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## Synthesis, Characterization, and Redox Studies of Thiolate, Thioether, Alkoxy, and Carboxylate Chelate Complexes with Bis(ethylenediamine)cobalt(III)<sup>1a</sup>

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The preparation and properties (ion exchange, electronic, and <sup>1</sup>H NMR absorption) of Co<sup>III</sup>(en)<sub>2</sub>(X-Y)<sup>n+</sup> complexes with X-Y = (H)ECH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, (H)ECH<sub>2</sub>CH<sub>2</sub>OH, (H)ECH<sub>2</sub>COO, (H)ECH(CH<sub>3</sub>)COO (E = S, O), CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, CH<sub>3</sub>SCH<sub>2</sub>COO, and NH<sub>2</sub>CH<sub>2</sub>COO as chelate ligands are described in conjunction with kinetic studies of their reactions with Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, V(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> as reductants. Inner-sphere rate enhancement factors of 35–3400 are observed for thiolate bridging over analogous alkoxide bridging to Cr(II) and attributed to a diminished steric accessibility of the oxygen atom and, perhaps, a ground-state elongation of the Co–N bond trans to an efficient sulfur bridge. Substitution control is evident in parallel inner-sphere reductions by V(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, whereas a comparative kinetic advantage for the thiolate class is again evident in outer-sphere reduction by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> although at a low reactivity level. Reduction pathways utilizing carboxylate bridging functions are found subject to both chelate and substituent steric effects and nonbridging ligand electronic effects, particularly from a cis thioether donor. In the absence of facile bridging ligands, the latter function appears to engender a relatively high degree of outer-sphere reactivity toward Cr(II). Rate laws, constants, and, where accessible, activation parameters are reported and discussed in the context of the limited data presently available for this class of chelating ligand.

### Introduction

Our interest in how coordinated thiolate and thioether functions affect the redox behavior of transition metal centers was aroused by the widespread occurrence of such coordination in iron–sulfur<sup>2</sup> and cytochrome *c*<sup>3</sup> electron-transfer proteins<sup>4</sup> as well as heme monooxygenases.<sup>4</sup> Our early studies<sup>5</sup> revealed that, relative to its alcoholate analogue, a thiolate coordinated to cobalt(III) functions extremely efficiently as a bridge in inner-sphere reactions, perhaps related to the efficient transfer mediation subsequently reported for sulfur-bridging thiocyanate.<sup>6</sup> We have since discovered high reactivities for thiolate functions in outer-sphere reactions also, at least for the tetrahedrally distorted Fe(II)–Fe(III) couple of rubredoxin.<sup>2e,7</sup> Additionally, thioether coordination to cobalt(III) appears to bestow unique kinetic redox features.<sup>8</sup> It is the purpose of this paper to amplify and extend observations in this area of coordinated sulfur redox chemistry, including alcoholate and carboxylate comparison reactions.

Certain features of the complexes are notable aside from possible biological relevance. The use of a divalent chalcogen donor atom, unlike one from groups 5 and 7, permits the introduction of substituents on that atom without precluding its function as an electron-transfer bridge. This allows exploration of the effects of chelation and steric modification on static and dynamic properties. For example, we have found chelated alcohol complexes to be substantially more acidic than closely similar monodentate complexes.<sup>9</sup> Kinetic anomalies also appear to arise from chelation in certain of our redox studies to be discussed. In the accompanying paper,<sup>10</sup> which deals with the substitution behavior of the chromium(III) product complexes,<sup>11,12</sup> evidence is presented for redox catalysis that is enhanced by pendent chelate functions.

### Experimental Section

**Equipment.** Visible and ultraviolet spectra (Table I) were measured on a Cary Model 14 spectrophotometer. Infrared spectra were measured in KBr pellets with a Perkin-Elmer Model 337 recording spectrophotometer. <sup>1</sup>H NMR spectra (Table II) were obtained at 37 °C using a Varian A-60A spectrometer. Fast reactions were analyzed using Polaroid photographs from a thermostated Durum-Gibson Model D-110 stopped-flow spectrophotometer. Aside from flushing the system with several rinses of deaerated reactant solutions, no special precautions were necessary where air-sensitive reductant concentrations exceeded ~5 × 10<sup>-4</sup> M. Slower reactions were followed using an all-glass mixing device<sup>13</sup> in the thermostated cell compartment of the Cary 14.

Table I. Spectral Parameters of Various Cobalt(III) Complexes<sup>a</sup>

Entry	Species	λ <sub>1</sub> (ε)	λ <sub>2</sub> (ε)	λ <sub>3</sub> (ε)
1	Co(en) <sub>2</sub> (SCH <sub>2</sub> -COO) <sup>+</sup>	518 (152)		282 (11 700)
2	Co(en) <sub>2</sub> (OCH <sub>2</sub> -COO) <sup>+</sup>	518 (132)	360 (140)	...
3	Co(en) <sub>2</sub> (HOCH <sub>2</sub> -COO) <sup>2+</sup>	499 (113)	348 (122)	...
4	Co(en) <sub>2</sub> (SCH(CH <sub>3</sub> )COO) <sup>+</sup>	517 (153)	360 sh (350)	282 (12 350)
5	Co(en) <sub>2</sub> (OCH(CH <sub>3</sub> )COO) <sup>+</sup>	517 (139)	360 (150)	...
6	Co(en) <sub>2</sub> (HOCH(CH <sub>3</sub> )COO) <sup>2+</sup>	499 (113)	349 (123)	...
7	Co(en) <sub>2</sub> (SCH <sub>2</sub> -CH <sub>2</sub> NH <sub>2</sub> ) <sup>2+</sup> <sup>b</sup>	482 (138)	370 sh (283)	282 (13 200)
8	Co(en) <sub>2</sub> (OCH <sub>2</sub> -CH <sub>2</sub> NH <sub>2</sub> ) <sup>2+</sup>	490 (98.7)	347 (104)	...
9	Co(en) <sub>2</sub> (HOCH <sub>2</sub> -CH <sub>2</sub> NH <sub>2</sub> ) <sup>3+</sup>	486 (79.4)	344 (87.8)	...
10	Co(en) <sub>2</sub> (SCH <sub>2</sub> -CH <sub>2</sub> O) <sup>+</sup>	524 (139)		283 (10 840)
11	Co(en) <sub>2</sub> (SCH <sub>2</sub> -CH <sub>2</sub> OH) <sup>2+</sup>	520 (156)		283 (14 560)
12	Co(en) <sub>2</sub> (OCH <sub>2</sub> -CH <sub>2</sub> O) <sup>+</sup>	523 (137)	382 (195?)	...
13	Co(en) <sub>2</sub> (HOCH <sub>2</sub> -CH <sub>2</sub> OH) <sup>3+</sup>	500 (112)	355 (82)	...
14	Co(en) <sub>2</sub> (CH <sub>3</sub> -SCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sup>3+</sup>	487 (172)	350 sh (276)	282 (7800)
15	Co(en) <sub>2</sub> (CH <sub>3</sub> -SCH <sub>2</sub> COO) <sup>2+</sup>	499 (168)	360 sh (250)	280 (7300)

<sup>a</sup> Wavelengths, λ, of maxima or shoulders (sh) are in nm; molar extinction coefficients, ε, given in parentheses, are in M<sup>-1</sup> cm<sup>-1</sup>, "... " signifies no band observed; no entry signifies shoulder not observed. Intense absorption was noted in certain complexes at higher energy (~240 nm) but not studied. <sup>b</sup> At 600 nm a shoulder (ε 41.4) was detected as similar to that at 593 nm (ε 38) in the analogous N-S cysteine complex.<sup>28</sup>

**Analyses.** Analyses for C, H, S, and N were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Cobalt was determined using 2,2',2''-terpyridine (terpy)<sup>14</sup> following complex decomposition by liquid fire (7 parts 70% HClO<sub>4</sub>–3 parts 70% HNO<sub>3</sub>). Development and measurement of absorption at 505 nm due to Co(terpy)<sub>2</sub><sup>2+</sup> were accomplished anaerobically, and a molar absorptivity of 1386 M<sup>-1</sup> cm<sup>-1</sup> determined with known solutions<sup>15</sup> was used rather than the

Table II. <sup>1</sup>H NMR of Various Protons Adjacent to Chalcogens<sup>a</sup>

Entry	Species	Medium	Methylene protons x	Methyl protons y	Methinyl protons	Ref
A. Thiolato and Alkoxy Species						
1	NaOOCCH <sub>2</sub> SD	D <sub>2</sub> O	3.51	...	...	b
2	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> S) <sup>+</sup>	D <sub>2</sub> O	3.10	...	...	c
3	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> S) <sup>+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	3.10	...	...	c
4	DOOCCH <sub>2</sub> OD	D <sub>2</sub> O	4.29	...	...	b
5	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> OD) <sup>2+</sup>	D <sub>2</sub> O	3.90	...	...	c
6	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> OD) <sup>2+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	4.26	...	...	c
7	DSCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ·DCI	D <sub>2</sub> O	2.85	...	...	b
8	Co(en) <sub>2</sub> (SCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sup>2+</sup>	D <sub>2</sub> O	2.20 mult	...	...	c
9	DOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	D <sub>2</sub> O	3.54	...	...	b
10	Co(en) <sub>2</sub> (OCH <sub>2</sub> CH <sub>2</sub> NH) <sup>2+</sup>	D <sub>2</sub> O-NaOD	3.19	...	...	c
11	Co(en) <sub>2</sub> (DOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sup>3+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	3.60	...	...	c
12	DOCH <sub>2</sub> CH <sub>2</sub> OD	D <sub>2</sub> O	3.68	...	...	b
13	Co(en) <sub>2</sub> (OCH <sub>2</sub> CH <sub>2</sub> O) <sup>+</sup>	D <sub>2</sub> O	3.00	...	...	c
14	Co(en) <sub>2</sub> (DOCH <sub>2</sub> CH <sub>2</sub> OD) <sup>3+</sup>	D <sub>2</sub> O-D <sub>2</sub> SO <sub>4</sub>	3.75	...	...	c
15	DOCH <sub>2</sub> CH <sub>2</sub> SD	D <sub>2</sub> O	3.69 t (xo) 2.68 t (xs)	...	...	b
16	Co(en) <sub>2</sub> (OCH <sub>2</sub> CH <sub>2</sub> S) <sup>+</sup>	D <sub>2</sub> O	3.00 mult (xo) 1.92 mult (xs)	...	...	c
17	Co(en) <sub>2</sub> (DOCH <sub>2</sub> CH <sub>2</sub> S) <sup>2+</sup>	D <sub>2</sub> O-D <sub>2</sub> SO <sub>4</sub>	~3.6 mult (xo) ~2.1 mult (xs)	...	...	c
18	DOOCCH(CH <sub>3</sub> )SD	D <sub>2</sub> O	...	1.48	3.65	c
19	Co(en) <sub>2</sub> (OOCCH(CH <sub>3</sub> )S) <sup>+</sup>	D <sub>2</sub> O	...	1.32	3.51	c
20	Co(en) <sub>2</sub> (OOCCH(CH <sub>3</sub> )S) <sup>+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	...	1.32	3.51	c
21	NaOOCCH(CH <sub>3</sub> )OD	D <sub>2</sub> O	...	1.30	4.09	b
22	Co(en) <sub>2</sub> (OOCCH(CH <sub>3</sub> )O) <sup>+</sup>	D <sub>2</sub> O	...	1.25	3.92	c
23	Co(en) <sub>2</sub> (OOCCH(CH <sub>3</sub> )OD) <sup>2+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	...	1.32	4.36	c
B. Thioether Species						
24	CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	D <sub>2</sub> O	2.08	...	...	b
25	CH <sub>2</sub> (SCH <sub>2</sub> COOH) <sub>2</sub>	CF <sub>3</sub> COOD	3.62	...	...	b
26	COOCCH(CH <sub>2</sub> SCH <sub>3</sub> )ND <sub>2</sub>	D <sub>2</sub> O	3.27	2.22	4.51	b
27	Co(en) <sub>2</sub> (OOCCH(CH <sub>2</sub> SCH <sub>3</sub> )NH <sub>2</sub> ) <sup>2+</sup>	D <sub>2</sub> O	3.05	2.22	3.62	d
28	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> SCH <sub>3</sub> ) <sup>2+</sup>	D <sub>2</sub> O	3.75	2.38	...	c
29	Co(en) <sub>2</sub> (OOCCH <sub>2</sub> SCH <sub>3</sub> ) <sup>2+</sup>	D <sub>2</sub> O-CF <sub>3</sub> COOD	3.75	2.38	...	c
30	Co(en) <sub>2</sub> (CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sup>3+</sup>	D <sub>2</sub> O	e	2.32	...	c

<sup>a</sup> Absorption downfield from external TMS in ppm. Where insufficiently soluble, perchlorate salts were solubilized using a slight deficiency of tetraphenylarsonium chloride. Acidification was usually with trifluoroacetic anhydride. <sup>b</sup> Sadtler NMR tables.

<sup>c</sup> This work. <sup>d</sup> Reference 28, using  $\delta_{\text{HOD}}$  4.60 ppm downfield from TMS. <sup>e</sup> Signal obscured by en absorption at 2.6–3.2 ppm.

reported value. Total chromium was determined spectrally by alkaline peroxide oxidation to chromate(VI) ion which was monitored at 373 nm where  $\epsilon$  was  $4815 \pm 15$ .<sup>15</sup> Chromium(II) was determined from the excess  $\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}$  absorption at 534 nm remaining after anaerobic reaction and allowance for absorbance due to  $\text{Co}^{2+}$  and  $\text{CrCl}^{2+}$ .<sup>21</sup>

**Kinetic Determinations.** Except where noted kinetic runs were made under pseudo-first-order conditions for the consumption of the cobalt(III) complex (usually at the low-energy maximum) in aqueous acidic solutions maintained with  $\text{LiClO}_4\text{-HClO}_4$  at  $I = 1.00$  M. Standard plots of  $\log(A_t - A_\infty)$  vs.  $t$  were linear through at least 90% reaction. The cobalt complexes were not as sensitive to room light as their chromium(III) analogues.<sup>12c</sup> Eyring treatments of  $\log(k/T)$  vs.  $1/T$  yielded activation parameters. Error limits are standard deviations from least-squares analyses using a Hewlett-Packard HP-65 calculator and program. The units for rate constants are molar and seconds. For two unmeasurably fast reactions a deficiency of reductant, R, was added to a solution containing equimolar amounts of the oxidant under investigation,  $\text{O}_1$ , and a second oxidant,  $\text{O}_2$ , whose rate of

reaction,  $k_2$ , with the reductant is kinetically parallel and known for the experimental conditions employed (e.g.,  $[\text{R}]_0:[\text{O}_1]_0:[\text{O}_2]_0 = 0.9:1.0:1.0$ ). The appropriate second-order differential rate laws can be rearranged and integrated to yield

$$\log \frac{[\text{O}_1]_t}{[\text{O}_1]_0} = \frac{k_1}{k_2} \log \frac{[\text{O}_2]_t}{[\text{O}_2]_0}$$

Thus, if  $[\text{O}_1]_\infty$  and  $[\text{O}_2]_\infty$  are determined by ion-exchange product isolation, then  $k_1$  may be found by solving at  $t = \infty$ .

**Ion-Exchange Procedures.** The charges of ions were inferred from their elution characteristics from cation-exchange columns of Bio-Rad AG (or Dowex) 50W-X2, 200–400 mesh ( $\text{Na}^+$  or  $\text{Li}^+$  form) calibrated with *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$ ,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ , and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  ions. Nitrogen pressure (1 atm) was used to increase the flow rate through the columns.

**Stoichiometry Studies.** After the reactions were allowed to occur with cobalt(III) in excess, with chromium(II) in excess and, in the case of the carboxylate chelates, with equal amounts of each, the

mixture was aerated and charged onto a calibrated ion-exchange column. With the carboxylate chelates the monomeric chromium(III) product was selectively eluted and analyzed as chromate(VI). With the amino chelates the remaining excess reagent was analyzed spectrally after elution of either the cobalt complex or the dimeric chromium(III) product of chromium(II) air oxidation.<sup>22</sup> The last approach gave results which were usually ~20% below those expected whereas the others were routinely within 10%.

**Gas Analysis.** After reaction of  $\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)^{3+}$  (6.0  $\mu\text{mol}$ ) with excess chromium(II) in 0.5 M acidic solution, the gastight reaction vessel was attached to a high-vacuum line and any volatile gaseous products were collected. The contents of the collection vessel were examined by standard vapor-phase chromatography. The authors are grateful to H. E. O'Neal for assistance with this analysis.

**Materials.** Common chemicals were of reagent grade unless otherwise specified. Deionized water was redistilled from alkaline permanganate and stored in glass bottles. Nitrogen for deaerating air-sensitive solutions was passed through two Cr(II) scrubbing towers. Lithium perchlorate was occasionally checked for purity by passage of solutions through an acidic cation-exchange column followed by titration of the eluent with sodium hydroxide. Substitution of solutions prepared from lithium carbonate and excess perchloric acid revealed no kinetic anomalies.

Stock solutions of Cr(III) (from chromium(III) perchlorate) at acidities between  $10^{-4}$  and 1 M were anaerobically reduced to Cr(II) using mossy or 20-mesh zinc which had been amalgamated with tetrachloromercurate ion in ~1 M HCl for 10 s following activation with 3 M HCl. Hexaammineruthenium(III) chloride (Matthey-Bishop) was similarly reduced anaerobically to  $\text{Ru}(\text{NH}_3)_6^{2+}$  following repeated recrystallization from hydrochloric acid to spectral integrity.<sup>23</sup> Vanadium(II) solutions were obtained anaerobically by the zinc amalgam reduction of vanadyl trifluoroacetate (from vanadyl sulfate and barium trifluoroacetate) in acidic solution.

2-Aminoethyl disulfide dihydrochloride was prepared<sup>24</sup> by the oxidation of 2-aminoethanethiol (0.1 mol of the hydrochloride neutralized with 0.1 mol sodium hydroxide in 30 ml of water) by hydrogen peroxide (10%, 10 ml). After 30 min, ten 100-ml ether extracts were evaporated at 40 °C. The resulting oil was treated with 25 ml of 12 M HCl and 200 ml of ethanol to yield a white solid which was filtered, washed with ethanol and ether, and suction-dried. 2,2'-Dithiopropanoic acid was prepared<sup>25</sup> by the addition of 1 mmol of 2-mercaptopropanoic acid to 1 mmol of iron(III) perchlorate in 200 ml of water. After 1 h several drops of concentrated  $\text{H}_2\text{SO}_4$  were added and the reaction mixture was extracted with three 50-ml portions of diethyl ether which was evaporated to dryness under a stream of nitrogen to yield a white solid (mp 113 °C uncor).

**Preparation of Cobalt Complexes.** Syntheses for the alkoxy complexes have been described.<sup>9</sup> (Mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate, (2-mercaptopropionato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate, and (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate were prepared by similar procedures of which the following is representative. Deoxygenated 98–100% ethylenediamine (0.057 mol) was added via syringe to a stirring, deoxygenated solution of  $\text{Co}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$  (0.028 mol) in 30 ml of water. After 15–30 min the solid disulfide (0.014 mol) or, in the case of  $(\text{NH}_2\text{CH}_2\text{CH}_2\text{S}-)_2\cdot 2\text{HCl}$ , a neutralized deoxygenated 15-ml solution was added. Isolation procedures after 30 min under nitrogen differed slightly. The mercaptoethylamine complex solution was filtered and, after addition of solid sodium perchlorate, yielded a purple-brown solid which was recrystallized from 0.1 M perchloric acid with slow cooling to yield dark brown needles. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})][\text{ClO}_4]_2$ : C, 15.87; H, 4.88; N, 15.42; S, 7.06. Found: C, 15.91; H, 5.07; N, 15.49; S, 7.02. From the mercaptoacetate reaction mixture a brown, solid mass was filtered and redissolved in 140 ml of hot (90 °C) water. After filtration, 30 g of  $\text{NaClO}_4\cdot\text{H}_2\text{O}$  was added with stirring and burgundy crystals separated on cooling. Recrystallization was accomplished by addition of 20 g of  $\text{NaClO}_4\cdot\text{H}_2\text{O}$  to 120 ml of hot solution. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{OOCCH}_2\text{S})][\text{ClO}_4]$ : C, 19.5; H, 4.88; N, 15.2; S, 8.67. Found: C, 19.5; H, 4.84; N, 15.13; S, 8.53. The mercaptopropionate product mixture was concentrated with stirring to 20 ml in a 150-ml beaker at 100 °C under a stream of nitrogen and cooled. After filtration and washing with 5 ml of hot water, the collected solid was dissolved in 100 ml of hot (90 °C) water, and the solution was filtered and cooled yielding light purple needles. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{OOCCH}(\text{CH}_3)\text{S})][\text{ClO}_4]$ : C, 21.97; H, 5.27;

N, 14.64; S, 8.36; Co, 15.40. Found: C, 21.75; H, 5.34; N, 14.61; S, 8.32; Co, 15.15.

(2-Mercaptoethanolato-*O,S*)bis(ethylenediamine)cobalt(III) perchlorate was prepared by adding 61 g of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  to a solution of 13 g of NaOH and 17 g of 2-mercaptoethanol in 250 ml of water. After 10 min the solution was filtered and excess sodium perchlorate added. The resulting solid was filtered and recrystallized by dissolution in minimal hot water, addition of sodium perchlorate, and cooling. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{O})][\text{ClO}_4]$ : C, 20.32; H, 5.68; N, 15.80; S, 9.03; Co, 16.61. Found: C, 20.32; H, 5.70; N, 15.91; S, 9.22; Co, 16.30. At least as indicated by elemental analysis, (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate can apparently be prepared analogously. Sodium hydroxide (4.0 g), cysteamine hydrochloride (5.7 g), and  $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$  (15.4 g) were mixed as solids, 200 ml of water was added, followed by excess sodium perchlorate after 15 min, and the resulting solid was recrystallized as before. Anal. Calcd for  $[\text{Co}(\text{trien})(\text{SCH}_2\text{CH}_2\text{NH}_2)][\text{ClO}_4]_2$ : C, 19.93; H, 5.00; N, 14.52; S, 6.65. Found: C, 19.83; H, 5.17; N, 14.53; S, 6.83.

Elemental analyses suggest that silver and mercury adduct complexes can be prepared. Addition of mercuric chloride to 1 g of  $[\text{Co}(\text{en})_2(\text{OCH}_2\text{CH}_2\text{S})][\text{ClO}_4]$  in 40 ml of water led to a red-orange color after about 2 min and a precipitate after about 5 min which was filtered after another 5 min, washed, and dried. One-fourth of the filtrate from the previous synthesis was treated with ~0.25 g of  $\text{K}_3[\text{Co}(\text{CN})_6]$ . The immediate precipitate was isolated as usual. Reaction of 0.1 g of  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{O})][\text{ClO}_4]$  in minimal water with 3 ml of 1 M silver perchlorate was followed after 15 min with addition of excess lithium perchlorate and, after stirring of the mixture overnight, a dark pink solid was isolated. In  $\text{D}_2\text{O}$  the  $^1\text{H}$  NMR spectrum observed retained methylene (O) absorption almost unshifted ( $\delta \sim 3.1$  ppm) while methylene (S) absorption had shifted downfield ( $\delta \sim 2.55$  ppm). The nature of the reactants, reaction times required,  $^1\text{H}$  NMR spectra and analyses lead us to tentatively formulate these three salts as follows. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OCH}_2\text{CH}_2\text{SHg})][\text{ClO}_4]_3$ : C, 9.33; H, 2.87; N, 7.27. Found: C, 9.08; H, 2.84; N, 6.92. Calcd for  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OCH}_2\text{CH}_2\text{SHg})][\text{Co}(\text{CN})_6]$ : C, 20.92; H, 3.22; N, 20.33. Found: C, 20.97; H, 3.45; N, 20.09. Calcd for  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OCH}_2\text{CH}_2\text{SAg})][\text{ClO}_4]_2$ : C, 12.42; H, 3.82; N, 9.66; S, 5.53. Found: C, 12.38; H, 3.77; N, 9.45; S, 5.29.

2-Methylthioethylaminebis(ethylenediamine)cobalt(III) perchlorate was prepared by adding a tenfold excess of methyl iodide to 0.82 g of  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)][\text{ClO}_4]_2$  in 60 ml of 66% (v/v) methanol-water. The flask was sealed and stirred vigorously for 36 h, with a change from dark brown to orange, followed by evaporation to dryness overnight from a beaker at 35 °C. The crude product was recrystallized twice from water (80 °C) by the addition of excess lithium perchlorate followed by cooling. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{CH}_3\text{SCH}_2\text{CH}_2\text{NH}_2)][\text{ClO}_4]_3$ : C, 14.78; H, 4.43; N, 12.31; S, 5.64. Found: C, 14.69; H, 4.36; N, 12.11; S, 5.49.

Methylthioacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared by adding a 25-fold excess of methyl iodide to a suspension of 1.8 g of  $[\text{Co}(\text{en})_2(\text{OOCCH}_2\text{S})][\text{ClO}_4]$  in 300 ml of 90% methanol-water. After stirring of the mixture for 24 h in a closed flask and for 3 h in an open flask a light pink solid was isolated and recrystallized twice from hot (90 °C) water by addition of sodium perchlorate until precipitation began followed by cooling. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{OOCCH}_2\text{SCH}_3)][\text{ClO}_4]_2$ : C, 17.40; H, 4.38; N, 11.60; S, 6.64. Found: C, 17.42; H, 4.26; N, 11.64; S, 6.75.

Glycinatobis(ethylenediamine)cobalt(III) perchlorate was prepared by adding slowly with stirring a solution of 6.8 g of  $[\text{Co}(\text{en})_2(\text{OOCCH}_2\text{NH}_2)]\text{Cl}_2$ <sup>26</sup> in 40 ml of water to a solution of 2.4 g of  $\text{AgClO}_4$  in 2 M  $\text{HClO}_4$ . The filtrate from silver chloride was reduced to a thick syrup on a rotary evaporator at 45 °C. After the mixture stood for several days, the resultant solid mass was filtered and dried for 2 days under aspirator suction and for 24 h in vacuo. Anal. Calcd for  $[\text{Co}(\text{en})_2(\text{OOCCH}_2\text{NH}_2)][\text{ClO}_4]_2$ : C, 15.94; H, 4.43; N, 15.49; Co, 13.04. Found: C, 16.13; H, 4.52; N, 15.52; Co, 13.25. Agreement was found with reported spectra.<sup>26</sup>

## Results

**Characterization of the Cobalt(III) Complexes.** Infrared spectra confirmed the coordination of carboxylate (strong absorption near 1635 and 1350  $\text{cm}^{-1}$ ) and the absence of the -S-H function (no 2500- $\text{cm}^{-1}$  absorption). The charges of

all species in Table I were confirmed by ion-exchange chromatography with the exception of entries 10–13 for which the formula weights of their isolated salts were confirmed (within 3.5%) by calibrated vapor-phase osmometry.

Chromatographic, electronic, and  $^1\text{H}$  NMR absorption data for the alkoxy chelates were collected under conditions appropriate to their acid–base characteristics.<sup>9</sup> Titrations confirmed that  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{O})^+$  is monobasic with a  $\text{p}K_a = 6.35$  ( $I = 0.30$  M) for its conjugate oxy acid in line with previous arguments.<sup>9</sup> No evidence for the protonation of our coordinated thiolates was encountered according to previous criteria.<sup>5</sup>

This conclusion is supported by the  $^1\text{H}$  NMR results in Table II. As with  $\text{Co}(\text{NH}_3)_5\text{OCH}_3^{2+}$ ,<sup>29</sup> proton resonances on the carbon adjacent to deprotonated alcoholate oxygen or thiolate sulfur bound to cobalt(III) are characteristically shifted upfield from the corresponding resonance in the protonated free ligand. Methylene and methinyl resonances are shifted 0.35–0.70 and  $\sim 0.15$  ppm, respectively. Protonation of alcoholate oxygen shifts the adjacent resonance back toward or beyond the free ligand resonance. No such change is detectable on acidification of thiolate complex solutions. Thus, spectral, potentiometric, and  $^1\text{H}$  NMR measurements all reflect the very low basicity of coordinated thiolate sulfur in these cationic complexes.  $\beta$ -Methyl resonances undergo less dramatic upfield shifts (see entries (II-19,22) (II refers to Table II)). In contrast, the thioether methyl resonance shifts downfield on coordination.

Electronic absorption studies complement other results in confirming the chelate formulations of Table I which, for  $\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})^+$  and  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$ , are also supported by x-ray structures.<sup>30</sup> As with chromium(III),<sup>10,12</sup> thiolate coordination gives rise characteristically to intense ultraviolet sulfur-to-metal charge-transfer transitions. With  $\text{Co}^{\text{III}}(\text{en})_2$  the energies are insensitive to variation in the auxiliary chelate function and, surprisingly, to methylation at sulfur.

In their  $\lambda_1$  ( $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ ) and  $\lambda_2$  ( $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ ) d–d transitions the alkoxy chelates exhibit higher molar absorptivities than their  $\text{M}^{\text{III}}(\text{en})_2(\text{monodentate})_2$  analogues. For example,  $\lambda$  ( $\epsilon$ ) for *cis*- $\text{Co}(\text{en})_2(\text{OH})(\text{OOCCH}_3)^+$  (512 (102), 365 (85)) and *cis*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OOCCH}_3)^{2+}$  (498 (100), 360 (77.5))<sup>31</sup> can be compared with data for entries I-2,3,5,6 and their monodentate hydrolysis products; *vide infra*. Data are available<sup>32,33</sup> for similar comparisons with entries I-8,9,12,13. The thiolato and thioether complexes have still higher extinction coefficients, presumably through intensity borrowing from the ultraviolet absorption. The data suggest very similar ligand field strengths for thiolate and alcoholate functions and a shift to higher energies on methylation of sulfur reminiscent of that occurring on protonation of oxygen. The acidity characteristics<sup>9</sup> and the nature of the reactions described below are also consistent with the formulations presented.

#### Decomposition Reactions of the Cobalt(III) Complexes.

None of the complexes incorporated water on recrystallization. With  $\text{Co}(\text{en})_2(\text{HOCH}_2\text{CH}_2\text{NH}_2)^{3+}$  and  $\text{Co}(\text{en})_2(\text{CH}_3\text{SCH}_2\text{CH}_2\text{NH}_2)^{3+}$  no anated products could be isolated from hot (90 °C) 3 M HBr<sup>34</sup> nor was there appreciable spectral change for the former complex over a period of 2 weeks in 1.0 M HClO<sub>4</sub>.  $\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})^+$  and  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$  undergo negligible decomposition over extended periods in acid,<sup>12c</sup> suggesting a comparable inertness for  $\text{Co}(\text{en})_2(\text{SCH}(\text{CH}_3)\text{COO})^+$ . In 0.1 M HClO<sub>4</sub>,  $\text{Co}(\text{en})_2(\text{HOCH}_2\text{COO})^{2+}$  and  $\text{Co}(\text{en})_2(\text{HOCH}(\text{CH}_3)\text{COO})^{2+}$  apparently dechelate slowly ( $k \approx 1.8 \times 10^{-6} \text{ s}^{-1}$ ) to monodentate aquocarbonylate products as judged by their spectral parameters  $\lambda$  ( $\epsilon$ ) (498 ( $\sim 100$ ), 360 ( $\sim 80$ )). Hydrolysis of

the ethylene glycol chelate also occurred slowly. In acidic solution,  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$  very slowly changed color to what may be a mixture of hydrolysis and redox products.<sup>2e</sup> Thus, all complexes retain their integrity in solution over the times of the redox reactions described below.

**Reduction by Chromium(II) Ion.** The stoichiometric ratio  $\Delta[\text{Co}(\text{III})]/\Delta[\text{Cr}(\text{II})]$  typically ranged from 0.87 to 0.99 with  $0.93 \pm 0.04$  as a mean for the reactions studied; with  $\text{Co}(\text{en})_2(\text{HOCH}_2\text{CH}_2\text{OH})^{3+}$  and  $\text{Co}(\text{en})_2(\text{HOCH}_2\text{CH}_2\text{S})^{2+}$  a 1:1 ratio was assumed. Only for the reaction of  $\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)^{3+}$  could no evidence be found for ligand transfer to chromium(III).<sup>35</sup> In all other cases the primary reactions are inner sphere as indicated by mechanistic features and ion-exchange and/or spectral characteristics of the primary or secondary chromium(III) products which, except with the  $\text{Co}(\text{en})_2(\text{HOCH}_2\text{CH}_2\text{OH})^{3+}$  and  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$  reactions, were isolated by ion exchange. These products are treated subsequently<sup>10</sup> and will be discussed here only inasmuch as mechanistic issues demand.

All of the reactions were found to be pseudo first order in the cobalt(III) complex and first order in chromium(II), except where noted, usually over a tenfold variation in the latter in the vicinity of  $10^{-3}$  M. Thus, the rate law

$$-d[\text{Co}(\text{III})]/dt = k[\text{Co}(\text{III})][\text{Cr}(\text{II})]$$

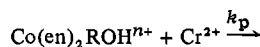
obtains at any particular acidity.

After reaction with  $\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})^+$ ,  $\text{Co}(\text{en})_2(\text{SCH}(\text{CH}_3)\text{COO})^+$ , and  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$  (and presumably  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$  although this was not checked) the isolated chromium(III) product exhibited the ultraviolet absorption characteristic of chromium(III)–thiolate coordination.<sup>10,12</sup> This and the absence of alternative bonding sites for chromium(II) on  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$  established a thiolate-bridging mechanism for this reaction. The rate,  $k = 3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, was independent of acidity over the range studied, 0.040–0.50 M. Linear regression of 23 individual runs at four temperatures between 8 and 25 °C led to values of  $\Delta H^\ddagger = 7.26 \pm 0.28 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -13.5 \pm 1.0 \text{ eu}$  which reproduced experimental averages within 1.6% except at 15 °C where the experimental average was  $\sim 4\%$  lower.

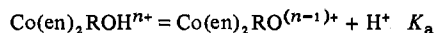
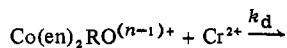
Rates with  $\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})^+$  and  $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$  called for competitive experiments against *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$  which is reported to react with Cr(II) with  $k_2 = (6.6 \pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at  $[\text{H}^+] = 0.010 \text{ M}$ ,  $I = 0.10 \text{ M}$  (HClO<sub>4</sub>–NaClO<sub>4</sub>), and 18.6 °C.<sup>36</sup> Under these conditions and assuming second-order rate laws, the respective rate constants were found to be  $k_1 = (6.4 \pm 0.5) \times 10^6$  and  $k_1 = (6.0 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>36</sup> No variation with acidity was detectable down to 0.005 M. Thiolate bridging is almost certainly operative for both fast reactions. An alcohol bridge is expected to be even less effective than a water bridge.<sup>37</sup> The rate of  $2.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  recorded below for  $\text{Co}(\text{en})_2(\text{OOCCH}_2\text{SCH}_3)^{2+}$  reduction represents, at the least, an upper limit for carboxylate bridging. Carboxylate bridging with  $\text{Co}(\text{en})_2(\text{OOCCH}_2\text{S})^+$  would require an unprecedented nonbridging ligand acceleration by  $2 \times 10^4$  above this rate. Moreover, in the accompanying paper<sup>10</sup> we shall describe a fleeting chromium(III) product of this reaction, believed to be  $\text{Cr}(\text{H}_2\text{O})_5\text{SCH}_2\text{COOH}^{2+}$ , which gives rise to chelated  $\text{Cr}(\text{H}_2\text{O})_4(\text{SCH}_2\text{COO})^+$  and then, under the *same* conditions, to  $\text{Cr}(\text{H}_2\text{O})_5(\text{OOCCH}_2\text{SH})^{2+}$ .

The rate with a 2-methyl substituent in  $\text{Co}(\text{en})_2(\text{SCH}(\text{CH}_3)\text{COO})^+$ ,  $k = 1.54 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C and  $I = 0.10 \text{ M}$ , could be followed at 282 nm and is independent of  $[\text{H}^+]$  between 0.10 and 0.010 M. Studies at four temperatures between 25 and 45 °C yielded  $\Delta H^\ddagger = 1.1 \pm 0.2 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -31 \pm 1 \text{ eu}$ . Evidence analogous to that adduced for the preceding case supports a thiolate-bridged mechanism.

Analogous alcoholate-bridged pathways occur for the reduction of each of the alcohol complexes for which reaction of a protonated and a deprotonated complex can be envisaged, i.e.



with



The appropriate differential rate expression is  $-d[\text{Co(III)}]/dt = k_{\text{obsd}}[\text{Co(III)}]_{\text{total}}$  where  $k_{\text{obsd}} = k_2[\text{Cr(II)}]$ . In general

$$k_2 = \frac{k_p + k_d K_a / [\text{H}^+]}{1 + K_a / [\text{H}^+]}$$

which reduces to  $k_2 = k_p + k_d K_a [\text{H}^+]^{-1}$  when  $K_a / [\text{H}^+] \ll 1$  and  $k_2 = k_d$  when  $K_a / [\text{H}^+] \gg 1$ .

With  $\text{Co(en)}_2(\text{HOCH}_2\text{CH}_2\text{NH}_2)^{3+}$  reaction is inner sphere (4+ chromium product by ion exchange) with no alternative to alkoxy bridging. The inefficiency of the protonated path<sup>37</sup> is underscored by 19 runs at  $0.50 \text{ M} > [\text{H}^+] > 0.050 \text{ M}$  which conformed to the equation  $k_2 = (-0.041 \pm 0.022) + (0.166 \pm 0.002)[\text{H}^+]^{-1}$ , the first term being indistinguishable from  $k_p = 0$ . At the lowest feasible initial acidity,  $5.5 \times 10^{-5} \text{ M}$ , and  $[\text{Co(III)}] = 6.0 \times 10^{-6} \text{ M}$  (to avoid complications from metal hydroxides)  $k_2 = 935 \pm 50 \text{ M}^{-1} \text{ s}^{-1} \approx k_d$ . Eleven runs at three temperatures between 12 and 25 °C yielded  $\Delta H_d^\ddagger = 5.14 \pm 0.54 \text{ kcal/mol}$  and  $\Delta S_d^\ddagger = -27.7 \pm 1.9 \text{ eu}$  which reproduced experimental averages within 1.4%. From the kinetic data an apparent  $K_a = 1.78 \times 10^{-4}$  at  $I = 1.0 \text{ M}$  can be derived in reasonable agreement with values of  $K_a = 3.47 \times 10^{-4}$  ( $I = 0.10 \text{ M}$ ) and  $2.58 \times 10^{-4}$  ( $I = ?$ ) obtained directly at lower ionic strengths.<sup>9,34</sup>

In less extensive experiments, data on  $\text{Co(en)}_2(\text{HOCH}_2\text{CH}_2\text{OH})^{2+}$  over the range  $0.10 \text{ M} > [\text{H}^+] > 0.010 \text{ M}$  conformed to the equation  $k_2 = (-16.2 \pm 11.2) + (18.0 \pm 0.2)[\text{H}^+]^{-1}$ , the first term again being indistinguishable from zero. A  $K_a = 2.5 \times 10^{-3}$  determined at  $I = 0.10 \text{ M}$ <sup>9</sup> was used to estimate  $k_d \approx 7.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C.

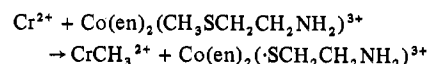
Over about the same acid range for  $\text{Co(en)}_2(\text{HOCH}_2\text{COO})^{2+}$ ,  $k_2 = (38.4 \pm 0.7) + (0.988 \pm 0.015)[\text{H}^+]^{-1}$ , while for  $\text{Co(en)}_2(\text{HOCH}(\text{CH}_3)\text{COO})^{2+}$ ,  $k_2 = (7.44 \pm 0.12) + (0.0221 \pm 0.0014)[\text{H}^+]^{-1}$ . The first term for each must be associated with carboxylate bridging in view of the bridging inefficiency documented earlier for the protonated alkoxy function and arguments advanced previously.<sup>5</sup> A directly measured  $K_a = 4.36 \times 10^{-4}$  ( $I = 1.0 \text{ M}$ ) (which did not vary significantly with ionic strength down to  $I = 0.10 \text{ M}$  as has been found elsewhere<sup>34</sup>) was used to estimate  $k_d = 51 \text{ M}^{-1} \text{ s}^{-1}$  for the latter complex. At an initial  $[\text{H}^+] = 8.0 \times 10^{-5} \text{ M}$  direct rates of  $k_d \approx 50 \text{ M}^{-1} \text{ s}^{-1}$  were observed but with ~20% fluctuations in value. With  $\text{Co(en)}_2(\text{HOCH}_2\text{COO})^{2+}$  a directly measured  $K_a = 1.0 \times 10^3$  ( $I = 1.0 \text{ M}$ ) yielded  $k_d = 0.99 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  whereas direct kinetic measurements at  $[\text{H}^+] = 1.0 \times 10^{-4} \text{ M}$  gave  $k_d = 1.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . Limited temperature studies between 15 and 35 °C under the latter conditions indicated that  $\Delta H_d^\ddagger \approx 2.2 \text{ kcal/mol}$  and  $\Delta S_d^\ddagger \approx -36 \text{ eu}$  for the deprotonated path. The kinetic comparisons now available with noncarboxylate alkoxy chelate ligands ensure that this path utilizes alkoxy bridging.

The rate of reduction of  $\text{Co(en)}_2(\text{OOCCH}_2\text{NH}_2)^{2+}$ ,  $k = 2.22 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, was independent of acidity between 0.010 and 0.10 M and  $\text{Cr}(\text{H}_2\text{O})_5(\text{OOCCH}_2\text{NH}_3)^{3+}$  was the initial product.<sup>10</sup> Studies at three temperatures between 13 and 34 °C yielded  $\Delta H^\ddagger = 8.93 \pm 0.13 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -27.0 \pm 0.4 \text{ eu}$ .

The rate of reduction of  $\text{Co(en)}_2(\text{OOCCH}_2\text{SCH}_3)^{2+}$  by

$\text{Cr(II)}$  is independent of acid concentration over the range 0.010–0.10 M with  $k = 274 \pm 9 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. Studies at four temperatures between 20 and 37 °C yielded  $\Delta H^\ddagger = 8.44 \pm 0.05 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -19.1 \pm 0.2 \text{ eu}$ .  $\text{Cr}(\text{H}_2\text{O})_5(\text{OOCCH}_2\text{SCH}_3)^{2+}$  was the only reaction product isolable by ion exchange (~90%). Under conditions where  $t_{1/2} \approx 0.03 \text{ s}$  for the redox reaction ( $[\text{Cr(II)}] \approx 0.093 \text{ M}$ ) no absorbancy changes were detectable on the Cary 14 after 30 s at 570 nm, 60 s at 440 nm ( $[\text{Co(III)}] = 4.1 \times 10^{-3}$ ), or 120 s at 285 nm ( $[\text{Co(III)}] = 1.6 \times 10^{-4}$ ). These observations appear to exclude the intermediates,  $\text{Cr}(\text{H}_2\text{O})_5(\text{CH}_3\text{SCH}_2\text{COOH})^{3+}$  and  $\text{Cr}(\text{H}_2\text{O})_4(\text{CH}_3\text{SCH}_2\text{COO})^{2+}$ , required by a thioether-bridged mechanism yielding the observed product and, supported by earlier arguments,<sup>8</sup> to substantiate a carboxylate bridging mechanism.

The rate of reduction of  $\text{Co(en)}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)^{3+}$  by chromous ion was found to be independent of acid between 0.050 and 0.50 M with  $k = 0.381 \pm 0.012 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. Three or four runs at each of three other temperatures between 12 and 32 °C yielded  $\Delta H^\ddagger = 5.48 \pm 0.19 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -42.1 \pm 0.6 \text{ eu}$ . Only  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  could be isolated by ion exchange. This and the absence of any evidence for subsequent reaction when the redox reaction was monitored at 487 nm for 3–6 half-lives under first-order conditions where  $t_{1/2} \approx 70 \text{ s}$  are consistent with the reaction being outer sphere. Nevertheless, because of the slowness of the reaction and the rapidity of chromium(III)–carbon bond hydrolysis<sup>38</sup> we felt obliged to test the possibility that the redox reaction might be initiated by chromium(II) cleavage of a carbon–sulfur bond, i.e.



Three hours after initiation of the reaction described in the Experimental Section no appreciable methane (or evacuable gas other than argon) could be detected by standard high-vacuum and gas chromatographic procedures. Accepting this reaction as being outer sphere in the absence of contrary evidence, the kinetic parameters of the chromous reductions are tabulated by reaction category and considered further under Discussion.

**Reduction by Vanadium(II) and Hexaammineruthenium(II) Ions.** The results with these reductants are summarized in Table III. The stoichiometric ratio  $\Delta[\text{Co(III)}]/\Delta[\text{V(II)}]$  was found to range from 1.03 to 1.06 by ion-exchange separation and spectral analysis of the excess cobalt(III) complex. The rate laws were first order in  $[\text{V}(\text{H}_2\text{O})_6^{2+}]$  over 4–5-fold variations near  $10^{-2} \text{ M}$  and independent of  $[\text{H}^+]$  over the ranges indicated. Reasonable bridging groups are present in the first three complexes, and, according to well-established criteria,<sup>39,40</sup> all rate parameters are consistent with inner-sphere reactions governed by rate-limiting substitution on vanadium(II). With  $\text{Co(en)}_2(\text{HOCH}_2\text{CH}_2\text{OH})^{3+}$ , however, the activation parameters are similar to those observed with  $\text{UO}_2^{2+}$ <sup>41</sup> on which basis an outer-sphere mechanism has been assigned.<sup>40</sup> Our results presumably reflect again the bridging inefficiency of the ROH function and an outer-sphere reduction of  $\text{Co(en)}_2(\text{HOCH}_2\text{CH}_2\text{OH})^{3+}$ .

Slow reductions by  $\text{Ru}(\text{NH}_3)_6^{2+}$  were complicated by its slow decomposition at higher concentrations.<sup>13,42</sup> Stoichiometries were assumed to be 1:1 and only data obtained within the first hour after preparation were considered reliable for determination of the rate constant under second-order conditions.

## Discussion

**Synthesis of the Cobalt(III) Complexes.** Our thiolate syntheses were designed<sup>5</sup> on the basis of principles underlying the preparation of  $\text{CrSH}^{2+}$ ,<sup>27</sup> i.e., the 1-equiv oxidative ad-

**Table III.** Kinetic Results with  $V(H_2O)_6^{2+}$  and  $Ru(NH_3)_6^{2+}$ 

A. $V(H_2O)_6^{2+}$ , $I = 1.00$ M ( $LiClO_4-HClO_4$ )					
Complex	$[H^+]$ , M	$k(25^\circ C)$ , $M^{-1} s^{-1}$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	
$Co(en)_2(OOCCH_2S)^+$	0.05-0.5	9.6	$11.6 \pm 0.5$	$-15.1 \pm 1.6$	
$Co(en)_2(OOCCH_2OH)^{2+}$	0.01-0.5	15.3	$10.2 \pm 0.4$	$-19.0 \pm 1.5$	
$Co(en)_2(SCH_2CH_2OH)^{2+}$	0.01-0.5	6.5	$12.0 \pm 0.7$	$-14.5 \pm 2.4$	
$Co(en)_2(HOCH_2CH_2OH)^{3+}$	0.1-0.5	40.6	$7.4 \pm 0.3$	$-26.4 \pm 1.0$	
B. $Ru(NH_3)_6^{2+}$					
Medium	$I$ , M	$[H^+]$ , M	$10^3 [Co(III)]$ , M	$10^3 [Ru(II)]$ , M	$k(25^\circ C)$ , $M^{-1} s^{-1}$
(a) $Co(en)_2(OOCCH_2OH)^{2+}$					
HCl-NaCl	0.15	0.100	5.00	2.33	3.2
(b) $Co(en)_2(OOCCH_2O)^+$					
$NH_4Cl-NH_3$	0.50	$\sim 5 \times 10^{-10}$	47.5	30.0	$<10^{-2}$
$NH_4Cl-NH_3$	0.50	$\sim 5 \times 10^{-10}$	45.9	12.5	$\sim 10^{-3}$
(c) $Co(en)_2(OOCH_2S)^+$					
HCl-NaCl	0.15	0.10	5.00	1.83	0.11
HCl-NaCl	0.10	0.0010	0.198	0.136	0.18
HCl-NaCl	0.10	0.0010	0.195	0.140	0.12

dition of a disulfide to a labile reducing center with capture of thiolate by the inert oxidized center. Extensions to monodentate<sup>12a</sup> and chelate<sup>12c</sup> chromium(III) species have been reported. Two ethylenediamines seem necessary in  $Co(en)_2^{2+}$  to develop sufficient reducing strength toward aliphatic disulfides. The availability of a *deprotonated* auxiliary chelate function ( $NH_2^-$ ,  $^-OOC^-$ ) may be influential, thermodynamically or kinetically, since  $Cr(en)_2^{2+}$ <sup>12c</sup> and  $Co(en)_2^{2+}$  react with amino or carboxylate chelates in *basic* solution to give the chelated M(III) product whereas  $Cr^{2+}$  in *acidic* solution is unreactive toward the protonated disulfides ( $^+NH_3^-$ ,  $HOOC^-$ ) but is reactive with monodentate aromatic (more reducible) disulfides.<sup>12a</sup>

The syntheses of  $Co(en)_2(SCH_2CH_2O)^+$  and  $Co(trien)-(SCH_2CH_2NH_2)^{2+}$  were based on procedures for cysteine.<sup>28</sup> Thioether chelates were prepared by methylation in contrast with dechelation when a third chelate function is present.<sup>28</sup> (Dechelated silver and mercury thiolate adducts appear preparable although we cannot be certain of our monodentate formulations with present evidence.)

**Outer-Sphere Reactions.** The results of Table IIIB suggest that  $Co(en)_2(SCH_2COO)^+$  is reduced by  $Ru(NH_3)_6^{2+}$  about 100 times more rapidly than is  $Co(en)_2(OCH_2COO)^+$ , probably as the result of the greater ease of activation of the elongated trans Co-N<sup>30</sup> and weaker Co-SR (relative to Co-OR) bonds. However, the rate is considerably slower than that of the reduction of  $Co(NH_3)_5X^{2+}$  with  $X^- = Cl^-$  ( $k = 2.6 \times 10^2$ ),  $Br^-$  ( $k = 1.6 \times 10^3$ ), and  $I^-$  ( $k = 6.7 \times 10^3$ ).<sup>13</sup> This is likely attributable to more difficult activation of the chelate ligands (see below) and the greater thiolate basicity suggestive of relatively greater resistance to activation of the Co-S bond ( $Co(NH_3)_6^{3+}$  and  $Co(NH_3)_5OH^{2+}$  are reduced with  $k = 0.011$  and  $0.04$ , respectively<sup>13</sup>). In this light the thiolate function seems to bestow reasonable outer-sphere reactivity on cobalt(III) once allowances are made for its basicity and the influence of the chelate ligands.

The rates of reduction of  $Co(en)_2(OCH_2COO)^+$  and  $Co(en)_2(HOCH_2COO)^{2+}$  are comparable to those of  $Co(NH_3)_5OH^{2+}$  and  $Co(NH_3)_5H_2O^{3+}$  ( $k = 3.0$ ), respectively.<sup>13</sup> This suggests that the introductions of a more easily activated cis carboxylate function and the more difficultly activated

**Table IV.** Kinetic Parameters for Outer-Sphere Chromium(II)-Cobalt(III) Pathways

En-try	Complex	$k$ , $M^{-1} s^{-1}$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	Ref
1	$Co(en)_2(CH_3SCH_2-CH_2NH_2)^{3+}$	$3.8 \times 10^{-1}$	5.5	-42	a, 35
2	$Co(NH_3)_5(NCNC-(NH_2)_2)^{3+}$	$2.9 \times 10^{-2}$	8.3	-37	b
3	$Co(NH_3)_5(OC-(NH_2)_2)^{3+}$	$1.9 \times 10^{-2}$	10.6	-31	b
4	$Co(NH_3)_5(4-pyridone)^{3+}$	$9.6 \times 10^{-3}$			c
5	$Co(NH_3)_5py^{3+}$	$4.3 \times 10^{-3}$	9.8	-36	37
6	$Co(NH_3)_6^{3+}$	$\sim 8.9 \times 10^{-5}$			59
7	$Co(en)_3^{3+}$	$\sim 2 \times 10^{-5}$			d

<sup>a</sup> This work. <sup>b</sup> F. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, **93**, 625 (1971). <sup>c</sup> E. S. Gould, *ibid.*, **90**, 1740 (1968). <sup>d</sup> J. P. Candlin, J. Halpern and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

chelate rings are approximately compensatory in these systems.

Table IV summarizes kinetic data against which the apparently outer-sphere  $Co(en)_2(CH_3SCH_2CH_2NH_2)^{3+}-Cr(H_2O)_6^{2+}$  reaction can be compared. The higher reactivity of the thioether complex arises from a lower enthalpy of activation in spite of the presence of amine chelates which might be expected to offer greater resistance to activation (compare IV-6 and IV-7). This result is consistent with a cobalt-thioether bond that is relatively easily stretched to lower the energy of the cobalt "e<sub>g</sub>" acceptor orbital in the activated complex. Additionally, the relatively small  $\Delta H^\ddagger$  raises the possibility that thioether coordination might cause a ground-state elongation of the trans cobalt-nitrogen bond (as has already been found for  $Co(en)_2(SCH_2COO)^+$  and  $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ <sup>30</sup>) resulting in a related kinetic enhancement.

**Inner-Sphere Reactions.** Our results can be considered within the usual conceptual framework<sup>4,40</sup> as reflecting variations in bridging<sup>6b</sup> or nonbridging<sup>36,40,43-56</sup> groups and/or the introduction of a chelate link between two such functions. Data selected as relevant background have been collected in Table V. While changes in  $\Delta H^\ddagger$  have been held predominantly responsible for certain nonbridging ligand variations,<sup>48,53,54</sup> no such rationale seems uniformly extractable from the present data (compare V-2-5,7-12), perhaps partly due to experimental uncertainties. Note the sensitivity to change in the trans position (involved intimately with the acceptor orbital), which in the case of reduction by chromium(II) extends to  $\Delta S^\ddagger$  as well as  $\Delta H^\ddagger$  (V-7-10). The lower entropy barrier<sup>56</sup> with the cis oxidants may reflect a substantial release into the solvent of the water trans to the bridging group on Cr(II) (an "e<sub>g</sub>" reductant).

**Carboxylate-Bridged Reactions.** Our results are summarized in Table VI with available comparisons. The more rapid reduction of VI-2 compared to that of VI-1 resides in  $\Delta S^\ddagger$  and has been attributed to a diminished steric restriction.<sup>60</sup> The increase in  $\Delta H^\ddagger$  on changing from ammonia (VI-1) to ethylenediamine (VI-3) spectator ligands finds precedent (V-1,2,6,7) and rationalization in terms of more difficult activation of the chelate ring<sup>51,54</sup> and/or the Co-N bonds.<sup>40</sup> However, the rate is accelerated due to an increased  $\Delta S^\ddagger$  which is ascribed to a greater precursor stability when the carbonyl function, to which chromium(II) probably binds,<sup>60</sup> is constrained to be more accessible by chelation via the amine function. The effect can be expected to extend, with allowances for other variations, to chelated carboxylates in general.

In changing the chelated complement from amine (VI-3) to thioether (VI-4), a 125-fold enhancement can be compared with the iron(II) reductions of cis- $Co(en)_2(NH_3)Cl^{2+}$  vs.

Table V. Selected Ligand Effects in Monodentate-Bridged Cobalt(III)-Amine Reductions<sup>a</sup>

Entry	Reaction	$k, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$	Ref
1	$\text{Co}(\text{NH}_3)_2\text{Br}^{2+}-\text{Fe}^{2+ b}$	$8.9 \times 10^{-4}$	15.5 ( $\pm 0.3$ )	-20.4 ( $\pm 1.0$ )	53
2	$\text{cis-Co}(\text{en})_2(\text{NH}_3)\text{Br}^{2+}-\text{Fe}^{2+}$	$6.1 \times 10^{-6}$	17.6 ( $\pm 1.5$ )	-23.2 ( $\pm 5.0$ )	53
3	$\text{cis-Co}(\text{en})_2(\text{H}_2\text{O})\text{Br}^{2+}-\text{Fe}^{2+}$	$2.8 \times 10^{-4}$	15.4 ( $\pm 0.8$ )	-23.2 ( $\pm 2.7$ )	53
4	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}-\text{Fe}^{2+ c}$	$1.4 \times 10^{-3}$	12.5 ( $\pm 1.2$ )	-30 ( $\pm 5$ )	57
5	$\text{cis-Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}-\text{Fe}^{2+}$	$3.5 \times 10^{-2}$	14.1 ( $\pm 0.5$ )	-18 ( $\pm 2$ )	50
6	$\text{Co}(\text{NH}_3)_5\text{OH}^{2+}-\text{Cr}^{2+}$	$1.7 \times 10^6$	4.6	-18	59
7	$\text{cis-Co}(\text{en})_2(\text{NH}_3)\text{OH}^{2+}-\text{Cr}^{2+}$	$2.0 \times 10^5$	5.6 ( $\pm 1.9$ )	-15.5 ( $\pm 6$ )	47
8	$\text{cis-Co}(\text{en})_2(\text{H}_2\text{O})\text{OH}^{2+}-\text{Cr}^{2+}$	$7.9 \times 10^5$	5.8 ( $\pm 2.1$ )	-12 ( $\pm 7$ )	47
9	$\text{trans-Co}(\text{en})_2(\text{NH}_3)\text{OH}^{2+}-\text{Cr}^{2+}$	$2.2 \times 10^5$	1.8 ( $\pm 1.4$ )	-28 ( $\pm 5$ )	47
10	$\text{trans-Co}(\text{en})_2(\text{H}_2\text{O})\text{OH}^{2+}-\text{Cr}^{2+}$	$2.6 \times 10^6$	2.0 ( $\pm 2.1$ )	-22 ( $\pm 7$ )	47
11	$\text{cis-Co}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}-\text{Cr}^{2+ d}$	$2.4 \times 10^5$	-2 ( $\pm 3$ )	-41 ( $\pm 4$ )	36
12	$\text{cis-Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}-\text{Cr}^{2+ d}$	$4.0 \times 10^5$	1 ( $\pm 4$ )	-29 ( $\pm 11$ )	36
13	$\text{cis-Co}(\text{en})_2(\text{H}_2\text{O})\text{F}^{2+}-\text{Cr}^{2+ d}$	$1.4 \times 10^5$	0 ( $\pm 6$ )	-34 ( $\pm 20$ )	36
14	$\text{trans-Co}(\text{en})_2(\text{H}_2\text{O})\text{Br}^{2+}-\text{Fe}^{2+}$	$9.4 \times 10^{-2}$	12.6 ( $\pm 0.3$ )	-20.8 ( $\pm 1.1$ )	53

<sup>a</sup>  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ),  $25^\circ \text{C}$ . <sup>b</sup> Others report  $\Delta H^\ddagger = 13.3 (\pm 1.2) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -28 (\pm 5) \text{ eu}$  ( $I = 1.0 \text{ M}$ )<sup>57</sup> and  $\Delta H^\ddagger = 15.6 (\pm 0.6) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -20 (\pm 2) \text{ eu}$  ( $I = 1.7 \text{ M}$ ).<sup>58</sup> <sup>c</sup> Reference 58 gives  $\Delta H^\ddagger = 14.5 (\pm 0.6) \text{ kcal/mol}$  and  $\Delta S^\ddagger = -23 (\pm 2) \text{ eu}$  at  $I = 1.7 \text{ M}$ . <sup>d</sup>  $I = 0.10 \text{ M}$ .

$\text{cis-Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$  (25-fold increase)<sup>46</sup> and of  $\text{cis-Co}(\text{en})_2\text{Cl}_2^+$  vs.  $\text{cis-Co}(\text{NH}_2(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{NH}_2)\text{Cl}_2^+$  (840-fold increase).<sup>46,62</sup> With this *single*, *cis*-cochelated thioether function (VI-4), a factor of  $\sim 55$  in the rate increase is attributable to an increase in  $\Delta S^\ddagger$ , which can be rationalized in terms of the lower demands placed on surrounding solvent by the larger and less hydrogen-bonding thioether function, relative to *cis*  $\text{H}_2\text{O}$  or  $\text{NH}_3$ . Such a solvation-dominated, nonbridging ligand influence has not previously been documented to our knowledge.

A 17-fold rate enhancement from chelated amine (VI-3) to alcohol (VI-5) is smaller than the 130-fold enhancement accompanying a roughly analogous monodentate change (VI-6 vs. VI-1), which may have to do with the chelating methylene substituent introducing greater resistance to activation. The similarity in rates between VI-5 and VI-6 suggests that the effects of ethylenediamine substitution and chelated carboxylate accessibility in VI-5 are compensatory. Steric inhibition seems evident in the rate of reduction of VI-7 relative to VI-5, perhaps due to enthalpic instability of the precursor complex (compare VI-1 and VI-8).

**Chalcogenide-Bridged Reactions.** The systems of Table VII were the principal subjects of this research. In attempting to evaluate the bridging efficiencies of chalcogenide functions, comparison can first be made with oxidants lacking a chelate linkage to the bridging atom. The presence of an ethylene linkage in VII-1a decreases the rate relative to V-7 by a factor of 210, primarily through a decrease in  $\Delta S^\ddagger$ . Precursor instability is likely responsible on two counts: diminished basicity of the chelated alkoxide<sup>9</sup> and steric restriction by the methylene substituent on oxygen.

The importance of a steric factor<sup>5</sup> appears supported by a 35-fold rate increase with the thiolate analogue (VII-1b). One source of the lower  $\Delta S^\ddagger$  barrier almost certainly lies in a diminished interference, by the methylene substituent, with  $\text{Cr}(\text{H}_2\text{O})_5^{2+}$  attachment to the larger sulfur atom. Less solvent electrostriction<sup>56,63</sup> around the activated complex at this approach distance would also contribute to a less negative  $\Delta S^\ddagger$  (compare V-1 vs. V-4). The net increase in  $\Delta H^\ddagger$  probably resides in the less basic thiolate function. Thus, any relative ease of precursor activation arising from the ground-state elongation of the Co-N bond *trans* to sulfur<sup>30</sup> and a greater ease of Co-S bond stretching<sup>5</sup> are apparently overcome by enthalpic instability of the precursor (compare V-1 and V-4).

A change in chelated nonbridging function from amine (VII-1a) to alcohol (VII-2a) results in the expected rate increase for the alkoxide-bridged systems. The decreased rates relative to the unchelated V-7 and V-8 analogues almost certainly have parallel sources given the similarities in chelate backbones.

Changing the nonbridging chelate function from amine to alcohol in the thiolate-bridged category (VII-1b to VII-2b) enhances the rate  $\leq 200$ -fold<sup>64</sup> (compared to 7.7-fold for alkoxide bridging, VII-1a vs. VII-2a). This factor is 4-300 times larger than with comparable monodentate-bridged systems (compare V-2 vs. V-3, V-7 vs. V-8, V-11 vs. V-12, and *cis-Co}(\text{en})\_2(\text{NH}\_3)\text{Cl}^{2+}-\text{Fe}(\text{II}),  $k = 1.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , vs. *cis-Co}(\text{en})\_2(\text{H}\_2\text{O})\text{Cl}^{2+}-\text{Fe}(\text{II}),  $k = 4.6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ <sup>46</sup>). These observations establish the thiolate-bridging function, at least when it is a chelate donor on Co(III), as being especially sensitive to this type of *cis* nonbridging ligand change. The high enhancement factor may reflect a greater sensitivity to activation of the chelate ring containing sulfur or contributions from superexchange, discussed in the subsequent paper,<sup>10</sup> with the exceptionally oxidizable thiolate bridges.**

Even more striking is the rate enhancement by at least 830 on changing from alkoxide (VII-2a) to thiolate (VII-2b) bridging. This far exceeds enhancement factors on changing from fluoride to chloride with Cr(II) (V-12 vs. V-13) or from *cis-Co}(\text{en})\_2(\text{H}\_2\text{O})\text{Cl}^{2+} ( $k = 4.6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ <sup>46</sup>) to *cis-Co}(\text{en})\_2(\text{H}\_2\text{O})\text{Br}^{2+} ( $2.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ <sup>53</sup>) with Fe(II). (Even the enhancement factor from VI-1a to VI-1b appears substantial in this light.) In explanation, some combination of three possibilities seems inescapable: (a) a unique kinetic pattern emerges when bridging functions are incorporated in chelating ligands; (b) divalent sulfur is particularly efficient as a bridging atom;<sup>5,6</sup> (c) alkoxide oxygen is particularly inefficient as a bridging atom because of steric restrictions in spite of its basicity advantage toward sterically undemanding protons. Without denying (a) or (b) we wish to focus attention on (c) for which we draw support from the  $\Delta S^\ddagger$  comparisons of V-7, VII-1a, -1b, -3a, and -4b (considered further below). One important conclusion can be stated: with the possible exceptions of selenium and tellurium, *divalent sulfur is unique as a donor atom in allowing* (but not necessarily enforcing) *a high level of inner-sphere reactivity while bearing a substituent significantly larger than the proton.***

The possible importance of this characteristic for the reactions of thiolate-coordinated metalloproteins<sup>2,4</sup> cannot be assessed at present for lack of demonstrated inner-sphere mechanisms; e.g., see ref 7. Nevertheless, the principle may prove operative since a redox metal center must find attachment to its protein through some donor atom substituent larger than hydrogen, most frequently carbon.

In turning to more detailed considerations, alkoxide-bridged oxidants react more slowly with carboxylate (VII-3a) than with alcohol (VII-2a) as the auxiliary chelate function. (A double-bridged mechanism, inaccessible to our chelated system, has been postulated for the most similar available monodentate comparison, *cis-Co}(\text{NH}\_3)\_4(\text{OH})(\text{OOCCH}\_3)^{2+},<sup>61</sup> for which*



Table VI. Carboxylate-Bridged Reductions of Cobalt(III)-Amine Complexes by Chromium(II)<sup>a</sup>

Entry	Oxidant	$k, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$	Ref
1	$\text{Co}(\text{NH}_3)_5(\text{OOCCH}_3)^{2+}$	0.35	8.2	-33	60b
2	$\text{Co}(\text{NH}_3)_5(\text{OOCCH}_3)^{2+}$	7.2	8.3	-27	60
3	$\text{Co}(\text{en})_2(\text{OOCCH}_2\text{NH}_2)^{2+}$	2.22	8.9 ( $\pm 0.1$ )	-27 ( $\pm 0.4$ )	b
4	$\text{Co}(\text{en})_2(\text{OOCCH}_2\text{SCH}_3)^{2+}$	274	8.4 ( $\pm 0.1$ )	-19 ( $\pm 0.2$ )	b
5	$\text{Co}(\text{en})_2(\text{OOCCH}_2\text{OH})^{2+}$	38.4			b
6	<i>cis</i> - $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{OOCCH}_3)^{2+}$	47			61
7	$\text{Co}(\text{en})_2(\text{OOCCH}(\text{CH}_3)\text{OH})^{2+}$	7.44			b
8	$\text{Co}(\text{NH}_3)_5(\text{OOCCH}(\text{CH}_3)_2)^{2+}$	0.0096	11.1	-31	60

<sup>a</sup> 25 °C,  $I = 1.0 \text{ M}$ . <sup>b</sup> This work.Table VII. Chalcogenide-Bridged Reductions of Cobalt(III)-Amine Complexes by Chromium(II)<sup>a</sup>

Entry	Oxidant (alkoxide bridged)	$k, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$	Entry	Oxidant (thiolate bridged)	$k, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$	S:O rate enhancement factor
1a	$\text{Co}(\text{en})_2(\text{OCH}_2\text{CH}_2\text{NH}_2)^{2+}$	$9.4 \times 10^2$	5.1 ( $\pm 0.4$ )	-28 ( $\pm 2$ )	1b	$\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$	$3.3 \times 10^4$	7.3 ( $\pm 0.3$ )	-13.5 ( $\pm 1$ )	35
2a	$\text{Co}(\text{en})_2(\text{OCH}_2\text{CH}_2\text{OH})^{2+}$	$7.2 \times 10^3$			2b	$\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$	$6.0 \times 10^6$			830
3a	$\text{Co}(\text{en})_2(\text{OCH}_2\text{COO})^+$	$1.9 \times 10^3$	~2.2	~36	3b	$\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})^+$	$6.4 \times 10^6$	(~1) <sup>d</sup>	(~-24) <sup>d</sup>	3400
4a	$\text{Co}(\text{en})_2(\text{OCH}(\text{CH}_3)\text{COO})^+$	50	(~-2) <sup>d</sup>	(~-43) <sup>d</sup>	4b	$\text{Co}(\text{en})_2(\text{SCH}(\text{CH}_3)\text{COO})^+$	$1.5 \times 10^5$	1.1 ( $\pm 0.2$ )	-31 ( $\pm 1$ )	3000

<sup>a</sup> 25 °C,  $I = 1.0 \text{ M}$  ( $\text{ClO}_4^-$ ), except where noted otherwise. <sup>b</sup>  $I = 0.10 \text{ M}$  ( $\text{ClO}_4^-$ ), 18.6 °C. <sup>c</sup>  $I = 0.10 \text{ M}$  ( $\text{ClO}_4^-$ ), 25 °C. <sup>d</sup> Estimates; see text.

$k_d \approx 5.6 \times 10^5$  if  $K_a < 5.0 \times 10^{-6}$ .<sup>66</sup>) The remarkable S:O enhancement factor of at least 3400 (VII-3) further supports the efficacy of bridging thiolate.

Methyl substitution on the carboxylate ligands (VII-4) decreased the rates by a surprisingly similar factor of ~40 within either alkoxide- or thiolate-bridged systems (internally comparable in ionic strength) leaving the S:O enhancement factor about the same. The most likely inference to be drawn is that the only competitive bridge to either oxygen or sulfur is on the hydrogen side, bridge formation being comparatively blocked in proximity of the methyl substituent. Thus, the activation demands could increase in parallel for the two systems and would, according to this rationale, seem primarily attributable to ~7-eu decreases in  $\Delta S^\ddagger$  on methyl substitution from VII-3a to VII-4a (~-43 eu) and from VII-3b (~-24 eu) to VII-4b. While the values in parentheses are unmeasured estimates to be viewed with caution, such an interpretation finds favor in comparison with the 6-eu variation between VI-1 and -2 and in a ~12-eu advantage in  $\Delta S^\ddagger$  for thiolate (VII-3b,4b) over alkoxide (VII-3a,4a) complexes which is consistent with the 14-eu advantage for VII-1b over VII-1a.

Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  that are higher and S:O rate ratios that are lower, respectively, with ethylenamine (VII-1) than with the methylenecarboxylate (VII-3,4) chelate skeletons suggest differences in their kinetic characteristics. No basis for such differences is apparent in the spectroscopic (Tables I and II) or acidity<sup>9</sup> data. While comparison of VII-3b,4b with V-9,10 seems consistent with kinetic enhancement from the elongated Co-N bond trans to sulfur,<sup>30</sup> no explanation is afforded thereby of the activation parameters with similarly distorted VII-1b compared to VII-1a,3a which are presumably less distorted. The more negative activation entropies with the carboxylate chelates are surprising in view of an opposing effect expected from their lower charge.<sup>56,63</sup> Perhaps relatedly, with chromium(II) as reductant (Table V) there is no precedent for the magnitude by which  $\Delta H^\ddagger$  is lower for the carboxylate than for the amine chelates based on cis non-bridging ligand changes.<sup>67a</sup> A tentative rationalization of the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  differences in terms of different requirements for the chelate backbones, particularly when one class has a protruding carbonyl function requiring solvation,<sup>67b</sup> can be offered from the limited data now available.

Rate constants for thiolate-bridged reductions of  $\text{Cr}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$  and  $\text{Cr}(\text{en})_2(\text{SCH}_2\text{COO})^+$  by  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  have recently been reported as  $1.1 \times 10^{-4}$  and  $\leq 1.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>68</sup> That the former is significantly smaller than with a variety of *unsubstituted* bridging functions<sup>68</sup> need not surprise us in view of the comparisons of VII-1b with V-7,<sup>10</sup> for example, among the kinetically less sensitive cobalt(III) systems. Our advocacy of the efficiency of thiolate bridging is taken with respect to bridging atoms bearing substituents of comparable size and steric hindrance. If our contentions are correct, inner-sphere reduction of  $\text{Cr}(\text{en})_2(\text{OCH}_2\text{CH}_2\text{NH}_2)^{2+}$  should be exceedingly slow.

The rate constant with mercaptoacetate, which may reflect carboxylate bridging,<sup>68</sup> does seem slow relative to our results and  $\text{Co}^{\text{III}}/\text{Cr}^{\text{III}}$  rate ratios appear anomalously high.<sup>68</sup> This has been attributed,<sup>68</sup> in part, to the lack of ground-state elongation of the Cr-N bond trans to sulfur.<sup>30</sup> We wish to offer a possible concomitant effect. Since inner-sphere chromium(III)-amine reductions are much more sensitive kinetically to changes in bridging ligands than corresponding cobalt(III) reductions (see, e.g., ref 68), it would not be surprising if they were more sensitive to sterically inhibiting substituents on a bridging atom even as large as sulfur.

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**Registry No.** [Co(en)<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)] [ClO<sub>4</sub>]<sub>2</sub>, 40330-50-5; [Co(en)<sub>2</sub>(OOCCH<sub>2</sub>S)] ClO<sub>4</sub>, 26743-67-9; [Co(en)<sub>2</sub>(OOCCH(CH<sub>3</sub>)S)] ClO<sub>4</sub>, 60828-75-3; [Co(en)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>O)] ClO<sub>4</sub>, 60803-56-7; [Co(trien)(SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)] [ClO<sub>4</sub>]<sub>2</sub>, 60803-58-9; [Co(en)<sub>2</sub>(H<sub>2</sub>O)(OCH<sub>2</sub>CH<sub>2</sub>SHg)] [ClO<sub>4</sub>]<sub>3</sub>, 60803-43-2; [Co(en)<sub>2</sub>(H<sub>2</sub>O)(OCH<sub>2</sub>CH<sub>2</sub>SHg)] [Co(CN)<sub>6</sub>]<sub>3</sub>, 60803-42-1; [Co(en)<sub>2</sub>(H<sub>2</sub>O)(OCH<sub>2</sub>CH<sub>2</sub>Sag)] [ClO<sub>4</sub>]<sub>2</sub>, 60803-44-3; [Co(en)<sub>2</sub>(CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)] [ClO<sub>4</sub>]<sub>3</sub>, 60803-59-0; [Co(en)<sub>2</sub>(OOCCH<sub>2</sub>NH<sub>2</sub>)] [ClO<sub>4</sub>]<sub>2</sub>, 60803-60-3; [Co(en)<sub>2</sub>(OOCCH<sub>2</sub>NH<sub>2</sub>)] [ClO<sub>4</sub>]<sub>2</sub>, 60635-87-2; Co(H<sub>2</sub>O)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>, 15305-50-7; (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>·2HCl, 56-17-7; *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl, 14040-33-6; [Co(trien)Cl<sub>2</sub>]Cl, 15555-97-2; [Co(en)<sub>2</sub>(OOCCH<sub>2</sub>NH<sub>2</sub>)] Cl<sub>2</sub>, 14408-57-2; Co(en)<sub>2</sub>(OCH<sub>2</sub>COO)<sup>+</sup>, 46240-06-6; Co(en)<sub>2</sub>(HOCH<sub>2</sub>COO)<sup>2+</sup>, 38731-30-5; Co(en)<sub>2</sub>(OCH(CH<sub>3</sub>)COO)<sup>+</sup>, 46360-38-7; Co(en)<sub>2</sub>(HOCH(CH<sub>3</sub>)COO)<sup>2+</sup>, 38641-66-6; Co(en)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sup>2+</sup>, 38641-65-5; Co(en)<sub>2</sub>(HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sup>3+</sup>, 41742-37-4; Co(en)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>OH)<sup>2+</sup>, 60828-73-1; Co(en)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)<sup>+</sup>, 46137-98-8; Co(en)<sub>2</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OH)<sup>3+</sup>, 38673-81-3; Co(en)<sub>2</sub>(OOCCH<sub>2</sub>OD)<sup>2+</sup>, 60803-61-4; Co(en)<sub>2</sub>(DOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sup>3+</sup>, 60803-62-5; Co(en)<sub>2</sub>(DOCH<sub>2</sub>CH<sub>2</sub>OD)<sup>3+</sup>, 60803-63-6; Co(en)<sub>2</sub>(DOCH<sub>2</sub>CH<sub>2</sub>S)<sup>2+</sup>, 60804-22-0; DOOCCH(CH<sub>3</sub>)SD, 60762-10-9; Co(en)<sub>2</sub>(OOCCH(CH<sub>3</sub>)OD)<sup>2+</sup>, 60804-23-1; Co(en)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OH)<sup>2+</sup>, 60804-24-2; Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, 20574-26-9; V(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, 15696-18-1; Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, 19052-44-9.

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