340 *Inorg. Chem.* **1985**, *24*, 340–346

pound 3 (R = C_2H_5) was purified by sublimation (60 °C (0.1 mm); mp 59–67 °C). The two geometrical isomers of 3 (R = CH_3) were separated by liquid chromatography[18] using CH_2Cl_2/C_6H_{14} (60:40) solvent (mp: cis, 152–154 °C; trans, 134–137 °C). Attempted chromatography of 3 (R = C_2H_5) resulted in extensive decomposition, presumably by hydrolysis.

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Supplementary Material Available: Table I for cyclotriphosphazenes showing mass spectral and elemental analysis data (2 pages). Ordering information is given on any current masthead page.

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Reduction of Cysteinesulfenato and Cysteinesulfinato Derivatives of Cobalt(III) by Chromium(II)

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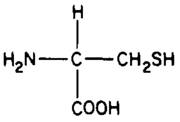
The reductions of the (cysteinesulfenato)bis(ethylenediamine)cobalt(III), abbreviated $[Co(en)_2(CysO)]^{2+}$, and the (cysteinesulfinato)bis(ethylenediamine)cobalt(III), abbreviated $[Co(en)_2(CysO_2)]^{2+}$, complexes by Cr(II) proceeded rapidly. The actual reduction of the cysteinesulfenato derivative was too fast to be measured directly but was estimated to be $>3 \times 10^4$ M^{-1} s^{-1}. Two electrons were rapidly consumed by the oxidant. It was postulated that one of these was used in inner-sphere attack by Cr(II) at the sulfur atom and the other remained on the sulfur ligand producing a radical intermediate. Three fast reactions followed reduction: the first was attributed to S–O bond fission ($k^{25 °C} = 39.5$ s^{-1}, $\Delta H^* = 10 \pm 1$ kcal/mol, $\Delta S^* = -16 \pm 3$ eu), the second was assigned to formation of an encounter pair from two radical ions followed by coupling to give the cystine dimer of Cr(III) ($k^{25 °C} = 5.4 \pm 0.2$ s^{-1}, $\Delta H^* = 11 \pm 2$ kcal/mol, $\Delta S^* = -19 \pm 6$ eu), and the third reaction was attributed to the Cr(II)-catalyzed aquation of the dimeric Cr(III)–cystine product ($k^{25 °C} = 2.9 \pm 0.4$ M^{-1} s^{-1}, $\Delta H^* = 9 \pm 2$ kcal/mol, $\Delta S^* = -26 \pm 11$ eu). The reduction of the cysteinesulfinato derivative occurred by attack of Cr(II) at sulfur to produce the Cr(III)–sulfur-bonded intermediate of cysteinesulfinic acid ($k^{25 °C} = (1.46 \pm 0.07) \times 10^3$ M^{-1} s^{-1}, $\Delta H^* = 4.4 \pm 0.3$ kcal/mol, $\Delta S^* = -29 \pm 1$ eu). This was followed by a slow Cr(II)-catalyzed aquation of the Cr(III)–sulfinic acid product ($k^{25 °C} = (2.5 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1}, $\Delta H^* = 21 \pm 2$ kcal/mol, $\Delta S^* = -1 \pm 5$ eu). These results are compared to work done on related systems.

The oxidation–reduction chemistry of metal-coordinated sulfur-containing organic ligands has received considerable attention over the past decade primarily as a result of the observation that sulfur (from the amino acids cysteine or methionine) is frequently found either close to the active site or directly bonded to the metal centers of proteins having important redox functions.[1,2] Bennett and his co-workers[3–5] first showed that thiolato sulfur could serve as an extremely efficient electron-transfer bridge between metal centers. Balahura and Lewis[6] found that a coordinated cysteine ligand having a sulfur atom directly bonded to the cobalt(III) center was rapidly reduced by Cr(II), again utilizing the sulfur as a bridge. Electron transfer via a noncoordinated thioether function in the reduction of methylcysteine and methionine complexes of cobalt(III) did not occur. Instead, reduction was found to take place through the coordinated carboxylate function.[6]

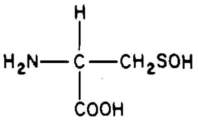
In an impressive series of reduction experiments[3,7] and X-ray structural studies,[8,9] it was shown that the remarkable efficiency of thiolate sulfur in mediating electron transfer to $(en)_2Co^{III}$ (where en is ethylenediamine) was due to its ability to exert a very strong ground-state trans effect (GSTE), thus decreasing the activation energy required for electron transfer. Sulfur was not, however, able to exert a similar effect in the corresponding $(en)_2Cr^{III}$ complexes. Nevertheless, since iron is frequently found in the active site of proteins and since the electron-transfer chemistry of iron is usually faster than that of cobalt, it is a reasonable conjecture that sulfur is present in these proteins because of its electron-mediating abilities.

Other sulfur-containing amino acids appear to be involved in biological transformations, including the oxidation products of cysteine (**1**), that is cysteinesulfenic acid (**2**) and cysteinesulfinic acid (**3**).



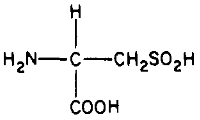
$H_2N{-}CH(COOH){-}CH_2SH$

1



$H_2N{-}CH(COOH){-}CH_2SOH$

2



$H_2N{-}CH(COOH){-}CH_2SO_2H$

3

Sulfenic acids (RSOH) in general are very unstable, elusive species,[10–18] and indeed, only a few have ever been isolated.[19–23] The instability of the sulfenic acid moiety is attributed to its high reactivity as either a nucleophile or an electrophile. The observation that protein sulfenic acids may play a regulatory role in enzyme-catalyzed reactions provides a particularly strong incentive for studying the chemistry of these species.[24] In an important

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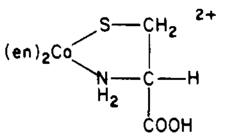
(1) Sutin, N. *Adv. Chem. Ser.* **1977**, *No. 162*, 156.
(2) Jones, T. E.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1975**, *97*, 7485.
(3) Lane, R. H.; Bennett, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1089.
(4) Gilroy, M.; Sedor, F. A.; Bennett, L. E. *J. Chem. Soc., Chem. Commun.* **1972**, 181.
(5) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Eisenhardt, P. F.; Bennett, J. P., Jr.; Ewall, R. X.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 93.
(6) Balahura, R. J.; Lewis, N. A. *Inorg. Chem.* **1977**, *16*, 2213.
(7) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1976**, *15*, 139.
(8) Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690.
(9) Elder, R. C.; Kennard, G. J.; Payne, D. M.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 1296.
(10) Kice, J. L.; Cleveland, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 104.
(11) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.
(12) Vinkler, E.; Klivenyi, F. *Int. J. Sulfur Chem.* **1973**, *8*, 111.
(13) Davis, F. A.; Jenkins, R. H., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7969.
(14) Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Org. Chem.* **1981**, *46*, 3467.
(15) Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 7016.
(16) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 197.
(17) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.
(18) Davis, F. A.; Friedman, A. J.; Nadir, U. K. *J. Am. Chem. Soc.* **1978**, *100*, 2844.
(19) Fries, K. *Chem. Ber.* **1912**, *45*, 2659.
(20) Bruice, T. C.; Markiw, P. T. *J. Am. Chem. Soc.* **1957**, *79*, 3150.
(21) Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 317.
(22) Jenny, W. *Helv. Chim. Acta* **1958**, *41*, 326.
(23) Chou, T. S.; Burgtorf, J. R.; Ellis, A. L.; Lammert, S. R.; Kukolja, S. R. *J. Am. Chem. Soc.* **1974**, *96*, 1609.

review article, Allison[24] has documented several indirect pieces of evidence suggesting that sulfenic acids are the oxidation products of protein sulfhydryl groups when these side chains are isolated, by the folding of the protein, for example, so that they are prevented from reacting with each other to form disulfides. In addition, the reactivity of the sulfenic acid derivative of glyceraldehyde 3-phosphate dehydrogenase (GPD) with a variety of nucleophiles has shown that protein sulfenic acids are excellent electrophilic centers that are well adapted for participation in oxidation catalysis.[24]

Because of their highly reactive nature, very little information is available on the chemistry of free sulfenic acids. When coordinated to a metal, however, they are greatly stabilized[25] and the metal complexes have, therefore, provided us in this work with a vehicle for the investigation of the reduction chemistry of the cysteinesulfenic acid molecule. The kinetics of the H_2O_2 oxidation of the (cysteineato)bis(ethylenediamine)cobalt(III) complex to the sulfenic derivative have already been studied,[26] but the reduction chemistry of coordinated sulfenic acids has not hitherto been reported, except for a brief qualitative study involving reduction by thiol in *N*,*N*-dimethylformamide.[27]

Sulfinic acids (RSO_2H), on the other hand, are quite stable, and their transition-metal derivatives have been known for some time.[28,29] Cysteinesulfinic acid (CSA) is an important intermediary compound in the metabolism of sulfur-containing amino acids.[30] In fact, the main oxidative pathway of cysteine in bacteria and animal tissues involves CSA as an intermediate. The synthesis of the sulfur-containing amino acid, taurine, occurs from cysteine via CSA. Taurine is present in rather large amounts in brain tissue where it has a heterogeneous distribution in the various brain areas.[31] Both a neurotransmitter and a neuromodulator role have been postulated for this particular amino acid.[32-34] Other studies have indicated that the CSA–taurine system may be important in the neuronal functions. For example, one may induce seizures in laboratory animals by the administration of CSA.[35]

These observations serve as a contrast to the lack of quantitative information on the reduction chemistry of CSA and sulfenic acids and the influence of oxidized sulfur on the rates and mechanisms of redox transformations. The reduction of the parent complex, (cysteinato)bis(ethylenediamine)cobalt(III) (**4**), has been reported in an earlier investigation.[6] In this work, we report the reactions of the cysteinesulfenic acid (**5**) and cysteinesulfinic acid (**6**) complexes of cobalt(III) with Cr(II).



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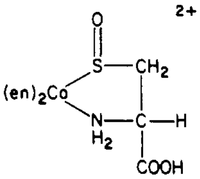

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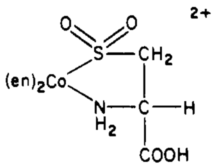

6

Experimental Section

Reagents. All reagent solutions were prepared in water that was deionized with a Barnstead high-capacity ion exchanger, then distilled with a Branstead Fi-stream glass distillation apparatus, and finally redistilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate solutions were made by dissolving anhydrous grade $LiClO_4$ (G. Frederick Smith Chemical Co.) in water and filtering the resulting solution through a 0.22-μm Durapore hydrophilic filter (Millipore Filter Corp.). Triplicate portions of the filtrate were then standardized by determining the amount of hydrogen ion released from an Amberlite IR120(H) analytical grade resin (BDH Chemicals Ltd.).

The perchloric acid solutions were prepared by dilution of 70% doubly distilled, reagent grade $HClO_4$ (G. Frederick Smith Chemical Co.). Aliquots of this solution were titrated to a bromothymol blue end point to determine the concentration. Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate (G. Frederick Smith Chemical Co.) in aqueous perchloric acid using zinc–mercury amalgam. The concentration of Cr(II) in the final solution was determined every 3 days by a standardization procedure described earlier.[36]

All standard solutions were stored under high-purity argon and were handled by using standard syringe techniques in an argon atmosphere.

Preparations. $[Co(en)_2(CysO)]ClO_4$. (Cysteinesulfenato)bis(ethylenediamine)cobalt(III) perchlorate (**5**) was prepared according to the method of Sloan and Krueger.[25] After the reaction was complete, the reaction mixture was diluted 10 times and was ion exchanged on an SP-Sephadex (SP-25-120) resin. The major orange band formed was separated from small yellow and brown bands by eluting with a 0.05 M NaCl solution. The resin containing the desired orange product was then physically removed from the column and was placed into a second column. Several column volumes of water were used to wash the resin to ensure that it was free of chloride ion. The product was then eluted in a concentrated form with a saturated aqueous $NaClO_4$ solution. Dark crystals separated upon cooling the eluent. These were filtered and dried at the pump. Anal. Calcd for $[CoC_7H_{21}N_5SO_3]ClO_4$: C, 20.3; H, 5.30; N, 16.9, S, 7.72. Found: C, 20.2; H, 5.44; N, 16.5; S, 7.83.

$[Co(en)_2(CysO_2)]ClO_4$. (Cysteinesulfinato)bis(ethylenediamine)cobalt(III) perchlorate (**6**) was also prepared following the method of Sloan and Krueger[25] and was ion exchanged as described for the sulfenato derivative. The desired product did not precipitate from the saturated $NaClO_4$ solution directly. It was obtained as a yellow powder by solvent exchange with 2-propanol. Anal. Calcd for $[CoC_7H_{21}N_5SO_4]ClO_4$: C, 19.6; H, 4.90; N, 16.3; S, 7.45. Found: C, 19.4; H, 5.20; N, 16.1; S, 7.62.

$[Cr(OH_2)_5(CysO_2)]^+$ by Electron Transfer. The sole product of the reaction between $[Co(en)_2(CysO_2)]^+$ and Cr(II) was a green Cr(III) compound. The reaction was performed by combining either 100 or 200 μmol of the cobalt(III) species with 200 or 400 μmol of Cr(II) in 10–20 mL of 0.1 M $HClO_4$. In all cases (1:1 or 2:1 ratio of Cr(II) to Co(III)), the same product was obtained. The product mixture was diluted 10 times and was passed through a column containing Sephadex SP 25-120 ion-exchange resin. The green Cr(III) product identified as $[Cr(OH_2)_5S(O)_2CH_2CH(NH_2)COO]^+$ was eluted with a solution of 0.25 M $NaClO_4$ in 0.05 M $HClO_4$ and was characterized by UV–visible spectroscopy.

$[Cr(OH_2)_5(CysO_2)]^+$ by Substitution. Cysteinesulfinic acid (1.0 g), prepared by the method of Toennies and Lavine,[37] was mixed with 3.5 mL of 0.5 M $[Cr(OH_2)_6]^{3+}$ in a 0.2 M $HClO_4$ solution. The mixture was stirred for 24 h. Several 0.5-mL portions of this mixture were ion exchanged on Sephadex SP 25-120. The green chromium(III) product obtained had the same electronic spectrum as that isolated from the electron-transfer studies (vide supra).

Kinetic Measurements. All of the fast reactions were performed on a Dionex D-110 stopped-flow spectrophotometer, interfaced to an Explorer II digital oscilloscope (Nicolet Instrument Corp.). The water bath on the stopped-flow instrument was connected to a Lauda NB-D temperature-controlled bath having an R2U electronic relay unit. The temperature was controlled with a mercury-contact thermoregulator and was monitored in the water bath of the stopped-flow instrument with an ASTM thermometer calibrated from 0 to 50 °C (Fisher Scientific).

The slow aquation of the $[Cr(OH_2)_5(CysO_2)]^+$ complex was studied with an Hitachi EPS-3T spectrophotometer. The quartz cell containing the reactants was placed into a metal cell block through which water flowed to stabilize the temperature. The water temperature was maintained by an external Lauda NB-D water bath having an R2U electronic relay unit. A small probe was inserted into the metal cell holder, and a YSI Model 72 proportional temperature controller sensed the temperature of this probe and controlled it to the desired value. The actual temperature of the reaction mixture was monitored by an ASTM thermometer inserted into a duplicate cell. All components of the reaction mixture were allowed to equilibrate before the reductant, Cr(II), was added to initiate the reaction.

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(24) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293.
(25) Sloan, C. P.; Krueger, J. H. *Inorg. Chem.* **1975**, *14*, 1481.
(26) Herting, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Inorg. Chem.* **1978**, *17*, 1649.
(27) Lydon, J. D.; Deutsch, E. *Inorg. Chem.* **1982**, *21*, 3180.
(28) Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elden, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.
(29) Jacobson, S. E.; Reich-Rohrwig, P.; Wojcicki, A. *Inorg. Chem.* **1973**, *12*, 717.
(30) Cederblad, G. *Biochem. Med.* **1980**, *24*, 103.
(31) Recasens, M.; Benezra, R. "Amino Acid Neurotransmitters"; DeFeudis, F. V., Mandel, P., Eds.; Raven Press: New York, 1981; p 545.
(32) Davidson, A. N.; Kaczmarek, L. K. *Nature (London)* **1971**, *234*, 107.
(33) Pasantes-Morales, H.; Klethi, J.; Urban, P. F.; Mandel, P. *Physiol. Chem. Phys.* **1972**, *4*, 339.
(34) Gruener, R.; Bryant, H. J. *J. Pharmacol. Exp. Ther.* **1975**, *194*, 514; *Chem. Abstr.* **1975**, *83* 158486*M*.
(35) Iwata, H.; Yamagami, S.; Mizuo, H.; Baba, A. *Jpn. J. Pharm.* **1980**, *30*, 8189; *Chem. Abstr.* **1981**, *94*, 186033*g*.
(36) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1533.

Table I. Kinetic Data for the First Reaction in the Chromium(II) Reduction of $[Co(en)_2(CysO]^+$ (μ = 1.00 M ($LiClO_4$))

temp,[a] °C	$[H^+]$,[b] M	$[Co(en)_2(CysO)]^+ \times 10^3$,[b] M	$[Cr(II)] \times 10^2$,[b] M	k_{obsd},[c] s^{-1}
25.0	0.10	3.19	6.28	38.6
	0.10	3.22	9.66	38.9
	0.10	3.30	13.2	38.9
	0.10	3.14	18.8	41.3
	0.10	3.24	25.9	42.1
	0.20	3.11	6.23	40.7
	0.40	3.16	6.13	48.5
	0.60	3.16	6.33	55.7
	0.80	3.20	6.19	59.6
35.0	0.10	3.22	6.40	70.5
45.0	0.10	3.15	6.29	127

[a] The temperatures were controlled to ±0.1 °C, or better. [b] Concentrations were initial values in molar units. [c] The values shown are averages of two or three runs per data point. The complete sets of data are available as Supplementary Material.

Table II. Kinetic Data for the Second Reaction in the Chromium(II) Reduction of $[Co(en)_2(CysO)]^+$ (μ = 1.00 M ($LiClO_4$))

temp,[a] °C	$[H^+]$,[b] M	$[Co(en)_2(CysO)]^+ \times 10^3$,[b] M	$[Cr(II)] \times 10^2$,[b] M	k_{obsd},[c] s^{-1}
25.0	0.10	3.16	6.31	5.46
	0.10	3.22	9.66	5.06
	0.10	3.30	13.2	4.95
	0.10	3.24	25.9	5.33
	0.20	3.06	6.13	6.03
	0.40	3.16	6.14	6.72
	0.60	3.17	6.37	7.53
	0.80	3.20	6.20	7.70
35.0	0.10	3.22	6.41	11.0
45.0	0.10	3.15	5.25	17.2

[a] The temperatures were controlled to ±0.1 °C or better. [b] Concentrations were initial values in molar units. [c] The values shown are averages of two or three runs per data point. The complete sets of data are available as Supplementary Material.

All reactions were carried out under pseudo-first-order conditions, i.e. the reductant was always present in greater than 20-fold excess over the oxidant. The ionic strength was controlled to 1.00 in each experiment with the standard $LiClO_4$ solution.

Physical Measurements. The ultraviolet and visible spectra of the various metal complexes were obtained on either an Hitachi EPS-3T or a Perkin-Model 330 spectrophotometer. All microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Results

I. The Sulfenato System. The cobalt(III) complex of the cysteinesulfenic acid was unstable in solution, and it was therefore necessary to work with freshly prepared solutions. This instability has been noted by previous investigators.[26,29]

Three consecutive reactions were observed in the reaction of Cr(II) with $[Co(en)_2(CysO)]^+$. The first and third reactions were monitored at 400 nm at which wavelength both showed a decrease in absorption with time. The second reaction did not give an appreciable absorbance change in the visible region but produced a sharp increase in absorbance at 285 nm, at which wavelength this reaction was studied. The kinetic data for these reactions are collected in Tables I, II, and III.

The first two reactions observed showed a first-order dependence on the cobalt(III) concentration but were independent of the concentration of chromium(II). A slight acid dependence was observed for both steps. The rate law for each of the first two reactions, then, has the form

$$-\frac{d[\text{oxidant}]}{dt} = (a + b[H^+])[\text{oxidant}] \qquad (1)$$

Table III. Kinetic Data for the Third Reaction in the Chromium(II) Reduction of $[Co(en)_2(CysO)]^+$ (μ = 1.00 M ($LiClO_4$))

temp,[a] °C	$[H^+]$,[b] M	$[Co(en)_2(CysO)]^+ \times 10^3$, M	$[Cr(II)] \times 10^2$,[b] M	$k_2 \times 10^3$,[e,f] $M^{-1} s^{-1}$
25.0	0.10	2.33	12.8[c]	2.79
	0.20	3.17	6.33[d]	6.33
	0.40	3.16	6.14[d]	15.1
	0.60	3.15	6.33[d]	16.9
	0.80	3.20	6.19[d]	22.6
35.0	0.10	3.22	6.41[e]	5.88
45.0	0.10	3.15	6.30[e]	8.06

[a] The temperatures were controlled to ±0.1 °C, or better. [b] Concentrations were initial values in molar units. [c] Concentrations of [Cr(II)] varied from 6.04×10^{-2} to 25.9×10^{-2} M with no change in k_2; average of six runs given. [d] Average of two runs. [e] Average of three runs. [f] The complete sets of data are available as Supplementary Material.

Table IV. Summary of Rate Constants and Activation Parameters for the Reactions Involved in the Chromium(II) Reductions of the Sulfenato and Sulfinato Derivatives of (Cysteinato)bis(ethylenediamine)cobalt(III)[a]

compd	reaction studied	$k^{25\,°C}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$[Co(en)_2(CysO)]^+$ (5)	1st[b]	39.5 ± 0.7 s^{-1}	10 ± 1	−16 ± 3
	2nd[b]	5.4 ± 0.2 s^{-1}	11 ± 2	−19 ± 6
	3rd[b]	2.9 ± 0.4 $M^{-1} s^{-1}$	9 ± 2	−26 ± 11
$[Co(en)_2(CysO_2)]^+$ (6)	1st	(1.46 ± 0.07) × 10^{-3} $M^{-1} s^{-1}$	4.4 ± 0.3	−29 ± 1
	2nd	(2.5 ± 0.1) × 10^{-3} $M^{-1} s^{-1}$	21 ± 2	−1 ± 5

[a] The rate constants shown were computer generated from the activation parameters. [b] Values shown are for rate constants measured at $[H^+]$ = 0.10 M since these reactions are $[H^+]$ dependent.

Table V. Product Analysis Data for the Chromium(II) Reduction of $[Co(en)_2(CysO)]^+$ at 25.0 °C

amt used, μmol		amt recovered, μmol		
$[Co(en)_2(CysO)]^+$	[Cr(II)]	$[Co(en)_2(CysO)]^+$	[Co(II)]	[Cr(II)]/[Co(III)]
96	100	41.2	50.7	1.97
98	100	48.2	47.3	2.11
96	100	32.6	48.2	2.07

The third reaction followed pseudo-first-order kinetics and is presumed to be the attack of chromium(II) on a chromium(III) intermediate. Again, a slight acid dependence was seen. The rate law is of the form

$$-\frac{d[Cr(III)]}{dt} = (a + b[H^+])[Cr(III)][Cr(II)] \qquad (2)$$

The rate constants and activation parameters for these three reactions are collected in Table IV.

A slow fourth reaction, giving an increase in absorbance at 550 nm, was also observed on the stopped-flow instrument. The reaction rate was not very reproducible, but the rate constant was approximately 5×10^{-2} M^{-1} s^{-1}. To see whether this slow reduction were due to the reaction between Cr(II) and the proposed product cystine, we studied this reaction independently. Again, we saw the same irreproducible behavior giving an estimated rate constant of 6×10^{-2} M^{-1} s^{-1}. The difficulty encountered in obtaining good rate data is probably due to the instability of cystine in perchloric acid media. A blank study was performed by using cysteine in place of cystine. In this case, there was no absorbance change at 550 nm.

Each equivalent of $[Co(en)_2(CysO)]^+$ required 2 equiv of Cr(II) for complete reaction. The results of the product studies are given in Table V. The only product isolated from the ion-exchange

Table VI. Kinetic Data for the First Reaction in the Chromium(II) Reduction of $[Co(en)_2(CysO_2)]^+$ (μ = 1.00 M ($LiClO_4$))

temp,[a] °C	$[H^+]$,[b] M	$[Co(en)_2$-$(CysO_2)]^+ \times 10^3$,[b] M	$[Cr(II)] \times 10^2$,[b] M	$k_2 \times 10^3$,[d] $M^{-1}\ s^{-1}$
25.0	0.10	0.906	5.76	1.46[c]
	0.40	1.11	4.44	1.39
	0.80	1.11	4.44	1.49
35.0	0.10	1.11	4.44	1.88
	0.10	1.11	13.7	1.87
	0.40	1.11	4.44	1.89
	0.80	1.11	4.44	1.93
45.0	0.10	1.11	4.44	2.54
	0.10	1.11	13.3	2.35
	0.40	1.11	4.44	2.54
	0.80	1.11	4.44	2.48

[a] The temperatures were controlled to ±0.1 °C, or better. [b] Concentrations were initial values in molar units. [c] Average of seven runs, [Cr(II)] varied from 0.781×10^{-2} to 12.9×10^{-2} M with no change in k_2. [d] The complete sets of data are available as Supplementary Material.

Table VII. Kinetic Data for the Second Reaction in the Chromium(II) Reduction of $[Co(en)_2(CysO_2)]^+$ (μ = 1.00 M ($LiClO_4$))

temp,[a] °C	$[H^+]$,[b] M	$[Co(en)_2$-$(CysO_2)]^+ \times 10^4$,[b] M	$[Cr(II)] \times 10^2$,[b] M	$k_2 \times 10^3$,[e] $M^{-1}\ s^{-1}$
25.0	0.10	1.38	5.87	2.53[c]
35.0	0.10	1.38	5.83	7.57[c]
45.0	0.10	1.19	8.45	24.4[d]
	0.40	1.38	6.00	26.3
	0.80	1.38	5.89	23.5

[a] Temperatures were controlled to ±0.1 °C, or better. [b] Concentrations were initial values in molar units. [c] Average of three runs. [d] Average of four runs, [Cr(II)] varied from 5.74×10^{-2} to 14.7×10^{-2} M with no change in k_2. [e] The complete sets of data are available as Supplementary Material.

column was $[Cr(OH_2)_6]^{3+}$. Apparently, 1 equiv of Cr(II) was used by the ligand cysteinesulfenic acid and another equivalent was required for the electron-transfer reaction at the cobalt(III) metal center (vide infra).

The nature of the organic product formed in the reaction cannot be absolutely established, but it is probably cystine. We were unable to isolate this material in a pure state because its solubility was very similar to other components of the final solution. To establish that the sulfur atoms of the product were not oxidized, we treated the final solution with HCl and an excess of KI. Only a trace amount of iodine appeared. Compounds containing S═O bonds are known to liberate iodine quantitatively when subjected to this treatment.[37,38]

II. The Sulfinato System. Two consecutive reactions were observed in the Cr(II) reduction of $[Co(en)_2(CysO_2)]^+$. The first reaction was followed at 430 nm on the stopped-flow instrument, and the second reaction was monitored at 265 nm on the Hitachi EPS-3T spectrophotometer. Both reactions showed a decrease in absorbance with time at their respective wavelengths. The kinetic data are listed in Tables IV, VI, and VII.

Both reactions follow pseudo-first-order kinetics, and the rate was found to be independent of the acid concentration of the medium. Each, therefore, has a rate law of the form

$$-\frac{d[\text{oxidant}]}{dt} = k[\text{Cr(II)}][\text{oxidant}] \qquad (3)$$

Table VIII. Product Analysis Data for the Chromium(II) Reduction of $[Co(en)_2(CysO_2)]^+$ at 25.0 °C

amt used, μmol		amt recovered, μmol	
$[Co(en)_2$-$(CysO_2)]^+$	[Cr(II)]	$[Cr(H_2O)_5$-$(CysO_2)]^{2+}$	% product
200	400	183	91.5
100	200	90.9	90.9
100	200	90.3	90.3
100	400	98.6	98.6

Product analyses of kinetic mixtures of $[Co(en)_2(CysO_2)]^+$ and Cr(II) showed a single band that was assigned to be the inner-sphere product $[Cr(OH_2)_5S(O)_2CH_2CH(NH_2)(COO)]^+$. The product analysis data for the reduction process and the electronic spectra of this species and related complexes are collected in Tables VIII and IX, respectively. The product (**19**) was assigned to be a monodentate species by considering the extinction coefficient of its longest wavelength band (see Table IX). An extinction coefficient of 20–30 is typical of a compound having a monodentate ligand (**15**–**18**) whereas that of a chelated derivative has a value of 50–70 (**11**–**14**). As is usually the case, 1 mol of Cr(II) is consumed/mol of Co(III) initially present (see Table VIII).

The metal-to-ligand bonding was presumed to be through the sulfur atom rather than through oxygen for two reasons. First, chromium(III) complexes having only oxygen ligands do not show a peak in the UV region of the spectrum above 210 nm (**16**–**18** in Table IX). Second, cobalt(III) complexes (**4**, **7**) show that metal–sulfur-bonded species have a peak in the UV region at 280–290 nm as do the sulfenato (**5**, **8**) and the sulfinato (**6**, **9**) derivatives. The oxygen-bonded sulfinato linkage isomer (**10**), however, has a peak shifted almost 40 nm to lower energy. The chromium(III) product in the present study has a peak in the ultraviolet region that is shifted slightly to higher energy with respect to the sulfur-bonded derivative. By comparison to the analogous cobalt complexes, such a shift would not be anticipated for an oxygen-bonded isomer and the bonding in the chromium(III)–cystine derivative, therefore, likely occurs through the sulfur atom.

Discussion

The Sulfenato System. The Cr(II) reductions of cobalt(III) complexes in which there is a cobalt–sulfur bond present, i.e. the reactions of the cysteinato,[6] mercaptoacetato,[3] 2-mercaptopropionato,[5] and 2-(methylthio)ethylamino[5] complexes of cobalt(III), have previously been studied, and all were found to be extremely fast. As is usually the case, 1 mol of Cr(II) is consumed/mol of the cobalt(III) species present. The requirement in our studies for an extra mole of Cr(II) for each mole of the (sulfenato)cobalt(III) complex means that two electrons are being consumed in this process in some fashion. It is known that free sulfenic acids are susceptible to nucleophilic attack by reducing agents such as thiols.[46] Also, sulfenato complexes of cobalt(III) are reduced to the corresponding thiolato complexes by excess thiol in *N*,*N*-dimethylformamide.[27] These reactions are acid catalyzed, since protonation of the oxygen atom of the sulfenato moiety makes it a better leaving group.

In the mechanism shown in Scheme I, the strong tendency toward reduction of the coordinated sulfenic acid is expressed. The reductant, Cr(II), presumably attacks the S–O function, leaving an odd electron on the sulfur atom. Attack of another Cr(II) occurs on the sulfur atom, which results in reduction of the cobalt(III) center and production of a Cr(III) sulfur-bonded intermediate. Both reactions had a half-life of less than 1 ms and could not be observed on the stopped-flow instrument. Therefore, the order in which they occur cannot be absolutely established. A lower limit on the rates of these reductions may be calculated to be $3 \times 10^4\ M^{-1}\ s^{-1}$.

The next step, which we also observed on the stopped-flow instrument, was attributed to sulfur–oxygen bond fission. The metal species exists as an equilibrium mixture of protonated and unprotonated forms, with the former reacting the fastest. The

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(37) Toennies, G.; Lavine, T. F. *J. Biol. Chem.* **1936**, *113*, 571.

(38) Toennies, G. *J. Biol. Chem.* **1937**, *122*, 27.

(39) Mäcke, H.; Houlding, V.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6889.

(40) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 102.

Table IX. Electronic Spectra of $[Cr(OH_2)_5(CysO_2)]^+$ and Related Complexes

complex	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})				ref
$[Co(en)_2(SCH_2CH(COOH)(NH_2))]^{2+}$ (**4**)	600 (37, sh)	483 (126)		283 (11700)	25
$[Co(en)_2(S(O)CH_2CH(COO)(NH_2))]^+$ (**5**)		480 (600, sh)	371 (5910)	287 (3750)	25
$[Co(en)_2(S(O)_2CH_2CH(COO)(NH_2))]^+$ (**6**)		430 (190)		287 (11900)	25
$[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ (**7**)	600 (44, sh)	482 (142)		282 (13800)	28
$[Co(en)_2(S(O)CH_2CH_2NH_2)]^{2+}$ (**8**)		470 (500)	365 (6700)	284 (3700)	28
$[Co(en)_2(S(O)_2CH_2CH_2NH_2)]^{2+}$ (**9**)		432 (230)		288 (14200)	28
$[Co(en)_2(OS(O)CH_2CH_2NH_2)]^{2+}$ (**10**)		512 (134)	326 (4100)		39
$[Cr(OH_2)_4(SCH_2CH(COO)(NH_2)]^{2+}$ (**11**)	580 (50.3, sh)	483 (136)		282 (26000)	6
$[Cr(OH_2)_4(SCH_2CH_2NH_2)]^{2+}$ (**12**)	518 (69.3)	440 (46.9, sh)		266 (5680)	40
$[Cr(OH_2)_4(SCH(CH_3)COO)]^{\bullet}$ (**13**)	545 (71.2)	440 (52.2)		254 (5050)	40
$[Cr(OH_2)_4(SCH_2COO)]^+$ (**14**)	548 (70)	437 (55)		262 (5270)	7
$[Cr(OH_2)_5(SCH_2CH_2NH_2)]^+$ (**15**)	580 (21.6)	437 (33.8)		273 (4640)	40
$[Cr(OH_2)_4OOCCH_2SH]^{2+}$ (**16**)	568 (26.0)	411 (25.1)			40
$[Cr(OH_2)_4OOCCH_2OH]^{2+}$ (**17**)	568 (24.5)	411 (30.5)			40
$[Cr(OH_2)_5(OOCCH_2SCH_3)]^{2+}$ (**18**)	567 (26.7)	412 (25.9)			40
$[Cr(OH_2)_5S(O)_2CH_2CH(NH_2)(COO)]^+$ (**19**)	596 (20 ± 1)	420 (23 ± 1)		255 (980 ± 30)	this work[a]
	595 (19 ± 1)	420 (21 ± 1)		254 (960 ± 30)	this work[b]

[a] Values obtained from products of the electron-transfer experiments. [b] Values obtained from substitution experiments.

proton may attach itself to the oxygen or sulfur atom, but it probably prefers oxygen.[27] The acid equilibrium of the carboxylate group is not expected to influence the kinetics, because it is rather far away from the reaction site. Therefore, the oxygen atom is eliminated in the form of either an hydroxide ion or a water molecule. The product is a radical cysteine complex of chromium(III). The reaction was followed by observing the decrease in absorbance at 400 nm. Such a decrease would be expected for a chromium(III) complex undergoing a transformation from M–S–O to M–S bonding by analogy to the observed spectra of the $[Co(en)_2(CysO)]^+$ and $[Co(en)_2(Cys)]^+$ in this region (Table IX). Since the protonated oxygen in cysteinesulfenic acid is expected to be a better leaving group than the unprotonated oxygen, a rate enhancement was observed with increasing acid concentration.

The rate law derived for this step in the mechanism is

$$-\frac{d[Cr(III)]}{dt} = \left(\frac{k_1 + K_a k_2[H^+]}{1 + K_a[H^+]}\right)[Cr(III)] \qquad (4)$$

where Cr(III) is equal to the total concentration of both the protonated and unprotonated forms of the intermediate Cr(III) species, which is in turn equal to the initial concentration of the cobalt(III) complex. If K_a is very small, then $K_a[H^+] \ll 1$, and the rate expression (4) reduces to

$$-\frac{d[Cr(III)]}{dt} = (k_1 + k_2K_a[H^+])[Cr(III)] \qquad (5)$$

Hence, this equation takes the form of the observed rate law of eq 1. A plot of k_{obsd} vs. $[H^+]$ for this reaction gives the intercept $k_1 = 36.8 \pm 0.8$ s^{-1} and slope $k_2K_a = 29 \pm 2$ M^{-1} s^{-1}. The protonation constant of $[Co(en)_2S(O)CH_2CH_2NH_2)]^{2+}$ has been estimated to be less than 0.1 M^{-1} at $\mu = 1.0$ M.[28] If we accept this an an upper value for the K_a of complex **22**, then $k_2 \leq 3.0$ s^{-1}.

The second reaction observed on the stopped-flow instrument is again independent of the chromium(II) concentration. We attribute this reaction to coupling of the radical intermediates to yield the cystine dimer (complex **22**; see Scheme I). Since second-order kinetics would be expected if two radical ions diffuse together and couple in this step and since the reaction rate instead showed a first-order dependence on the initial Co(III) concentration, we propose that the radical ions come together to form an encounter complex that then couples in the slow step. A term exhibiting a positive hydrogen ion dependence was presented in the observed rate law. This can be accommodated if the encounter complex exists in a proton equilibrium (see Scheme I). Two possible sites for protonation exist—the nitrogen of the amine and the oxygen of the carboxylate group. The nitrogen is almost certainly already protonated at the pH range in which we are working[42] so we show the proton on the carboxylate groups. Presumably the protonated ligand has a different conformation in solution that would stabilize the approach of the two highly charged radical species perhaps by a hydrogen-bonded interaction. The driving force for this radical coupling process must be very strong to overcome the Coulombic barrier involved in bringing the two highly positively charged ions together in this step. The sharp increase in absorbance at 285 nm for this reaction is consistent with the formation of a normal chromium–sulfur-bonded complex. The radical ligand would be expected to produce a LMCT peak at much higher energy. From the mechanism proposed in Scheme I, we derive the following rate expression:

$$-d[Cr(III)]/dt = [(k_3K_{EC} + k_4K_a''K_{EC}[H^+])/(1 + K_a''[H^+])][Cr(III)]^2 + [(k_3 + K_4K_a''[H^+])/(K_a''[H^+] + 1)][Cr(III)] \qquad (6)$$

where $[Cr(III)]_0$ is equal to the initial concentration of the [Co(III)] complex used. If $K_a'' \ll 1$ and if K_{EC} is very small, this equation reduces to give

$$k_{obsd} = k_3 + k_4K_a''[H^+] \qquad (7)$$

which is the same as the kinetically observed rate law (eq 1). A plot of k_{obsd} against $[H^+]$ gives an intercept $k_3 = 4.9 \pm 0.2$ s^{-1} and a slope $K_a'k_4 = 3.9 \pm 0.4$ M^{-1} s^{-1}. Assuming that the pK_a of the COOH group is approximately the same as that of the free cysteine ligand,[42] then $K_a' = 1.1 \times 10^{-2}$ M^{-1} and $k_4 \approx 350$ s^{-1}.

We ascribe the third reaction studied on the stopped-flow instrument to the Cr(II)-catalyzed decomposition of the chromium(III)–cystine dimer (**23**). This reaction is also enhanced by the presence of acid, again possibly because the approach of Cr(III) is conformationally easier when the cystine ligand is protonated and the molecule is held in a favorable orientation for Cr(II) attack (see Scheme I).

The rate expression derived for this step from Scheme I is

$$-d[Cr(III)]/dt = [(k_5 + K_a''k_6[H^+])/(1 + K_a''[H^+])][Cr(III)][Cr(II)] \qquad (8)$$

Assuming that K_a'' again corresponds to protonation of the carboxylate function, then the expression reduces to

$$k_{obsd} = k_5 + k_6K_a''[H^+] \qquad (9)$$

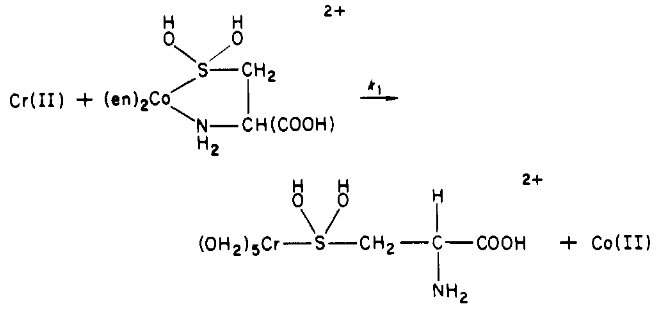
which is equivalent to the observed rate expression given in eq 7. Plotting k_{obsd} vs. $[H^+]$ produces a straight line having an intercept $k_5 = 1 \pm 2$ s^{-1} and a slope $k_6K_a'' = 28 \pm 3$ M^{-1} s^{-1}. If $K_a'' = 1.1 \times 10^{-2}$ M^{-1}, then $k_6 \approx 2.5 \times 10^3$ s^{-1}. These results imply that there is, within experimental error, no reaction involving the unprotonated species.

Table X. Comparison of Rate Constants and Activation Parameters for the Chromium(II) Reduction of Various Sulfur-Containing Cobalt(III) Species

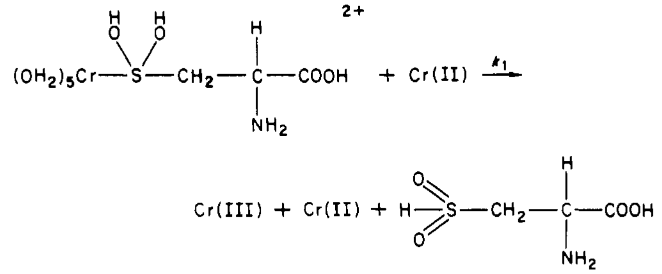
compd^a	$k_2^{25\,°\mathrm{C}}$, $\mathrm{M^{-1}\,s^{-1}}$	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	ref
$[\mathrm{Co(en)_2}(\mathit{S}\mathrm{CH_2CH(COOH)}(\mathit{N}\mathrm{H_2}))]^{2+}$ (**4**)	$(2.4 \pm 0.3) \times 10^5$			6
$[\mathrm{Co(en)_2}(\mathit{S}\mathrm{(O)CH_2CH(COOH)}(\mathit{N}\mathrm{H_2}))]^{2+}$ (**5**)	$>3 \times 10^4$			this work
$[\mathrm{Co(en)_2}(\mathit{S}\mathrm{(O)_2CH_2CH(COOH)}(\mathit{N}\mathrm{H_2}))]^{2+}$ (**6**)	$(1.46 \pm 0.07) \times 10^3$	4.4 ± 0.3	-29 ± 1	this work
$[\mathrm{Co(en)_2}(\mathit{N}\mathrm{H_2CH(CH_2SCH_3)(CO}\mathit{O}\mathrm{))}]^{2+}$ (**20**)	0.56 ± 0.01	9 ± 1	-28 ± 4	6
$[\mathrm{Co(en)_2}(\mathit{N}\mathrm{H_2CH(CH_2CH_2SCH_3)(CO}\mathit{O}\mathrm{))}]^{2+}$ (**21**)	0.416 ± 0.006	9.7 ± 0.9	-28 ± 3	6
$[\mathrm{Co(en)_2}(\mathit{S}\mathrm{CH_2CH_2}\mathit{N}\mathrm{H_2})]^{2+}$ (**15**)	3.3×10^4	7.3 ± 0.3	-13 ± 1.0	5
$[\mathrm{Co(en)_2}(\mathit{S}\mathrm{CH(CH_3)CO}\mathit{O})]^{+}$ (**13**)	1.5×10^5	1.1 ± 0.2	-13 ± 1	5
$[\mathrm{Co(en)_2(CH_3}\mathit{S}\mathrm{CH_2CH_2}\mathit{N}\mathrm{H_2})]^{3+}$ (**12**)	3.8×10^{-1}	5.5	-42	5

^{a} Coordinating atoms are italic.

The Sulfinato System. There were two consecutive reactions observed in the Cr(II) reduction of $[\mathrm{Co(en)_2(CysO_2)}]^+$. The first corresponded to the reduction of the cobalt complex i.e.



The second, slow reaction observed for this process was attributed to the Cr(II)-catalyzed decomposition of the Cr(III) intermediate to $\mathrm{Cr(OH_2)_6}^{3+}$ and free ligand i.e.

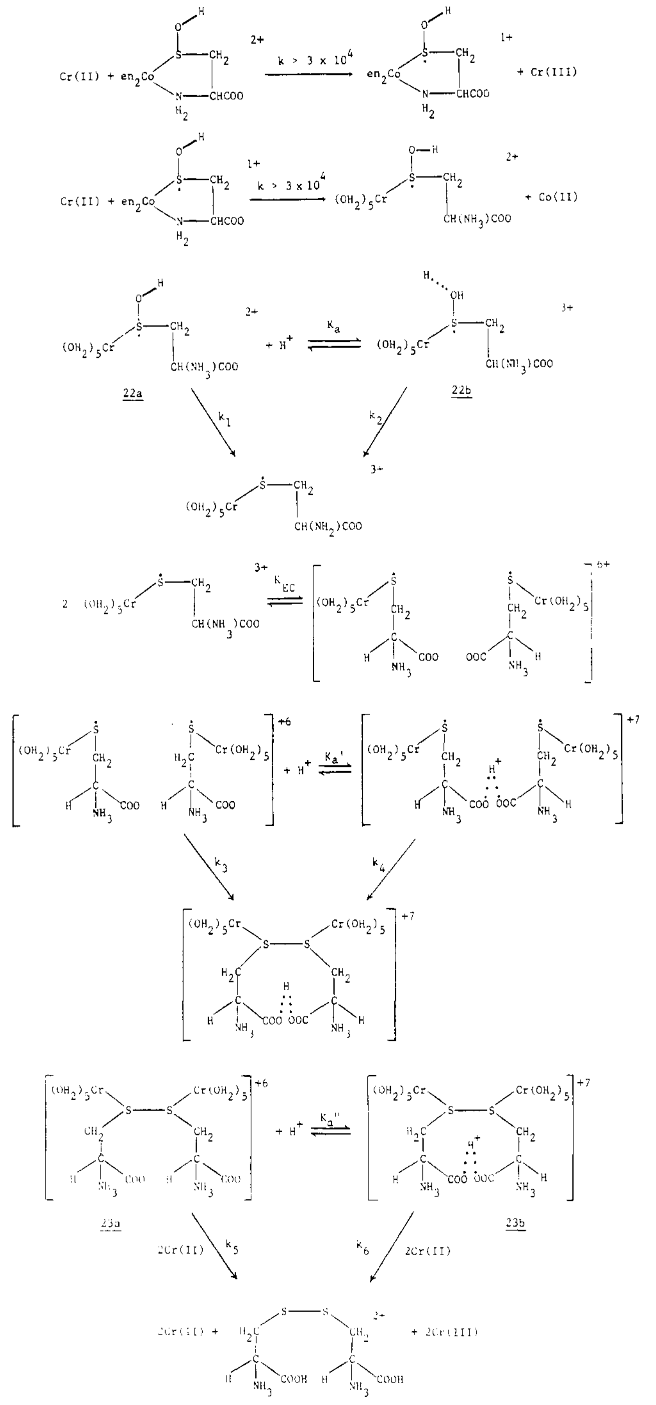


The green Cr(III) product was isolated and characterized (vide supra).

As can be seen from Table X, the rate of reduction of this complex is less than that of the parent cysteinato complex, as anticipated. The reduction of the sulfenato derivative **5** is probably intermediate in rate between that of the cysteinato species **4** and the sulfinato complex **6**. We were unable to measure the reduction rate of the sulfenato derivative exactly because of very small absorbance changes at low reactant concentrations. Thus, we have established that, as long as sulfur is coordinated to the oxidizing center, the rate of electron transfer is high, even when the sulfur atom is oxidized to the 0 or +2 oxidation state. It would be instructive to measure the reduction rate of the linkage isomer of **6** or some similar O-bonded sulfinato derivative to determine whether sulfur can exert its influence on the reduction rate when it is not directly bonded to the metal oxidizing site. Work done by Shea and Haim[41] on the thiocyanato linkage isomers of cobalt(III) would lead us to anticipate that the effect of sulfur would be much less when it is not coordinated to the oxidant.

Comparison to Other Systems. All $\mathrm{(en)_2Co^{III}}$ complexes having a coordinated thiolate sulfur are reduced very rapidly by Cr(II) (see **4**, **13**, and **15** in Table X). This remarkable efficiency in electron mediation is likely responsible for the fact that sulfur is ubiquitous among redox proteins. As the formal oxidation state of the coordinated sulfur atom increases along the thiolato–sulfenato–sulfinato series (−2, 0, +2), the electronegativity of the ligand increases.[28] This would be expected to result in a corresponding decrease in the rate of reduction of the cobalt(III)

Scheme I



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[41] Shea, C.; Haim, A. *J. Am. Chem. Soc.* **1971**, *93*, 3055.

[42] White, A.; Handler, P.; Smith, E. L. "Principles of Biochemistry"; 3rd ed.; McGraw-Hill: New York, 1964; p 108.

346 *Inorg. Chem.* **1985**, *24*, 346-355

complex. The reduction step for the sulfenato complex was not observed, but the sulfinato derivative did react about 160 times more slowly than the parent cysteinato complex. This contrasts markedly with the reduction rate that occurs when an alkyl substituent is placed on sulfur (**12** and **15** in Table X); in these reactions, the substituted derivative is reduced almost 10^5 times slower than the parent thiolato species. It is interesting to note that the coordinated sulfenato system produces the coupled product, cystine, upon reduction, in the same way as is postulated to occur when sulfur radical ions are produced in purely organic systems.[43] There is no evidence in our work that the metal complexes are able to compete with the radical for the dimerization process, even in an intramolecular fashion. Sulfur compounds such as cysteamine and cysteine have been proposed to act as radical repair agents that protect against the effects of ionizing radiation.[44,45] It seems clear from our work that they would also protect the metal centers of proteins from the effects of very reducing radicals since the sulfur radicals would preferentially couple to form dimers rather than pass the electron onto a metal.

Acknowledgment. We are grateful to the Research Corp. for a Cottrell Grant that aided this work in its early stages. We are further indebted to the National Institutes of Health for a grant that allowed for the completion of this study (Grant No. GM31383).

Registry No. **5**, 94110-44-8; **6**, 62698-05-9; Cr, 7440-47-3; [Cr(OH_2)$_5$(CysO_2)]$^+$, 94136-14-8.

Supplementary Material Available: Full sets of kinetic data for Tables I-III, VI, and VII (8 pages). Ordering information is given on any current masthead page.

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(43) Hoffman, M. Z.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 990.

(44) Adams, G. E.; McNaughton, G. S.; Micheal, B. D. *Trans. Faraday Soc.* **1968**, *64*, 902.

(45) Adams, G. E.; Armstrong, R. C.; Charlesby, A.; Michael, B. D.; Willson, R. L. *Trans. Faraday Soc.* **1969**, *65*, 732.

(46) Oae, S. "Organic Chemsitry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; pp 406-13.

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Electronic Absorption and Emission Spectra of Dioxorhenium(V) Complexes. Characterization of the Luminescent ^3E_g State

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The low-temperature single-crystal-polarized electronic absorption spectra of three *trans*-dioxorhenium(V) ions, $ReO_2L_4^z$ (L = CN^-, z = 3−; L = $^1/_2$en, z = 1+; L = py, z = 1+), have been investigated. The spectra display up to four distinct band systems that exhibit vibrational progressions in a high-energy (750–800-cm^{-1}) mode. The two lowest energy band systems (500–550 nm) are assigned to components of a $^3E_g[b_{2g}(xy)^1e_g(xz,yz)^1 \leftarrow b_{2g}(xy)^2]$ excited state that is split by spin–orbit coupling interactions. The next higher energy band (400–450 nm) is assigned to the corresponding ^1E_g state, whereas the fourth band (ca. 300 nm) must arise from a different one-electron excitation. Luminescence from at least two of the lowest energy ^3E_g components in the cyanide and pyridine complexes has been detected, and the zero-field splitting between the two emitting states is 10–20 cm^{-1}. At 5 K, only the lowest energy component is populated and the luminescence spectra from this state display progressions in a ca. 900-cm^{-1} mode that corresponds to the symmetric rhenium–oxygen stretching vibration. Franck–Condon analyses of the luminescence bands indicate distortions of 0.09 (1) and 0.07 (1) Å along each Re–O bond for the cyanide and pyridine complexes, respectively. The lower energy of the corresponding progressions in absorption and the π-antibonding character of the ^3E_g state suggest that the excited-state distortion is an elongation. The luminescence spectrum of the pyridine complex also exhibits a progression in a 190-cm^{-1} mode indicative of a 0.03 (1) Å distortion along the symmetric Re–py stretching coordinate. The lifetime of the ^3E_g state at room temperature varies from 10 to 300 μs in crystals and is about 10 μs for $ReO_2(py)_4^+$ (and its substituted pyridine analogues) in aprotic solvents. The luminescence of these dioxorhenium species, however, is rather efficiently quenched by protic solvents such as water and alcohols.

Introduction

The importance of oxidation reactions of organic compounds and the capacity of many metal–oxo reagents to effect such transformations have stimulated a great deal of research into the structures and reactivity of these high-valent transition-metal complexes. Stoichiometric oxidation reactions of organic substrates by d^0 oxo complexes of Mn, Cr, Ru, and Os are quite well-known and extensively studied.[1] These reagents are commonly used in organic synthesis, and the mechanisms of their reactions have been examined both experimentally and theoretically.[2] In addition, metal oxides and mixed-metal oxides are currently used in catalytic oxidations, and oxo species are even suspected in biochemical oxygenase reactions.[3,4] Clearly, metal–oxo complexes are exceptionally valuable chemical reagents.

One of the goals of our research on metal–oxo species has been to develop reagents that will photochemically oxidize organic substrates. Since an electronically excited metal–oxo complex is one reagent in a reaction of this sort, we believe it is necessary to examine, in detail, by electronic spectroscopy, its physical and structural properties. We have already communicated our initial results from spectroscopic studies of some luminescent dioxorhenium(V) complexes.[5] In this paper we fully describe the electronic spectra and structures of these complexes as well as their excited-state decay properties in crystals and solutions.

Experimental Section

Procedures. Dichloromethane (Burdick and Jackson) was degassed with five freeze–pump–thaw cycles on a high-vacuum line ($<10^{-3}$ torr) and stored under vacuum over activated (heating under vacuum for 12

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(1) (a) Stewart, R. In "Oxidation in Organic Chemistry", Part A; Wiberg, K. B., Ed.; Academic Press: New York, 1962; pp 1–68. (b) Wiberg, K. B. Reference 1a, pp 69–184. (c) Lee, D. G.; van den Engh, M. In "Oxidation in Organic Chemistry"; Part B; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; pp 177–227. (d) Collin, R. J.; Jones, J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1974**, 1094–1097.

(2) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 3287–3294.

(3) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272–413.

(4) (a) Groves, J. T.; McClucky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859–861. (b) Loew, G. H.; Kert, C. J.; Hjelmeland, L. M.; Kirchner, R. F. *Ibid.* **1977**, *99*, 3534–3536. (c) Balch, A. L. *Ibid.* **1980**, *102*, 1446–1448. (d) Loew, G. H.; Herman, Z. S. *Ibid.* **1980**, *107*, 6174–6175. (e) Hanson, L. K.; Chang, C. K.; Davis, M. S.; Fajer, J. *Ibid.* **1981**, *103*, 663–670.

(5) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1373–1374.

0020-1669/85/1324-0346$01.50/0