $Z = 2$, $d_{calcd} = 1.54$, $d_{measd} = 1.52$ (1) g cm^{-3}. The $\theta/2\theta$ scan rate varied between 2.0 and 8.0°/min, and the scan ranged from 0.6° in 2θ below the calculated Kα_1 peak position to 0.8° above that calculated for Kα_2. The drift correction varied from 1.013 to 0.990 and was random in behavior. Absorption corrections were not applied since $\mu = 11.87$ cm^{-1} leading to an estimated maximum relative error of <3%. Within the sphere $2\theta > 45°$, 3629 reflections were measured in the forms hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$. From these, 2729 were obtained by averaging and in this set 2229 had $I > 2\sigma(I)$ with p set equal to 0.04.

Structure Solution and Refinement, $[(en)_2Co(S(CH_3)-CH_2CH_2NH_2)][Fe(CN)_6] \cdot 4H_2O$. This structure was solved using normal Patterson techniques and refinement proceeded without difficulty. Hydrogen atoms, fixed at calculated positions (N–H = 0.87 Å; C–H = 0.97 Å; tetrahedral geometry), were assigned isotropic temperature parameters[32] of $B = 4.0$ Å^2. In the final cycles of least-squares refinement, 278 parameters were varied including the overall scale factor, positional parameters, and anisotropic thermal parameters for all nonhydrogen atoms, but excluding hydrogen atom positional and thermal parameters. Convergence was achieved with $R_1 = 0.042$ and $R_2 = 0.036$,[33] with all correlation coefficients <0.3, confirming assignment of the space group Cc. Reflection of the model through $y = 1/2$ did not generate a superior model. In the last cycle of refinement the maximum shift per error was 0.04 and the average shift/error was 0.01. The two highest peaks (ca. 0.33 e Å^{-3}) on a final difference map were within 1.0 Å of the iron or cobalt atoms. Mean values of $w\Delta^2$ decreased by a factor of 2 with increasing (sin $\theta)/\lambda$ and increased by the same amount with increasing $|F_o|$, indicating that a larger value of p would have been appropriate in assigning weights. Neutral atom scattering curves as given by Cromer[34] were used for Co, Fe, S, N, C, and O; those of Stewart[35] were used for H. Anomalous dispersion corrections[36] were made for Co, Fe, and S. The values of $|F_o|$ and F_c are listed in Table A.[37]

Structure Solution and Refinement, $[(en)_2Co(S(CH_2C_6H_5)-CH_2COO)](SCN)_2$. Solution and refinement of this structure were as above, with the following differences in procedures and data. Intensity statistics did not determine between the possible space groups $P1$ and $P\bar{1}$. A solution was found using Patterson methods for space group $P\bar{1}$ and subsequently refined. Hydrogen atoms were fixed at their calculated positions (trigonal geometry for hydrogen atoms on the benzene ring) and assigned isotropic temperature parameters of $B = 4.0$ Å^2. In the final cycles of least-squares refinement 246 parameters were varied. Convergence with $R_1 = 0.037$ and $R_2 = 0.035$ confirmed the choice of space group. In the final cycle of refinement the maximum shift/error was 0.76 and the average shift/error was 0.08. The highest peaks (ca. 0.8 e Å^{-3}) in a final difference map were generally located between bonded pairs of nonhydrogen atoms. Mean values of $w\Delta^2$ did not vary significantly with (sin $\theta)/\lambda$ or $|F_o|$. Anomalous dispersion corrections[36] were made for Co and S. The values of $|F_o|$ and F_c are listed in Table B.[37]

Results

Characterization. In addition to the x-ray structure analyses described below, the title complexes are characterized by (1) the synthetic route employed for their preparation, (2) elemental analyses (Table I) of isolated salts which give empirical compositions in agreement with those predicted, (3) cation-exchange elution characteristics which are consistent with the
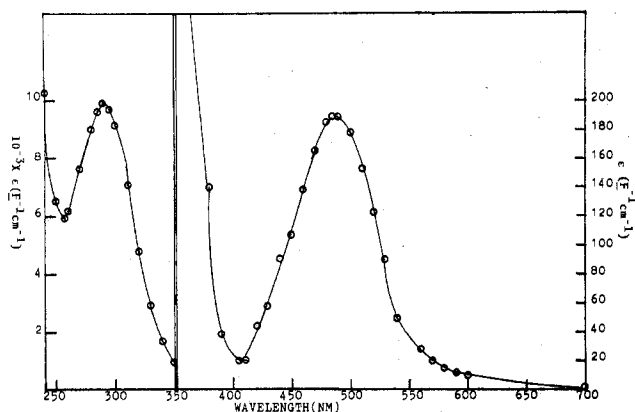
Figure 1. Visible and ultraviolet absorption spectra of [(en)$_2$Co-(S(CH$_2$C$_6$H$_5$)CH$_2$CH$_2$NH$_2$)]$^{3+}$ in dilute aqueous perchloric acid.
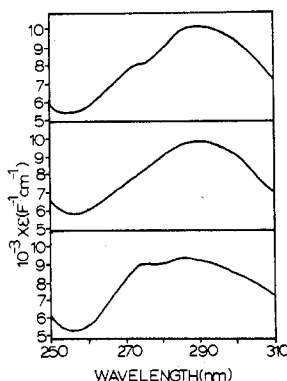

Figure 2. Ultraviolet absorption spectra of [(en)$_2$Co(S(R)-CH$_2$CH$_2$NH$_2$)]$^{3+}$ complexes in dilute aqueous perchloric acid: top, R = p-fluorobenzyl; middle, R = benzyl; bottom, R = p-methylbenzyl.
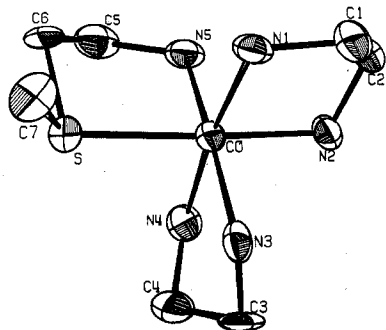

Figure 3. A perspective view of the cation [(en)$_2$Co(S(CH$_3$)-CH$_2$CH$_2$NH$_2$)]$^{3+}$ with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

assigned formal charges, and (4) the visible–UV and ^{1}H NMR spectral parameters listed in Tables II and III. With regard to the latter, the ^{1}H NMR spectra confirm the presence and identity of the organic moieties bonded to sulfur, while the visible–UV spectra exhibit 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 to a potentially oxidizing center.[11] Figure 1 shows the visible–UV spectrum of [(en)$_2$Co(S-(CH$_2$C$_6$H$_5$)CH$_2$CH$_2$NH$_2$)]$^{3+}$, while Figure 2 compares the UV LTMCT band of this benzyl complex with those of the related 4-fluorobenzyl and 4-methylbenzyl complexes.

Crystal Structures. In this section x-ray data are presented in pairs of analogous tables and figures, the first member of each pair containing data for [(en)$_2$Co(S(CH$_3$)-CH$_2$CH$_2$NH$_2$)][Fe(CN)$_6$]·4H$_2$O and the second member containing data for [(en)$_2$Co(S(CH$_2$C$_6$H$_5$)CH$_2$COO)](SCN)$_2$.

Table IV. Fractional Atomic Positional Parameters of [(en)$_2$Co(S(CH$_3$)CH$_2$CH$_2$NH$_2$)][Fe(CN)$_6$]^{a,b}

Atom	x	y	z
Co	0.50000 (–)	0.50248 (7)	0.50000 (–)
N(1)	0.6175 (5)	0.3782 (6)	0.5147 (4)
N(2)	0.5480 (4)	0.4960 (6)	0.6190 (3)
N(3)	0.5965 (5)	0.6439 (6)	0.5027 (4)
N(4)	0.3999 (5)	0.6350 (6)	0.4946 (4)
N(5)	0.4026 (5)	0.3688 (6)	0.4949 (4)
S(1)	0.4392 (2)	0.4948 (2)	0.3267 (1)
C(1)	0.6813 (6)	0.3685 (7)	0.6033 (5)
C(2)	0.6119 (6)	0.3815 (6)	0.6492 (4)
C(3)	0.5524 (7)	0.7652 (7)	0.5165 (5)
C(4)	0.4377 (7)	0.7565 (8)	0.4711 (5)
C(5)	0.3191 (7)	0.3446 (8)	0.4126 (6)
C(6)	0.3647 (8)	0.3473 (7)	0.3497 (5)
C(7)	0.5355 (7)	0.4458 (8)	0.3205 (4)
Fe	0.00350 (11)	0.50221 (12)	0.74602 (8)
C(11)	−0.0962 (6)	0.4876 (7)	0.7972 (4)
C(12)	−0.0431 (6)	0.3398 (7)	0.6887 (4)
C(13)	0.1085 (6)	0.5226 (7)	0.6934 (4)
C(14)	0.0489 (7)	0.6555 (7)	0.8019 (5)
C(15)	−0.0926 (6)	0.5983 (7)	0.6604 (5)
C(16)	0.1086 (7)	0.4147 (7)	0.8339 (4)
N(11)	−0.1578 (6)	0.4834 (7)	0.8271 (4)
N(12)	−0.0696 (5)	0.2458 (6)	0.6560 (4)
N(13)	0.1667 (6)	0.5330 (7)	0.6598 (5)
N(14)	0.0785 (6)	0.7493 (5)	0.8390 (4)
N(15)	−0.1532 (6)	0.6528 (7)	0.6077 (5)
N(16)	0.1708 (7)	0.3566 (7)	0.8856 (5)
O(1)	0.0167 (6)	0.6204 (4)	0.4994 (5)
O(2)	0.7635 (4)	0.4889 (4)	0.9554 (3)
O(3)	0.8414 (5)	0.9303 (5)	0.6347 (3)
O(4)	0.6982 (5)	0.6916 (5)	0.7196 (4)

^{a} Estimated errors in the last digit are given in parentheses. This form is used throughout. ^{b} The numbering scheme for the cation is shown in Figure 3. In the anion C(11) through C(15) are coordinated to Fe, and C(n) is bonded to N(n).

Table V. Fractional Atomic Positional Parameters of [(en)$_2$CoS(CH$_2$C$_6$H$_5$)(CH$_2$CO$_2$)](SCN)$_2$^{a}

Atom	x	y	z
Co	0.48442 (7)	0.31639 (7)	0.30640 (20)
S(1)	0.55382 (13)	0.37803 (12)	0.20247 (4)
S(2)	0.02733 (15)	0.79789 (17)	0.17419 (5)
S(3)	0.87436 (19)	0.16729 (16)	0.46258 (5)
O(1)	0.2099 (3)	0.2981 (3)	0.2847 (1)
O(2)	−0.0253 (4)	0.2986 (4)	0.2097 (1)
N(1)	0.5636 (4)	0.5791 (4)	0.3417 (1)
N(2)	0.7649 (4)	0.3391 (4)	0.3292 (1)
N(3)	0.3910 (4)	0.2659 (4)	0.3946 (1)
N(4)	0.4156 (4)	0.0535 (4)	0.2810 (1)
N(5)	−0.2852 (5)	0.8564 (5)	0.2492 (1)
N(6)	0.6701 (5)	0.3696 (5)	0.5408 (1)
C(1)	0.7595 (6)	0.6336 (5)	0.3826 (2)
C(2)	0.8880 (4)	0.5341 (6)	0.3456 (2)
C(3)	0.2688 (6)	0.0718 (6)	0.3858 (2)
C(4)	0.3662 (7)	−0.0342 (5)	0.3400 (2)
C(5)	0.1521 (5)	0.3297 (5)	0.2285 (2)
C(6)	0.3194 (5)	0.4212 (5)	0.1869 (2)
C(7)	0.5209 (5)	0.1698 (5)	0.1414 (2)
C(8)	0.5202 (6)	0.2100 (5)	0.0712 (2)
C(9)	0.3383 (7)	0.1513 (6)	0.0322 (2)
C(10)	0.3356 (10)	0.1856 (7)	−0.0322 (2)
C(11)	0.5078 (13)	0.2782 (7)	−0.0564 (2)
C(12)	0.6895 (10)	0.3387 (7)	−0.0179 (2)
C(13)	0.6938 (7)	0.3043 (6)	0.0463 (2)
C(14)	−0.1523 (5)	0.8358 (5)	0.2185 (2)
C(15)	0.7554 (5)	0.2866 (5)	0.5088 (1)

^{a} The numbering scheme for the cation is shown in Figure 4. One anion is comprised of S(2), C(14), and N(5), while the other is comprised of S(3), C(15), and N(6).

Final atomic positional parameters, and their estimated standard deviations, for nonhydrogen atoms are given in Tables IV and V. The corresponding anisotropic thermal parameters

Table VI. Root-Mean-Square Amplitudes of Vibration of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)][Fe(CN)_6]$ ($\times 10^3$ Å)

Atom	Min	Mean	Max
Co	137	147	175
N(1)	165	182	212
N(2)	152	180	206
N(3)	132	162	183
N(4)	155	170	219
N(5)	170	194	244
S(1)	157	175	259
C(1)	145	194	240
C(2)	143	191	252
C(3)	128	218	247
C(4)	152	196	292
C(5)	175	184	323
C(6)	158	205	341
C(7)	205	248	278
Fe	146	151	180
C(11)	154	181	189
C(12)	131	170	200
C(13)	169	178	231
C(14)	165	191	214
C(15)	150	185	203
C(16)	138	186	247
N(11)	226	248	260
N(12)	182	207	227
N(13)	228	253	273
N(14)	187	195	271
N(15)	183	204	271
N(16)	189	236	324
O(1)	208	228	314
O(2)	205	232	243
O(3)	220	268	319
O(4)	242	254	351

Table VII. Root-Mean-Square Amplitudes of Vibration of $[(en)_2CoS(CH_2C_6H_5)(CH_2CO_2)](SCN)_2$ ($\times 10^3$ Å)

Atom	Min	Mean	Max
Co	140	148	169
S(1)	150	151	186
S(2)	177	230	275
S(3)	202	269	278
N(1)	156	178	193
N(2)	168	180	206
N(3)	163	179	195
N(4)	163	173	189
N(5)	228	248	270
N(6)	213	252	280
O(1)	143	171	210
O(2)	155	204	253
C(1)	157	222	233
C(2)	156	209	236
C(3)	198	228	264
C(4)	176	200	289
C(5)	162	174	186
C(6)	166	189	219
C(7)	149	178	207
C(8)	151	180	229
C(9)	179	240	275
C(10)	193	271	365
C(11)	172	218	450
C(12)	209	220	396
C(13)	192	210	297
C(14)	181	200	227
C(15)	137	199	227

may be found in Tables C[37] and D,[37] the root-mean-square displacements calculated therefrom are collected in Tables VI and VII, and the associated ellipsoids for the complex cations are shown in Figures 3 and 4. Bond lengths and angles not involving hydrogen atoms are presented in Tables VIII and IX and Tables X and XI, respectively. Tables E[37] and F[37] contain hydrogen atom positional parameters, while Tables XII and XIII detail possible hydrogen bonds.

Both crystal structures involve discrete cationic cobalt(III) complexes containing a coordinated thioether. The cobalt(III)

Table VIII. Bond Lengths of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)][Fe(CN)_6]$ (Å)

	Cation		
Co-S(1)	2.267 (10)	Co-N(3)	1.988 (6)
Co-N(1)	2.025 (7)	Co-N(4)	1.942 (6)
Co-N(2)	1.968 (9)	Co-N(5)	1.927 (7)
S-C(6)	1.834 (9)	N(4)-C(4)	1.500 (11)
S-C(7)	1.817 (12)	N(5)-C(5)	1.516 (15)
N(1)-C(1)	1.499 (13)	C(1)-C(2)	1.466 (15)
N(2)-C(2)	1.477 (10)	C(3)-C(4)	1.492 (15)
N(3)-C(3)	1.476 (10)	C(5)-C(6)	1.463 (17)

	Anion		
Fe-C(11)	1.904 (11)	Fe-C(14)	1.884 (8)
Fe-C(12)	1.979 (8)	Fe-C(15)	1.904 (13)
Fe-C(13)	1.994 (12)	Fe-C(16)	1.934 (14)
C(11)-N(11)	1.150 (13)	C(14)-N(14)	1.178 (10)
C(12)-N(12)	1.141 (9)	C(15)-N(15)	1.155 (12)
C(13)-N(13)	1.162 (15)	C(16)-N(16)	1.175 (12)

Table IX. Bond Lengths of $[(en)_2CoS(CH_2C_6H_5)(CH_2CO_2)](SCN)_2$ (Å)

	Cation		
Co-S(1)	2.274 (1)	Co-N(2)	1.949 (3)
Co-O(1)	1.913 (2)	Co-N(3)	1.980 (3)
Co-N(1)	1.977 (3)	Co-N(4)	1.955 (3)
S(1)-C(6)	1.802 (4)	N(1)-C(1)	1.491 (5)
S(1)-C(7)	1.842 (3)	N(2)-C(2)	1.490 (5)
O(1)-C(5)	1.291 (4)	N(3)-C(3)	1.482 (5)
O(2)-C(5)	1.225 (4)	N(4)-C(4)	1.476 (5)
C(1)-C(2)	1.503 (6)	C(8)-C(13)	1.365 (6)
C(3)-C(4)	1.468 (6)	C(9)-C(10)	1.382 (6)
C(5)-C(6)	1.521 (5)	C(10)-C(11)	1.347 (9)
C(7)-C(8)	1.513 (5)	C(11)-C(12)	1.383 (10)
C(8)-C(9)	1.390 (6)	C(12)-C(13)	1.378 (7)

	Anions		
S(2)-C(14)	1.632 (4)	N(5)-C(14)	1.167 (5)
S(3)-C(15)	1.640 (4)	N(6)-C(15)	1.152 (5)

Table X. Bond Angles of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)][Fe(CN)_6]$ (deg)

Cation
Cobalt Coordination Angles

S(1)-Co-N(1)	94.7 (2)	N(1)-Co-N(5)	92.3 (3)
S(1)-Co-N(2)	175.5 (3)	N(2)-Co-N(3)	92.2 (2)
S(1)-Co-N(3)	92.1 (2)	N(2)-Co-N(4)	92.0 (3)
S(1)-Co-N(4)	89.6 (2)	N(2)-Co-N(5)	89.0 (3)
S(1)-Co-N(5)	86.8 (3)	N(3)-Co-N(4)	85.1 (3)
N(1)-Co-N(2)	84.1 (3)	N(3)-Co-N(5)	178.1 (3)
N(1)-Co-N(3)	89.4 (3)	N(4)-Co-N(5)	93.3 (3)
N(1)-Co-N(4)	173.1 (3)		

Methyl 2-Aminoethyl Thioether Angles

S(1)-C(6)-C(5)	107.1 (6)	C(6)-C(5)-N(5)	110.1 (8)
C(7)-S-C(6)	99.4 (5)	C(5)-N(5)-Co	116.1 (6)
C(7)-S-Co	114.2 (2)	C(6)-S-Co	97.9 (3)

Ethylenediamine Angles

Co-N(2)-C(2)	109.9 (5)	Co-N(3)-C(3)	110.3 (5)
N(2)-C(2)-C(1)	107.4 (6)	N(3)-C(3)-C(4)	106.0 (6)
C(2)-C(1)-N(1)	108.8 (6)	C(3)-C(4)-N(4)	108.0 (6)
C(1)-N(1)-Co	108.5 (5)	C(4)-N(4)-Co	108.7 (5)

Anion

C(11)-Fe-C(12)	91.1 (4)	C(13)-Fe-C(16)	88.3 (4)
C(11)-Fe-C(13)	178.4 (4)	C(14)-Fe-C(15)	87.8 (3)
C(11)-Fe-C(14)	88.8 (4)	C(14)-Fe-C(16)	88.8 (3)
C(11)-Fe-C(15)	90.6 (4)	C(15)-Fe-C(16)	175.7 (4)
C(11)-Fe-C(16)	92.1 (4)	Fe-C(11)-N(11)	177.4 (7)
C(12)-Fe-C(13)	90.5 (3)	Fe-C(12)-N(12)	179.6 (15)
C(12)-Fe-C(14)	179.2 (9)	Fe-C(13)-N(13)	177.2 (7)
C(12)-Fe-C(15)	93.0 (3)	Fe-C(14)-N(14)	177.9 (8)
C(12)-Fe-C(16)	90.4 (3)	Fe-C(15)-N(15)	177.5 (7)
C(13)-Fe-C(14)	89.7 (4)	Fe-C(16)-N(16)	177.1 (7)
C(13)-Fe-C(15)	89.0 (4)		

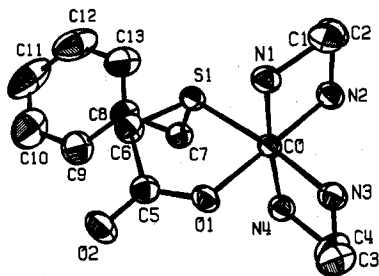centers are six-coordinate (five ammine nitrogen atoms and the thioether sulfur atom in $[(en)_2Co(S(CH_3)-$

Figure 4. A perspective view of the cation [(en)₂Co(S-(CH₂C₆H₅)CH₂COO)]²⁺ with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table XI. Bond Angles of
[(en)₂CoS(CH₂C₆H₅)(CH₂CO₂)](SCN)₂ (deg)

Metal Coordination Angles			
S(1)–Co–N(1)	89.7 (1)	N(1)–Co–O(1)	93.4 (1)
S(1)–Co–N(2)	92.2 (1)	N(2)–Co–N(3)	94.7 (1)
S(1)–Co–N(3)	173.0 (1)	N(2)–Co–N(4)	91.1 (1)
S(1)–Co–N(4)	95.7 (1)	N(2)–Co–O(1)	179.1 (5)
S(1)–Co–O(1)	87.9 (1)	N(3)–Co–N(4)	85.5 (1)
N(1)–Co–N(2)	85.7 (1)	N(3)–Co–O(1)	85.1 (1)
N(1)–Co–N(3)	89.6 (1)	N(4)–Co–O(1)	93.4 (1)
N(1)–Co–N(4)	173.9 (2)		

Ethylenediamine Angles			
Co–N(1)–C(1)	108.5 (3)	N(1)–C(1)–C(2)	106.5 (3)
Co–N(2)–C(2)	109.8 (3)	N(2)–C(2)–C(1)	107.5 (3)
Co–N(3)–C(3)	107.5 (2)	N(3)–C(3)–C(4)	108.9 (3)
Co–N(4)–C(4)	110.3 (2)	N(4)–C(4)–C(3)	108.4 (6)

Mercaptoacetate Angles			
Co–O(1)–C(5)	122.2 (2)	O(1)–C(5)–O(2)	123.8 (3)
Co–S(1)–C(6)	94.4 (1)	O(1)–C(5)–C(6)	116.0 (3)
Co–S(1)–C(7)	111.6 (1)	C(6)–S(1)–C(7)	101.4 (2)
S(1)–C(6)–C(5)	113.5 (3)	O(2)–C(5)–C(6)	120.1 (3)

Benzyl Angles			
S(1)–C(7)–C(8)	110.1 (3)	C(9)–C(10)–C(11)	120.0 (5)
C(7)–C(8)–C(9)	118.9 (3)	C(10)–C(11)–C(12)	121.0 (3)
C(7)–C(8)–C(13)	121.1 (3)	C(11)–C(12)–C(13)	119.4 (5)
C(8)–C(9)–C(10)	119.6 (4)	C(12)–C(13)–C(8)	120.0 (4)

Thiocyanate Angles			
S(2)–C(14)–N(5)	177.5 (4)	S(1)–C(15)–N(6)	179.3 (6)

Table XII. Possible Hydrogen Bonding in
[(en)₂Co(S(CH₃)CH₂CH₂NH₂)][Fe(CN)₆]ᵃ

A,H,B	H···B, Å	A···B, Å	A–H···B, deg
N(1),H(2),O(1)ᵇ	2.21	3.03	155.15
N(1),H(1),O(2)ᶜ	2.10	2.94	161.70
N(2),H(8),O(4)	2.17	3.01	162.94
N(2),H(7),O(3)ᵈ	2.21	3.03	157.15
N(3),H(9),N(15)ᵉ	2.47	3.27	153.54
N(3),H(10),N(14)ᶠ	2.26	3.04	148.06
N(4),H(16),N(12)ᵍ	2.19	2.97	150.14
N(4),H(15),N(16)ᶜ	2.23	3.04	155.65
N(5),H(18),O(3)ᵈ	2.12	2.96	163.02
N(5),H(17),O(1)ᵇ	2.22	3.04	157.43

A,B	A···B, Å	A,B	A···B, Å
N(11),O(2)ʲ	2.85	N(13),O(3)ᵍ	2.82
N(11),O(4)	3.11	N(15),O(3)ᵉ	2.98
N(11),O(1)ʰ	3.31	N(15),O(4)ᵉ	3.35
N(12),O(4)ᵍ	3.49	N(15),O(2)ⁱ	2.93
N(13),O(1)	2.99	N(16),O(1)ʰ	3.42
		O(1),O(2)ⁱ	3.48

ᵃ Includes any hydrogen bond where A···B distance ≤3.5 Å. ᵇ Transformed to x + ¹/₂, y − ¹/₂, z. ᶜ Transformed to x, 1 − y, z − ¹/₂. ᵈ Transformed to x − ¹/₂, y − ¹/₂, z. ᵉ Transformed to x + 1, y, z. ᶠ Transformed to x − ¹/₂, ³/₂ − y, z − ¹/₂. ᵍ Transformed to x + ¹/₂, y + ¹/₂, z. ʰ Transformed to x, 1 − y, z + ¹/₂. ⁱ Transformed to x + 1, 1 − y, z + ¹/₂. ʲ Hydrogen atoms of water were not located in this refinement.

**Table XIII.** Possible Hydrogen Bonding in
[(en)₂CoS(CH₂C₆H₅)(CH₂CO₂)](SCN)₂ᵃ

A,H,B	A···B, Å	A···B, Å	A–H···B, deg
N(1),H(1),N(6)ᵇ	2.163	2.968	153.58
N(1),H(2),N(5)ᶜ	2.240	3.066	158.39
N(2),H(8),O(2)ᶜ	2.100	2.890	150.55
N(3),H(10),N(6)ᵇ	2.374	3.122	144.10
N(4),H(15),N(5)ᵈ	2.198	2.989	151.04
N(4),H(16),S(2)ᵉ	2.498	3.332	160.42

ᵃ Includes any possible hydrogen bond where A···B distance ≤3.5 Å. ᵇ Transformed to 1 − x, 1 − y, 1 − z. ᶜ Transformed to 1 + x, y, z. ᵈ Transformed to 1 + x, y − 1, z. ᵉ Transformed to x, y − 1, z.

CH₂CH₂NH₂)]³⁺, four amine nitrogen atoms, a carboxylate oxygen atom, and the thioether sulfur atom in [(en)₂Co(S-(CH₂C₆H₅)CH₂COO)]²⁺) in a configuration that closely approximates octahedral. The major distortion from octahedral geometry results from steric crowding between an ammine ligand and the nonchelating alkyl group of the thioether. Thus, in [(en)₂Co(S(CH₃)CH₂CH₂NH₂)]³⁺ the methyl group interacts with N(1) causing it to bend away from the sulfur atom and toward N(2) [N(1)–Co–S(1) = 94.7 (2), N(1)–Co–N(2) = 84.1 (3)°]; in [(en)₂Co(S(CH₂C₆H₅)-CH₂COO)]²⁺ the benzyl group interacts with N(4) causing it to bend away from the sulfur atom and toward N(3) [N-(4)–Co–S(1) = 95.7 (1), N(4)–Co–N(3) = 85.5 (1)°]. In addition, both structures incorporate loose networks of hydrogen bonds (Tables XII and XIII) similar to those observed in related structures.[3,23,24,38] In all of these structures there is no obvious correlation between the hydrogen bonding of a given amine ligand and the associated Co–N bond length.

The geometry of the [Fe(CN)₆]³⁻ anion of [(en)₂Co(S-(CH₃)CH₂CH₂NH₂)][Fe(CN)₆]·4H₂O can best be described as octahedral with distortion along a trigonal axis. The face of the octahedron which is defined by N(11), N(14), and N(15) is significantly closer to the iron center than is the opposite face defined by N(12), N(13), and N(16) (average Fe–N distances of 3.058 (4) and 3.128 (25) Å, respectively). Similar distortions, characterized by widely varying M–C bond lengths, have been observed in other hexacyanometalate(III)

complexes.[39–42] The average C–N bond length in the [Fe-(CN)₆]³⁻ anion is 1.160 (14) Å, in agreement with other values reported for cyanometalate complexes ([Fe(CN)₆]³⁻, 1.143 (21) Å;[42] [Co(CN)₆]³⁻, 1.154 (24),[42] 1.155 (8),[39] 1.160 (18);[40] [Mn(CN)₆]³⁻, 1.142 (12) Å;[41] [Ni(CN)₅]³⁻, 1.156 (4) Å[43]). The thiocyanate anions of [(en)₂Co(S(CH₂C₆H₅)-CH₂COO)](SCN)₂ have reasonable bond lengths, thermal parameters, and bond angles, and are entirely as expected from other structure determinations.[23]

Discussion

Synthesis and Properties of Title Complexes. The general procedure used in this work for the synthesis of coordinated thioethers involves alkylation of a coordinated thiol in N,-N-dimethylformamide (DMF).

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + RX \xrightarrow{DMF}$$
$$(en)_2Co(S(R)CH_2CH_2NH_2)^{3+} + X^- \qquad (1)$$
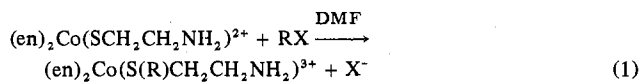
DMF provides a decidedly superior medium for these alkylation reactions, relative to the methanol–water medium previously used.[15,17] This is due both to the meritorious properties of DMF as a solvent for alkylation reactions[44] and also to the fact that most alkyl halides and coordination complex perchlorate salts are soluble in DMF and therefore reactions in this medium are homogeneous. Contrariwise, most alkyl halides and coordination complex perchlorates are only slightly soluble in methanol–water, and reactions in this

medium are generally heterogeneous. Thus the use of DMF as reaction solvent extends the general alkylation route to allow synthesis of complexes not accessible via the use of methanol–water; e.g., in methanol–water, cyclohexylmethyl bromide does not detectably react with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ over a period of months, but in DMF the reaction proceeds at a modest rate (50% completion in ca. 90 days). The advantageous use of DMF as a solvent for alkylation of coordinated thiols has previously been noted by Busch.[45]

All of the thioether complexes prepared in this work are very stable, showing no evidence for Co–S bond fission in acidic solution or in the solid (decomposition does occur in alkaline media). This observation is not at variance with the results of Kothari and Busch[15] who report the facile conversion of N,S-$[(en)_2Co(S(CH_3)CH_2CH(COO)NH_2)]^{2+}$ to N,O-$[(en)_2Co(OOCCH(CH_2SCH_3)NH_2)]^{2+}$ since in this particular complex the geometry of the "flexidentate" S-methylcysteinato ligand places the noncoordinated carboxylate group in an ideal position to displace the coordinated thioether group. Thus the cobalt–thioether bond cleavage reported by Kothari and Busch[15] seems to be a special case induced by the peculiar properties of the S-methylcysteinato ligand which promote intraligand substitution, whereas in general the cobalt–thioether bond is resistant to interligand substitution.

An intense ligand-to-metal charge-transfer (LTMCT) band, characteristic of coordinated chalcogens,[3,11] dominates the UV spectra of the thioether complexes prepared in this work (Table II). Figure 2 clearly shows that this band is composite in nature, arising from at least two distinct electronic transitions. This multiplicity may arise because (a) transitions originate on both bonding and nonbonding sulfur-centered levels or (b) transitions terminate on nondegenerate cobalt-centered antibonding levels, or (c) both situations (a) and (b) obtain. No matter what the origin of the multiplicity, the composite nature of the LTMCT band means that its observed position will largely be determined by the relative transition probabilities of the component transitions. Since there is no reason to assume that the "dominant" component will remain the same as the chalcogen ligand is varied, it becomes very difficult to correlate observed LTMCT band positions with the nature of the ligand or with a simple parameter such as the reducing power of the chalcogen ligand. For example, from Table II it is seen that for either the cysteamine or thioglycollate systems, altering the nature of the coordinated chalcogen from a thiol to a methyl thioether causes only a 2-nm blue shift in the observed LTMCT band position, whereas merely varying the R group on the thioether from methyl to benzyl leads to a ca. 10-nm red shift.

The visible spectra of the thioether complexes are dominated by the cobalt(III) $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition at ca. 500 nm. The $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transition expected at ca. 350 nm is almost always obscured by the tail of the UV LTMCT band, although in some cases a shoulder at ca. 350 nm is observed. The intensities of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions are somewhat greater than normal, presumably because of "intensity stealing" from the LTMCT band. For most of the $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes the $^1A_{1g} \rightarrow {}^1T_{1g}$ band lies in the range 486–490 nm independent of the R group. When R is 1-naphthylmethyl or 2-naphthylmethyl, the tail of the LTMCT band extends far enough into the visible region to cause the position of maximum absorbance to shift 5–10 nm to the blue. It is interesting that the visible spectrum of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ exhibits a shoulder at ca. 600 nm which presumably arises because the asymmetric field provided by five nitrogen atoms and one weak-field thiolato sulfur atom causes splitting of the $^1T_{1g}$ excited state.[15,46] However, none of the $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ complexes exhibit any noticeable absorbance at 600 nm or any noticeable splitting

of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band.[47] While this observation may be due to differing transition probabilities in the thiolato and thioether systems, it does suggest the possibility that in these complexes a coordinated thioether provides a somewhat stronger ligand field than does a coordinated thiolate. This suggestion receives support from the observation that in the thioglycollate system the thiolato complex absorbs at lower energy (518 nm) than do the thioether complexes (499 and 504 nm; see Table II). If true, this result implies considerable back-bonding from cobalt(III) to sulfur since, as first generalized by Williams, the principal difference between RS⁻ and RSR as ligands is that the former are more highly polarizable, but not as effective dπ acceptors as the latter.[48]

Structural Characteristics. Chronologically, the structural analysis of $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)][Fe(CN)_6]\cdot 4H_2O$ was completed first. This analysis confirmed the presence of a coordinated thioether and generally showed the structural features of the complex to be normal in all respects. However, the range of Co–N bond lengths (1.927 (7)–2.025 (7) Å; see Table VIII) and the relatively large esd's associated with these bond lengths made establishment of the thioether-induced structural trans effect, STE, very uncertain (0.00 (5) Å) and also raised suspicions of a possible quirk in the analysis. In order to resolve this situation a second structural analysis was undertaken on a compound, $[(en)_2Co(S(CH_2C_6H_5)\text{-}CH_2COO)](SCN)_2$, specifically chosen to have properties (cation charge, R group steric requirements, anion structure, hydrogen-bonding requirements, etc.) considerably different from those of the original compound. This analysis confirmed the results of the original and also yielded a smaller range of Co–N bond lengths (1.949 (3)–1.980 (3) Å; see Table IX) permitting a somewhat more precise calculation of the STE induced by coordinated thioether sulfur (0.02 (2) Å). The average Co–N bond lenghts in these two structures (1.97 (5) and 1.96 (2) Å) are in agreement with each other and with the average cis Co–N bond lengths observed in the analogous thiolato complexes (1.960 (9) and 1.965 (7) Å).[23] Overall, both structures are largely as expected with bond lengths and bond angles in agreement with those previously observed in similar structures.[3,23,24,38]

Interestingly, the most remarkable feature of these thioether complex structures is the *absence* of a significant STE. This result is somewhat surprising in view of the fact that coordinated sulfur induces a significant STE in the analogous thiolato,[23] sulfenato,[24] and sulfinato[3] complexes, as well as in pentaamminecobalt(III) complexes containing S-bonded SO_3^{2-} and RSO_2^{-}.[38] However, all these sulfur ligands which do induce a STE also carry a formal negative charge, while the thioether ligand is neutral. This difference would seem to be crucial since it is generally accepted[49] that charge donation from sulfur to cobalt(III) is the underlying cause of trans effects. This interpretation receives support from the recent observation[50] that the coordinated sulfur of (thiosulfato-S)-pentaamminecobalt(III) does not exert a significant STE; the coordinated sulfur of S-bonded thiosulfate presumably carries a formal charge which is close to 0. These studies allow us to establish[51] the following STE series for cobalt(III): SO_3^{2-} > RSO⁻ > RSO_2^{-} > RS⁻ > $S_2O_3^{2-}$ ≃ RSR. An analysis of this ordering will be published separately.[52]

The fact that thioether sulfur does not exert a significant STE when coordinated to cobalt(III) is also of interest in terms of Worrell's observations on the kinetics of ligand substitution in the *cis*-dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) cation.[22] Worrell finds that ligand substitution trans to a coordinated thioether is *not* enhanced relative to substitution trans to a nitrogen ligand. This is entirely consistent with the fact that substitution trans to S-bonded SO_3^{2-} and RSO_2^{-}, which do induce significant STE's, proceeds *more* rapidly than

substitution trans to nitrogen[38]. Thus, in cobalt(III) chemistry, there seems to be a definite correlation between structural trans effects and kinetic trans effects, presumably because a longer bond is a weaker bond that is more readily cleaved in either a dissociative or an associative process.[2]

Registry No. [Co(en)$_2$(S(CH$_3$)(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 60803-59-0; [Co(en)$_2$(S(CH$_3$)(CH$_2$)$_2$NH$_2$)]I$_3$, 54453-46-2; [Co(en)$_2$(S(CH$_3$)-(CH$_2$)$_2$NH$_2$)][Co(CN)$_6$], 65622-70-0; [Co(en)$_2$(S(CH$_3$)-(CH$_2$)$_2$NH$_2$)][Fe(CN)$_6$], 65622-69-7; [Co(en)$_2$(S(CH$_2$C$_6$H$_5$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-68-6; [Co(en)$_2$(S(CH$_2$C$_6$H$_5$)-(CH$_2$)$_2$NH$_2$)]I$_3$, 54453-52-0; [Co(en)$_2$(S(1-CH$_2$C$_{10}$H$_7$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65651-36-7; [Co(en)$_2$(S(2-CH$_2$C$_{10}$H$_7$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-92-6; [Co(en)$_2$(S(CH$_2$C$_6$H$_{11}$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-90-4; [Co(en)$_2$(S(CH$_2$CO$_2$CH$_3$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-88-0; [Co(en)$_2$(S(CH$_2$CO$_2$H)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-86-8; [Co(en)$_2$(S((CH$_2$)$_2$CO$_2$H)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-84-6; [Co(en)$_2$(S((CH$_2$)$_3$CO$_2$H)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-82-4; [Co(en)$_2$(S(p-CH$_2$C$_6$H$_4$F)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-80-2; [Co(en)$_2$(S(p-CH$_2$C$_6$H$_4$CH$_3$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-78-8; [Co(en)$_2$(S(CH$_2$CH$_3$)-(CH$_2$)$_2$NH$_2$)](ClO$_4$)$_3$, 65622-76-6; [Co(en)$_2$(S(CH$_2$C$_6$H$_5$)-CH$_2$COO)](SCN)$_2$, 65622-74-4; [(en)$_3$Co]$^{2+}$, 23523-25-3; [(en)$_2$Co(SCH$_2$CH$_2$N$_2$)](ClO$_4$)$_2$, 40330-50-5; [(en)$_2$Co-(SCH$_2$COO)]Cl, 42901-31-5; (hydroxymethyl)cyclohexane, 100-49-2.

Supplementary Material Available: Tables A–F giving $|F_o|$ and F_c, anisotropic thermal parameters, and hydrogen atom positional parameters (23 pages). Ordering information is given on any current masthead page.

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