bulk solvent involves negligibly small changes in the overall compressibility of the system.

The persistence of the first-order dependence of k_{an} on chloride concentration over the entire range of chloride ion studied[2,4,6] requires that the rate of water exchange with the substrates be significantly faster than k_{an}.[4] Similar arguments have been used[23] for the anation of $Co(CN)_5(OH_2)^{2-}$ where the results were discussed in terms of the ratio of the competitive rate constants for the water exchange and anation of the proposed $Co(CN)_5^{2-}$ intermediate.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft is gratefully appreciated.

Registry No. $RhCl_6^{3-}$, 21412-00-0; $RhCl_5(OH_2)^{2-}$, 15276-84-3; *cis*-$RhCl_4(OH_2)_2^-$, 15157-53-6; $K_3[RhCl_6]$, 13845-07-3; $K_2[RhCl_5(OH_2)]$, 15306-82-8.

References and Notes

(1) (a) State University of New York at Oswego. (b) University of Frankfurt.
(2) W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).
(3) K. Swaminathan and G. M. Harris, *J. Am. Chem. Soc.*, **88**, 4411 (1966).
(4) W. Robb and M. M. De V. Steyn, *Inorg. Chem.*, **6**, 616 (1967).
(5) M. J. Pavelich and G. M. Harris, *Inorg. Chem.*, **12**, 423 (1973).
(6) D. A. Palmer and G. M. Harris, *Inorg. Chem.*, **14**, 1316 (1975).
(7) W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).
(8) B. R. James and M. Kastner, *Can. J. Chem.*, **50**, 1708 (1972).
(9) R. J. Buchacek and G. M. Harris, *Inorg. Chem.*, **15**, 926 (1976).
(10) W. Plumb and G. M. Harris, *Inorg. Chem.*, **3**, 542 (1964).
(11) W. Robb, M. M. De V. Steyn, and H. Kruger, *Inorg. Chim. Acta*, **3**, 383 (1969).
(12) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).
(13) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).
(14) A linear extrapolation of ln K vs. $1/T$ (K) for the values of the equilibrium constants for the aquation reaction of $RhCl_6^{3-}$ at various temperatures[2] provides an estimate of $K < 1$ at −20 °C.
(15) F. K. Fleischman, E. G. Conze, D. R. Stranks, and H. Kelm, *Rev. Sci. Instrum.*, **45**, 1427 (1974).
(16) At these conditions the reaction is a first- and second-order reversible reaction and not strictly pseudo first order. Since $K = 7.1$ at 20 °C,[2] the k_{obsd} value obtained is thus an adequate approximation for k_{aq}.
(17) D. R. Stranks, *Pure Appl. Chem.*, **38**, 303 (1974).
(18) A. Billi, F. Malatesta, R. Zamboni, and A. Indelli, *J. Chem. Phys.*, **61**, 4787 (1974).
(19) D. A. Palmer and H. Kelm, *Inorg. Chim. Acta*, **19**, 117 (1976).
(20) D. A. Palmer and H. Kelm, *Inorg. Chem.*, **16**, 3139 (1977).
(21) W. E. Jones, L. R. Carey, and T. W. Swaddle, *Can. J. Chem.*, **50**, 2739 (1972).
(22) D. A. Plamer and H. Kelm, to be submitted for publication.
(23) R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).
(24) J. R. Ferraro and K. Nakamoto, *Inorg. Chem.*, **11**, 2290 (1972).
(25) J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Am. Chem. Soc.*, **93**, 3862 (1971).
(26) L. J. Basile, J. R. Ferraro, M. Choca, and K. Nakamoto, *Inorg. Chem.*, **13**, 496 (1974).
(27) R. A. Horne, Ed., "Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Properties", Wiley-Interscience, New York, N.Y., 1972, Chapter 13.
(28) D. R. Stranks and N. Vanderhoek, *Inorg. Chem.*, **15**, 2639 (1976).

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

Kinetics of Oxidation of (Cysteinato-*N,S*)bis(ethylenediamine)cobalt(III) and Related Thiolato Complexes to Sulfenatocobalt(III) Complexes

DANIEL L. HERTING, CAMILLA P. SLOAN, ARTHUR W. CABRAL, and JAMES H. KRUEGER*

Received October 27, 1977

The Λ-((*R*)-cysteinato-*N,S*)bis(ethylenediamine)cobalt(III) ion is oxidized by hydrogen peroxide to the N,S-bound cysteinesulfenato complex $(en)_2Co[(R)\text{-}NH_2CH(COO)CH_2S(O)]^+$ in a process that is first order in each reactant; $k_{SO} = 0.36\ M^{-1}\ s^{-1}$ at 20.3 °C, pH 5–7, 0.10 M ionic strength. The pH dependence of k_{SO} for the cysteinato species was obtained over the range 0.3–6.9, in which $[(en)_2Co[NH_2CH(COOH)CH_2S]^{2+}]$- and $[H^+][(en)_2Co[NH_2CH(COOH)CH_2S]^{2+}]$-dependent pathways also were observed. For the related complexes $(en)_2Co(NH_2CH_2CH_2S)^{2+}$ and $(en)_2Co[(S)\text{-}NH_2CH(COO)C(CH_3)_2S]^+$, $k_{SO} = 0.85\ M^{-1}\ s^{-1}$ and $0.14\ M^{-1}\ s^{-1}$, respectively. Oxidation of $\Lambda\text{-}(en)_2Co[NH_2CH(COO)CH_2S]^+$ produces a mixture of what is presumed to be the *S* and *R* forms of the chiral (sulfur) sulfenate, with second-order rate constants of formation of $0.27\ M^{-1}\ s^{-1}$ and $0.09\ M^{-1}\ s^{-1}$, respectively. Circular dichroism spectra were obtained and the stability and rate of oxidation to the sulfinato complex was studied for each of the diastereomers. The reactions are interpreted in terms of nucleophilic substitution by coordinated thiolate sulfur on peroxide oxygen. The relative order of reactivity toward hydrogen peroxide of several sulfur-containing nucleophiles is $H_3N^+CH(COO^-)CH_2S^- > (en)_2Co[NH_2(COO)CH_2S]^+ > SO_3^{2-} > (HOCH_2CH_2)_2S > NCS^-$. Thus, cobalt(III)-bound cysteinate, although less reactive than free $H_3N^+CH(COO^-)CH_2S^-$, exhibits considerable nucleophilic reactivity.

Introduction

We have reported previously the generation of sulfur-bound sulfenato (RSO^-) and sulfinato (RSO_2^-) cobalt(III) complexes via oxidation of N,S-coordinated cysteinate.[1] This oxidative process provides a convenient route to nonlabile complexes in which an otherwise highly reactive alkylsulfenate is stabilized through bonding to a metal center. Recently, Jackson, Sargeson, and Whimp have reported[2] the separation of diastereomers in the oxidation of $(en)_2Co[(R)\text{-}NH_2CH(COOH)CH_2S]^{2+}$, including, in particular, a crystallographic determination of the Λ-((*R*)-cysteine-*S*-sulfenato)bis(ethylenediamine)cobalt(III) ion. In addition, Deutsch, Elder, and co-workers[3] have described the oxidative synthesis and structural determination of the bis(ethylenediamine)(2-sulfinatoethylamine-*N,S*)cobalt(III) ion.

The oxidation of the cysteinato to cysteinesulfenato species by hydrogen peroxide provides a useful system in which the nucleophilic reactivity of coordinated thiolate can be examined. We report herein a study of the kinetics of oxidation of thiolato and of sulfenato complexes by H_2O_2 and a comparison of their reactivities with that of other sulfur nucleophiles. Principal attention has been focused on reactions of the Λ-((*R*)-cysteinato-*N,S*)bis(ethylenediamine)cobalt(III) cation, $\Lambda\text{-}(en)_2CoCyS^+$. Reactions of the related N,S-bound (*S*)-penicillaminato, $(en)_2CoPenS^+$, and cysteaminato (2-aminoethanethiolato), $(en)_2Co(cystS)^{2+}$, species were examined briefly.

Experimental Section

((*R*)-Cysteinato-*N,S*)bis(ethylenediamine)cobalt(III) Complexes. $(en)_2Co[(R)\text{-}NH_2CH(COO)CH_2S]ClO_4$ was prepared from L-cystine

0020-1669/78/1317-1649$01.00/0 © 1978 American Chemical Society

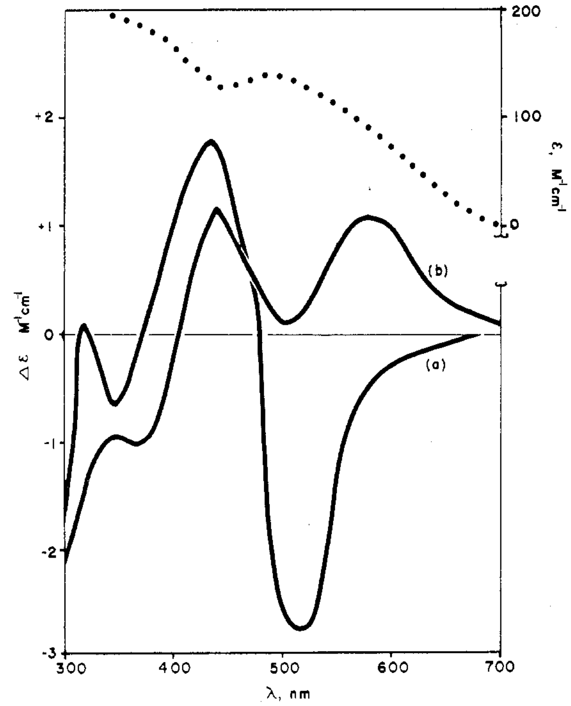


Figure 1. Left ordinate (—): circular dichroism spectra of complexes assigned as (a) Δ-$(en)_2CoCyS^+$ and (b) Λ-$(en)_2CoCyS^+$. Right ordinate (···): UV–visible spectrum for (a) and (b).

(Aldrich), as described previously.[1] The product solution was eluted with 0.5 M NaCl on a Bio-Rad AG 50W-X-4 column (200–400 mesh, Na^+ form). Separation into two major bands (in order of elution), a:b = 2.3:1, was observed. Circular dichroism spectra (Jasco-Durrum J-10 spectrometer) were obtained for a and b, as shown in Figure 1. On the basis of the sign of the longest wavelength CD band, which arises primarily from the $^1A \rightarrow {}^1E$ transition, the a and b species are tentatively assigned as the Δ and Λ diastereomers, respectively.[4] (These are abbreviated as Δ-$(en)_2CoCyS^+$ and Λ-$(en)_2CoCyS^+$ in subsequent discussions.) Several kinetics runs were made using each of the above solution fractions.

Addition of sodium perchlorate to the original product solution (pH ~9) resulted in crystallization of almost all of the cysteinatocobalt(III) material as the rather insoluble Λ perchlorate. (In contrast, the Δ perchlorate is extremely soluble in water.) Thus, conversion from the Δ to the Λ form occurred, since Δ-$(en)_2CoCyS^+$ predominated in the product solution. However, the Δ diastereomer is the more thermodynamically stable of the two in solution, since heating a Λ-fraction solution at 100 °C converted it to the Δ form, as judged by changes in the CD spectrum. Therefore, when Λ-$(en)_2CoCySClO_4$ solid was recrystallized from hot water, part of it was lost as the Δ species. The Λ perchlorate subsequently recovered, which was used in most of the kinetics runs, eluted as a single band on a cation resin and exhibited a CD spectrum identical with that assigned to Λ-$(en)_2CoCyS^+$. The high yield of Λ perchlorate from the original product solution appears to have been the result of labilization of the $\Delta \rightleftharpoons \Lambda$ system, which was forced to the right as the perchlorate crystallized. The presence of unreacted cobalt(II), hydroxide, and ethylenediamine in the product solution probably is responsible for labilization, since no change occurs upon addition of perchlorate to a pure Δ-solution fraction.

Attempts to prepare the cysteinato complex in the chloride form by crystallization from aqueous ethanol generally lead to a mixture containing some sodium chloride. However, one crop of crystals obtained by crystallization from aqueous ethanol over several days proved to be the Λ diastereomer. This material, being more soluble in water than the perchlorate, was used to determine pK_a for dissociation of Λ-$(en)_2Co[(R)\text{-}NH_2CH(COOH)CH_2S]^{2+}$. A 10.0-mL solution, initially containing 0.204 mmol of [Λ-$(en)_2CoCyS$]Cl and 0.100 mmol of $HClO_4$, was titrated potentiometrically in each determination.

((*R*)-Cysteinesulfenato-*N*,*S*)bis(ethylenediamine)cobalt(III) Complexes. The perchlorate solid was obtained from [Λ-$(en)_2CoCyS]ClO_4$, as described previously,[1] except that to minimize formation of the sulfinato complex, 0.10 M H_2O_2, in only 5% excess, was employed. Solutions containing the Λ-$(en)_2CoCySO^+$ species were prepared by H_2O_2 oxidation of Λ-$(en)_2CoCyS^+$. The diastereomers were separated on Bio-Rad AG 50W-X-4 (200–400 mesh, 20 cm, Na^+ form) by elution with 0.5 M NaCl. The relative amounts of the two sulfenatocobalt(III) species that separated were determined from areas of absorbance vs. fraction curves and from absorbances (370 nm) of the total volume of solution of each recovered.

In the handling and storage of solutions of these sulfenato complexes, it is recommended that exposure to light be minimized, due to the photosensitivity observed for dilute solutions.

(Cysteaminato-*N*,*S*)bis(ethylenediamine)cobalt(III) Complexes. $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was prepared[1,5] from cystamine dihydrochloride (Aldrich) and $CoCl_2{\cdot}6H_2O$ and recrystallized from water. A sample eluted as a single 2+ species with 1.0 M NaCl and gave no CD spectrum, consistent with the expected racemic nature of the product. The sulfenato perchlorate was prepared by oxidation with a stoichiometric amount of hydrogen peroxide and precipitated with 2-propanol. The orange powder obtained was dissolved in water and crystallized from a 3:1 2-propranol–water mixture. Both $[(en)_2Co(cystS)](ClO_4)_2$ and $[(en)_2Co(cystSO)](ClO_4)_2$ gave satisfactory elemental analyses.

((*S*)-Penicillaminato-*N*,*S*)bis(ethylenediamine)cobalt(III) Complexes. The penicillaminato complexes were prepared by oxidation of cobalt(II) chloride with D-penicillamine disulfide (Aldrich). D-Penicillamine disulfide (1.01 g, 3.4 mmol) was added to 9.0 mL of 10% aqueous ethylenediamine (13.5 mmol), which had been purged previously with nitrogen. Cobalt(II) chloride hexahydrate (1.60 g, 6.7 mmol) was added in small portions over 1 h. The pH was kept near 8.5 with concentrated KOH. The mixture was kept under N_2 at ~52 °C for 8 h. The product solution contained appreciable amounts of tris(ethylenediamine)cobalt(III) chloride and penicillamine disulfide. The $(en)_2Co$-(*S*)-$PenS^+$ complex was crystallized as either the hexafluorophosphate or tetraphenylborate salt. A crude PF_6^- salt, obtained using excess 2-propanol, was dissolved in water, and $Co(en)_3^{3+}$ was removed by passage through a Dowex 50W-X-4 column. The resulting solution was treated with a stoichiometric quantity of $NaB(C_6H_5)_4$ in dilute aqueous solution. Elemental analysis of the solid indicated the correct 5.00:1 N:S ratio expected for $[(en)_2CoPenS]B(C_6H_5)_4$ but revealed the presence of coprecipitated $NaB(C_6H_5)_4$ and NaCl. Since neither of these interfere with the H_2O_2 oxidation, several kinetics runs were made with this solid.

As an alternative procedure, a stoichiometric amount of NH_4PF_6 was added to the crude product solution, followed by addition of an equal volume of 2-propanol. $[Co(en)_3](PF_6)_3$ crystallized over 1–2 h and was removed. The filtrate was treated with additional NH_4PF_6 (50% of stoichiometric), and 2-propanol was added until a substantial quantity of solid $[(en)_2CoPenS]PF_6$ formed. This solid contained ≤1% of $Co(en)_3^{3+}$ (by ion exchange) and penicillamine disulfide (by ^1H NMR methyl resonances).

The hexafluorophosphate salt was eluted on Bio-Rad AG 50W-X-4, 200–400 mesh, with 0.5 M NaCl, resulting in separation into a major and a minor band. The corresponding complexes are tentatively assigned as Λ-$(en)_2Co$-(*S*)-$PenS^+$ and Δ-$(en)_2Co$-(*S*)-$PenS^+$, respectively, on the basis of CD spectra obtained for each: major species, $\Delta\epsilon_{522} > 0$; minor species, $\Delta\epsilon_{500} < 0$. Solutions of these separated species were used for kinetics measurements.

Kinetics. The reactions were followed using a Cary 16K spectrophotometer to monitor absorbance changes at the sulfenato maxima near 370 nm. Reactions were carried out in glass-stoppered 1-cm silica cells in a thermostated cell compartment. In most runs no provision was made for exclusion of oxygen since rates were shown to be independent of oxygen. Reagent grade 70% perchloric acid, buffer salts, and sodium perchlorate were used to maintain pH and ionic strength. Most runs were carried out with water redistilled from basic permanganate. In a number of runs, Na_2EDTA (10^{-3} M) was added to minimize effects of trace metal ions. The results were essentially independent of the presence or absence of added EDTA. Hydrogen peroxide solutions were prepared from Mallinckrodt reagent grade 30% H_2O_2 and were analyzed iodometrically,[6] using a 3% ammonium molybdate catalyst. In each analysis, potassium iodide was dissolved in water, followed by addition of acid, catalyst, and finally the H_2O_2, to preclude possible decomposition of peroxide on the surface of solid potassium iodide.

The stoichiometry of reaction 1 (vide infra) was verified by iodometric determination of hydrogen peroxide consumed and spec-

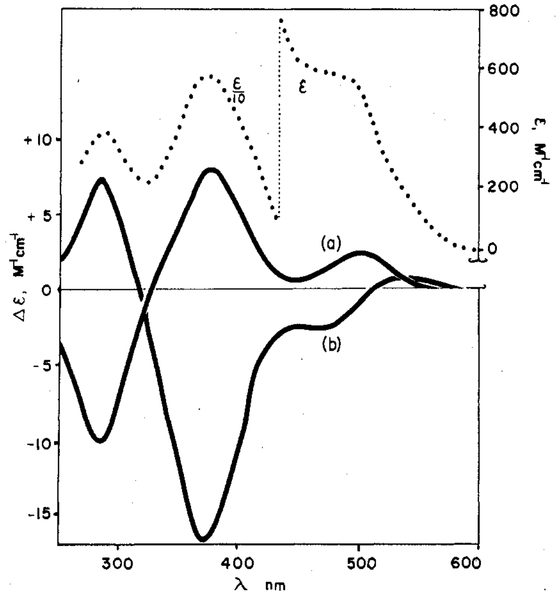


Figure 2. Left ordinate (—): circular dichroism spectra of complexes tentatively assigned as (a) Λ-$(en)_2Co[(S)$-cysteinesulfenate$]^+$ and (b) Λ-$(en)_2Co[(R)$-cysteinesulfenate$]^+$. Right ordinate (···): UV–visible spectrum for (a) and (b).

trophotometric determination of $(en)_2CoCySO^+$ produced in a mixture with $[H_2O_2]_0 = 5.14 \times 10^{-3}$ M and $[\Lambda\text{-}(en)_2CoCyS^+]_0 = 2.92 \times 10^{-3}$ M.

Results

Oxidation of Λ-$(en)_2CoCyS^+$. Kinetics of reaction 1 were

$$\Lambda\text{-}(en)_2CoCyS^+ + H_2O_2 \rightarrow \Lambda\text{-}(en)_2CoCySO^+ + H_2O \qquad (1)$$

determined under both first-order (excess H_2O_2) and second-order conditions. Subsequent oxidation of the sulfenato complex is much slower and does not interfere with rate measurements of reaction 1. In a series of runs with $[\Lambda\text{-}(en)_2CoCyS^+]_0$ in the range (0.6–1.4) × 10^{-4} M, plots of ln $(A_\infty - A)$ vs. t were linear over 3–4 half-lives.[7] First-order rate constants were determined over a (0.94–12.2) × 10^{-3} M range of $[H_2O_2]_0$. The results conformed to the rate law $-d[\Lambda\text{-}(en)_2CoCyS^+]/dt = k_{SO}[\Lambda\text{-}(en)_2CoCyS^+][H_2O_2]$, within experimental error. In solutions containing $[H_2PO_4^-] = [HPO_4^{2-}] = 0.010$ M, the average value of k_{SO} for 25 runs was 0.40 ± 0.02 M^{-1} s^{-1} (pH 6.9, 20.3 °C, ionic strength 0.10 M). Data obtained from 13 runs under second-order conditions, in which $[H_2O_2]_0/[\Lambda\text{-}(en)_2CoCyS^+]_0$ was varied from 0.58 to 6.85, confirmed the rate law ($k_{SO} = 0.42 \pm 0.02$ M^{-1} s^{-1}). Average values of k_{SO} at 11.6, 29.8, and 37.4 °C were 0.222, 0.648, and 0.997 M^{-1} s^{-1}, respectively, giving $\Delta H^{\ddagger} = 9.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27.7 \pm 1$ eu, from transition-state theory.

A number of runs were made in the pH 5–7 range in the absence of a phosphate buffer, yielding $k_{SO} = 0.36_5 \pm 0.02$ M^{-1} s^{-1} (20.3 °C, $\mu = 0.10$ M). Thus, values of k_{SO}, though independent of pH in the range 5–7, were systematically greater in phosphate media than in water. The effect increased with increasing buffer concentration at constant pH and was observed for hydrogen phthalate containing buffers near pH 5 as well. This small rate enhancement may arise from the greater reactivity of a hydrogen-bonded ion pair of HPO_4^{2-} with $(en)_2CoCyS^+$; it is not, however, an artifact created by the experimental conditions. Addition of phosphate buffer species did not change the visible or CD spectrum, stability, or tendency toward further oxidation of the sulfenate product.

Λ-Cysteinesulfenato Complexes. The sulfenato complexes contain a chiral sulfur center. Cation-exchange chromatography of solutions obtained from oxidation of Λ-$(en)_2CoCyS^+$ with H_2O_2 at pH 5–7 resulted in separation of two sulfenato complexes in the approximate ratio 2.9:1. The CD spectra of these are shown as a and b, respectively, in Figure 2. Jackson et. al.[2] have reported the separation of two sulfenates in this system. In their work the major species was crystallized as the 1:1 adduct $[(en)_2CoS(O)CH_2CH(COOH)NH_2](ClO_4)_2\cdot[(en)_2CoS(O)CH_2CH(COO)NH_2](ClO_4)$ and was shown to possess S configuration at sulfur. Thus, we have assumed that the major and minor species we obtained correspond to sulfenato complexes possessing S and R configurations at sulfur, Λ-(S)-$(en)_2CoCySO^+$ and Λ-(R)-$(en)_2CoCySO^+$, respectively. The R configuration at carbon is maintained and is not specifically designated in the formulas.

The $[\Lambda\text{-}(en)_2CoCySO]ClO_4$ solid that crystallized from 2-propanol–water media consisted essentially of the S diastereomer and small amounts of the cysteinesulfinato complex (≤3%).

In the oxidation step the S and R diastereomers were produced in a 2.9:1 ratio via parallel pseudo-first-order processes. Thus, $k_{SO}^S/k_{SO}^R = 2.9$ and, on the basis of the overall rate constant, 0.36 M^{-1} s^{-1}, $k_{SO}^S \simeq 0.27$ M^{-1} s^{-1} and $k_{SO}^R \simeq 0.09$ M^{-1} s^{-1} at pH 5–7.[8]

The sulfenato complexes are stable in solid form and, if protected from light, are relatively stable in aqueous solution. Approximately 5% decomposition occurred in solution in 10 days at 25 °C as judged by the decrease in absorbance of the characteristic charge-transfer peak at 371 nm. When exposed to light, dilute solutions of the sulfenates decomposed at a moderate rate (~35% in 12 h). However, by recording CD spectra as a function of time of solutions exposed to room light, it was found that initially pure Λ-(R)-$(en)_2CoCySO^+$ underwent a rapid reaction (~55% in 0.3 h) to give an approximately 3:1 S:R equilibrium mixture, as judged by the change in CD spectrum in the 371-nm region. Similarly, Λ-(S)-$(en)_2CoCySO^+$ was converted (~80% in 1.3 h) to essentially the same mixture, having a CD spectrum which closely resembled that obtained by summing the spectra for individual Λ-S and Λ-R sulfenates with a 3:1 weighting. This was confirmed by exposing a dilute solution of $[\Lambda\text{-}(S)\text{-}(en)_2CoCySO]ClO_4$ to room light for 14 h, followed by chromatographic separation of the resulting mixture into the individual S and R components. There was no evidence for conversion to Δ species, although small amounts (up to 20%) of Δ-(S)-$(en)_2CoCySO^+$ and Δ-(R)-$(en)_2CoCySO^+$ may have been present. The interconversions at sulfur occurred about 10 times more rapidly than decomposition, both in the dark and in light.

Absorbance at 371 nm was taken as a quantitative measure of sulfenato-complex concentration. On the basis of oxidation in solution of weighed amounts of $[\Lambda\text{-}(en)_2CoCyS]ClO_4$, ϵ_{371} is 5800 M^{-1} cm^{-1} for the 3:1 S:R mixtures obtained. Since no changes in A_{371} (allowing for decomposition) were observed during the interconversions of R and S sulfenates, we have used $\epsilon_{371}(R) = \epsilon_{371}(S) = 5800$ M^{-1} cm^{-1} in calculating sulfenate concentrations and Δϵ values.

For purposes of comparison with reactivity of the cysteinato complex, a brief study was made of the further, slow oxidation of Λ-$(en)_2CoCySO^+$ to Λ-$(en)_2CoCySO_2^+$.[1] As anticipated, CD spectra and chromatographic behavior were consistent with formation of a single N,S-bound cysteinesulfinato complex. A series of runs was made using the 3:1 mixture of S and R sulfenates generated by adding solutions of Λ-$(en)_2CoCyS^+$ to hydrogen peroxide solutions, the concentrations of which were in the range 0.5–1.1 M. Formation of Λ-$(en)_2CoCySO^+$ was complete within several minutes. The subsequent slow decrease in A_{371}, corresponding to production of the sulfinate, proceeded with approximately first-order kinetics. The pseudo-first-order rate constants were proportional to $[H_2O_2]_0$ over the limited range that could be studied. An average value of $k_{SO_2} = (2.0 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1} (9 runs) was obtained at 20.3 °C, pH 5–7, and 0.1 and 0.28 M $NaClO_4$. For solutions of the individual Λ-*S* and Λ-*R* sulfenato complexes, separated by elution with 0.5 M $NaClO_4$, $k_{SO_2}{}^S = 1.7 \times 10^{-4}$ M^{-1} s^{-1} and $k_{SO_2}{}^R = 3.0 \times 10^{-4}$ M^{-1} s^{-1} at 20.3 °C, pH 5–7, 0.28 M $NaClO_4$. Since the individual rate constants differ by only a factor of 2, the *R*–*S* mixture was oxidized with apparent pseudo-first-order kinetics under the reaction conditions. On the basis of a 3:1 composition, the predicted k_{SO_2} value of the mixture is 2.0×10^{-4} M^{-1} s^{-1}, in agreement with results obtained for the mixture of Λ sulfenates. The rates were ca. 30% greater in 0.28 M NaCl than in 0.28 M $NaClO_4$, indicative of ion pairing.

pH Dependence of Λ-(en)$_2$CoCyS$^+$ Oxidation. The observed pH dependence of k_{SO} for Λ-(en)$_2$CoCyS$^+$ is indicated by the experimental points in Figure 3. The data were correlated with rate law 2 in which the k_{2H^+} term represents oxidation

$$\frac{-d[\Lambda\text{-(en)}_2\text{CoCyS}^+]_T/dt}{[H_2O_2]} = k_{SO}[(\text{en})_2\text{CoCyS}^+] + k_{2H^+}[(\text{en})_2\text{CoCyS(H)}^{2+}] + k_{3H^+}[(\text{en})_2\text{CoCyS(H)}^{2+}][H^+] \quad (2)$$

of the protonated Λ-(en)$_2$Co[(*R*)-NH$_2$CH(COOH)CH$_2$S]$^{2+}$ ion and the k_{3H^+} term represents hydrogen ion dependent oxidation of Λ-(en)$_2$CoCyS(H)$^{2+}$. Defining k_2(obsd) as $(-d \ln [\Lambda\text{-(en)}_2\text{CoCyS}^+]_T/dt)/[H_2O_2]$

$$k_2(\text{obsd}) = \frac{k_{SO}K_a}{K_a + [H^+]} + \frac{k_{2H^+}[H^+]}{K_a + [H^+]} + \frac{k_{3H^+}[H^+]^2}{K_a + [H^+]} \quad (3)$$

where K_a is the acid-dissociation constant of Λ-(en)$_2$Co[(*R*)-NH$_2$CH(COOH)CH$_2$S]$^{2+}$, determined potentiometrically to be 4×10^{-3}.[9] Using $K_a = 4 \times 10^{-3}$ and $k_{SO} = 0.365$ M^{-1} s^{-1}, a least-squares fit of the data to eq 3 yielded $k_{2H^+} = 0.235 \pm 0.004$ M^{-1} s^{-1} and $k_{3H^+} = 0.544 \pm 0.014$ M^{-2} s^{-1} at 20.3 °C.[10] Calculated values of k_2(obsd) are illustrated by the curve in Figure 3.

A ratio of sulfenato species *S*:*R* of 1.3:1 was determined for a product solution resulting from oxidation at pH 1.5, where most of the reaction proceeds via the k_{2H^+} path. Values of $k_{SO}{}^S = 0.13$ M^{-1} s^{-1} and $k_{SO}{}^R = 0.1$ M^{-1} s^{-1} would account for the observed *S*:*R* ratio and $k_{2H^+} = 0.23$ M^{-1} s^{-1} at pH 1.5. Thus, upon protonation, only the $k_{SO}{}^S$ component of k_2(obsd) decreased significantly, apparently the result of conformational changes upon protonation that serve to limit the rate of attack of H_2O_2 along the axial direction at sulfur to form the Λ-*S* sulfenate species.

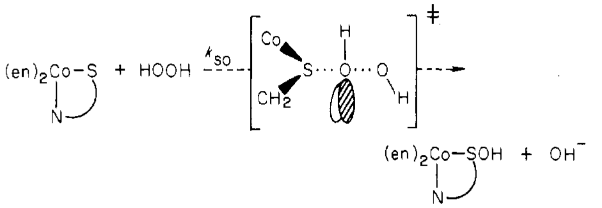
Oxidation of Δ-(en)$_2$CoCyS$^+$. The rate of oxidation of Δ-(en)$_2$CoCyS$^+$ was studied briefly, using both a Δ-fraction solution from ion exchange and a Δ-perchlorate solid. At 20.3 °C and $\mu = 0.1$ M, the second-order rate constant was 0.39 ± 0.03 M^{-1} s^{-1} (pH 5–7) and 0.43 ± 0.03 M^{-1} s^{-1} in 0.010 M phosphate buffer (pH 6.9). The rate was unchanged in perchloric acid media at pH 2.8 and 1.5, despite the fact that the Δ complex undergoes carboxylate protonation with the same pK_a, within experimental error, as the Λ diastereomer. A hydrogen ion dependent pathway, similar to that for Λ-(en)$_2$CoCyS$^+$, is suggested by the increased value of the second-order rate constant, 0.71 M^{-1} s^{-1}, observed at $[H^+] = 0.50$ M.

Oxidation of (en)$_2$Co(cystS)$^{2+}$ and (en)$_2$CoPenS$^+$. Oxidation of the cysteaminato complex to the sulfenate was second-order ($[H_2O_2]_0 = 0.0011$–0.0033 M) with an average second-order rate constant $k_{SO} = 0.94 \pm 0.03$ M^{-1} s^{-1} (20.3 °C, 0.1 M, phosphate buffer) and $k_{SO} = 0.86 \pm 0.03$ M^{-1} s^{-1} (in water, pH 5–7). Values of k_{SO} were nearly independent of pH over the range 6.9–2.0. (Values averaged about 5% lower in the range 2.0–3.0, but there was no evidence that the complex was undergoing protonation.) A first-order hydrogen ion dependence was observed in the range 0.16–0.48 M, similar to the behavior exhibited by Λ-(en)$_2$CoCyS$^+$, with $k_{3H^+} \approx 1.2$ M^{-2} s^{-1} at 0.48 M ionic strength.

Oxidation of a 2:1 Λ:Δ mixture of (en)$_2$CoPenS$^+$ proceeded with second-order constants $k_{SO} = 0.14 \pm 0.01$ M^{-1} s^{-1} (20.3 °C, pH 6.9) and $k_{SO} = 0.092 \pm 0.003$ M^{-1} s^{-1} (20.3 °C, pH 1.3). A kinetics run on the individual diastereomers showed that $k_{SO}{}^{\Lambda}/k_{SO}{}^{\Delta} = 1.4$ (in 0.17 M Cl^-), at both pH 6.9 and pH 1.5. Subsequent oxidation of the resulting mixture of penicillaminesulfenato complexes proceeded at an average rate of 1.9×10^{-4} M^{-1} s^{-1} (20.3 °C, pH 6.9).

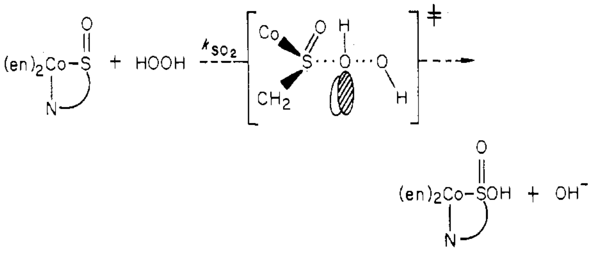
Discussion

Since hydrogen peroxide is generally thought to react with a reducing nucleophile via an S_N2 path, we adopt mechanisms 4 and 5 for formation of sulfenato and sulfinato complexes.



(4)

(subsequent rapid proton transfer)



(5)

The second-order kinetics, and the large, negative $\Delta S^{\ddagger}$ obtained for oxidation of Λ-(en)$_2$CoCyS$^+$, are consistent with this S_N2 scheme. Although k_{SO} values are affected somewhat by structural and electronic factors (vide infra), they may be used as a measure of nucleophilicity of thiolate sulfur, bound to cobalt(III).

Table I compares nucleophilic reactivity of Λ-(en)$_2$CoCyS$^+$ with that of a variety of sulfur nucleophiles. Although Λ-(en)$_2$CoCyS$^+$ is less reactive than free cysteinate, $H_3N^+CH(COO^-)CH_2S^-$, as expected, cobalt(III)-bound thiolate sulfur is an effective nucleophile, especially when compared with other sulfur nucleophiles. This behavior is similar to that observed for cobalt(III)-bound hydroxide, which retains substantial nucleophilic reactivity.[13]

Although postulated as intermediates, the highly reactive sulfenates have not been detected during oxidation of free thiolates to disulfides.[12,14,15] In contrast, H_2O_2 oxidation of thiolate bound to the nonlabile cobalt(III) center results in stabilization of the sulfenate produced and, hence, in modification not only of the rate of thiolate oxidation but also of the stoichiometry of its oxidation.[16]

Oxidation of both the cysteine- and penicillaminesulfenatocobalt complexes proceeds approximately 10^3 times less rapidly than that of the corresponding thiolate complexes. This behavior is a consequence of the inherently lower negative charge density and greater steric requirements of the sulfenate–sulfur center.

The penicillaminato complex was studied to determine the importance of steric and electronic effects on coordinated thiolate reactivity. Rate constants for Λ-(en)$_2$CoCyS$^+$ (0.36 M^{-1} s^{-1}) and (en)$_2$CoPenS$^+$ (0.14 M^{-1} s^{-1}) are surprisingly close, suggesting that the effect of adverse steric interactions

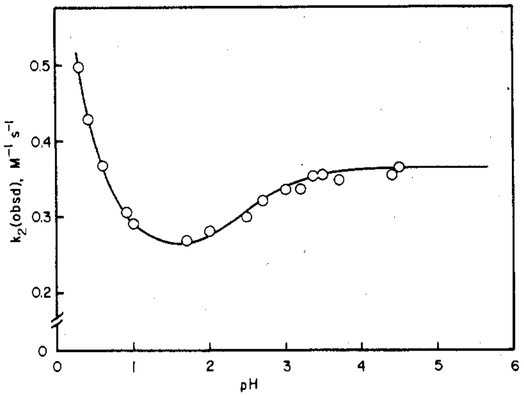


Figure 3. Plot of k_2(obsd) vs. pH for oxidation of Λ-((*R*)-cysteinato)bis(ethylenediamine)cobalt(III) perchlorate.

Table I. Comparison of Reactivity of Coordinated Thiolate with That of Other Sulfur Nucleophiles

$$\text{Nu} + \text{HO-OH} \rightarrow \text{NuOH}^+ + \text{OH}^- \text{ (rds)}$$

Nu	CyS^-	Λ-$(en)_2CoCyS^+$	SO_3^{2-}	R_2S^d	NCS^-
k_2,^{a} M^{-1} s^{-1}	12.4^b	0.36^c	0.2	0.0022	0.00052

[a] 25 °C; in H_2O; ref 11. [b] $H_3N^+CH(COO^-)CH_2S^-$, in H_2O; ref 12. [c] 20.3 °C; this study. [d] $R = CH_2CH_2OH$.

in the transition state is nearly compensated by increased nucleophilicity resulting from the inductive effect of replacement of hydrogens by methyls.[17]

The effect on reactivity of electron-withdrawing COOH at the β-carbon can be assessed by comparing rate constants for Λ-$(en)_2Co[NH_2CH(COOH)CH_2S]^{2+}$ (0.23 M^{-1} s^{-1}) and $(en)_2Co[NH_2CH_2CH_2S]^{2+}$ (0.86 M^{-1} s^{-1}), complexes which have the same charge and steric requirements.[18]

Although the decrease in k_{SO} for Λ-$(en)_2CoCyS^+$ (Figure 3) might be attributed to the inductive effect of replacing COO^- with COOH, this behavior appears to arise, at least in part, from conformational effects since Δ-$(en)_2CoCyS^+$ shows no such decrease and, for Λ-$(en)_2CoCyS^+$, only the $k_{SO}{}^S$ component decreases. A purely inductive effect should be operative in general for formation of the sulfenatocobalt complexes.

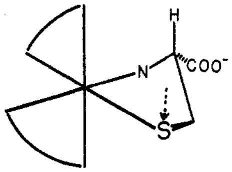
A hydrogen ion assisted pathway commonly is observed for attack of "free" nucleophiles on peroxide oxygen.[19] Although the actual site of interaction is unknown, the added proton is thought to lower the transition-state energy by providing for OH_2, rather than OH^-, as the leaving group during scission of the O–O bond (see eq 6 and 7). A hydrogen ion dependent

$$H_2O_2 + H^+ \rightleftarrows HOOH_2^+ \tag{6}$$

$$HOOH_2^+ + Nu^- \rightarrow NuOH + H_2O \tag{7}$$

pathway (k_{3H^+}) is observed for Λ-$(en)_2CoCyS^+$ and also for Δ-$(en)_2CoCyS^+$ and $(en)_2Co(cystS)^{2+}$. However, the contribution from this path is not significant unless pH < 1.5, consistent with the increase in positive charge associated with formation of the activated complex, e.g., Λ-$(en)_2Co[NH_2CH(COOH)CH_2S] \cdot HOOH_2^{3+}$.

The 2.9:1 mixture of chiral sulfenates in the oxidation of Λ-$(en)_2CoCyS^+$ is the result of competitive second-order processes that differ in the orientation of attack at the two lone pairs on sulfur. In the five-member cysteinate ring, an equatorial orientation of carboxylate is preferred. As a consequence, examination of structural models indicates that initial peroxide-oxygen attack at the axial lone pair on sulfur is favored, resulting in the sulfenate with *S* configuration. In subsequent oxidation of the sulfenates, reaction is somewhat more rapid for the Λ-(*R*)-$(en)_2CoCySO^+$ complex in which the remaining lone pair that reacts with H_2O_2 is in the favored axial position.



The cysteinesulfenato complexes are characterized by their large Δε values in the region of the 371-nm (visible) charge-transfer peak; $\Delta\epsilon_{372} = -16.7$ M^{-1} cm^{-1} for *R* and $\Delta\epsilon_{377} = 8.5$ M^{-1} cm^{-1} for *S*. These provide a sensitive criterion for cobalt–sulfur bond cleavage and $R \rightleftharpoons S$ interconversion. Although stable for days when protected from light, a dilute solution of a sulfenato complex can undergo rather rapid changes in CD spectrum when exposed to room light. The $R \rightleftharpoons S$ interconversions in light require Co–S bond breaking in a photoactivated species,[20] followed by re-forming of the cobalt–sulfur bond to give either the *R* or *S* diastereomer. Related photoisomerizations of $(NH_3)_5Co\text{–}NO_2^{2+}$ to the nitrito form[21] and of $(NH_3)_5Co\text{–}SCN^{2+}$ to the *N*-thiocyanato form[22] have been reported. The apparent equilibrium mixture of 3:1 Λ-*S*:Λ-*R* is the same, within experimental error, as that of the kinetically controlled product mixture obtained in oxidation of Λ-$(en)_2CoCyS^+$. This situation is coincidental but does reflect the fact that the interactions between the oxygen atom and the chelate rings are more favorable in the *S* form.

Acknowledgment. This work was supported by the National Institutes of Health under Grant No. GM 22063. We are grateful to Professor Kensal Van Holde, Department of Biochemistry and Biophysics, for assistance in obtaining the circular dichroism spectra and to Dr. Barbara Tomlonovic Halko for providing the [Λ-$(en)_2$CoCyS]Cl sample.

Registry No. Δ-$(en)_2CoCyS^+$, 66161-35-1; Λ-$(en)_2CoCyS^+$, 66161-34-0; Λ-(*S*)-$(en)_2CoCySO^+$, 66254-06-6; Λ-(*R*)-$(en)_2CoCySO^+$, 66211-49-2; $(en)_2Co(cystS)^{2+}$, 42901-32-6; Λ-$(en)_2CoPenS^+$, 66211-50-5; Δ-$(en)_2CoPenS^+$, 66212-54-2; Λ-$CoPenSO^+$, 66211-48-1; Δ-$CoPenSO^+$, 66161-26-0; $[(en)_2CoPenS]PF_6$, 66161-33-9; H_2O_2, 7722-84-1.

Supplementary Material Available: Tables of kinetics data (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. P. Sloan and J. H. Krueger, *Inorg. Chem.*, **14**, 1481 (1975).
(2) W. G. Jackson, A. M. Sargeson, and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 934 (1976).
(3) B. A. Lange, K. Lisbon, E. Deutsch, and R. C. Elder, *Inorg. Chem.*, **15**, 2985 (1976).
(4) S. F. Mason in "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism", F. Ciardelli and P. Salvadori, Ed., Heyden and Son, Ltd., New York, N.Y., 1971, Chapter 3.6.
(5) L. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973).
(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", 3rd ed, Macmillan, New York, N.Y., 1952, p 600.
(7) In a number of runs, small corrections to A_∞(obsd) were necessary to obtain linearity, but no systematic deviation from first-order behavior was noted.
(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", 2nd ed, Wiley, New York, N.Y., 1961, pp 160–162.
(9) This value is significantly larger than that ($pK_a = 3.7$) previously reported: V. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969).
(10) Rate constants were obtained at an ionic strength of 0.48 M in the range of $[H^+] = 0.1\text{–}0.48$ M, but test runs showed that k_2(obsd) is nearly independent of ionic strength.
(11) J. O. Edwards, "Inorganic Reaction Mechanisms", W. A. Benjamin, New York, N.Y., 1964, p 77.
(12) J. P. Barton, J. E. Packer, and R. J. Sims, *J. Chem. Soc., Perkin Trans. 2*, 1547 (1973).
(13) (a) D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 4981 (1974); (b) D. A. Buckingham and L. M. Engelhardt, *ibid.*, **97**, 5915 (1975).
(14) W. E. Savige and J. A. MacLaren in "The Chemistry of Organic Sulfur Compounds", Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N.Y., 1966, p 379.
(15) A. B. Roy and P. A. Trudinger, "The Biochemistry of Inorganic Compounds of Sulfur", Cambridge University Press, New York, N.Y., 1970, pp 289–295.

(16) CySOH + CyS$^-$ → CySSCy + OH$^-$ is very rapid in aqueous solution. We have shown that reaction of (en)$_2$CoCyS$^+$ with (en)$_2$CoCySO$^+$ does not occur at a significant rate under the reaction conditions.

(17) In contrast, it has been shown that steric effects dominate in the reaction of penicillaminethiolate ion (0.0065 M^{-1} s^{-1}) and cysteinethiolate ion (0.134 M^{-1} s^{-1}) with acrylonitrile: M. Friedman, "The Chemistry and Biochemistry of the Sulfhydryl Group in Amino Acids, Peptides and Proteins", Pergamon Press, New York, N.Y., 1973, pp 107–111.

(18) However, it is possible that conformational differences in the complexes may account for a part of the difference in rates.

(19) Reference 11, p 79.

(20) For example, absorption within the 371-nm LMCT band could give rise to a (en)$_2$Co^{II}NH$_2$,·SO radical pair.

(21) (a) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968); (b) F. Scandola, C. Bartocci, and M. A Scandola, *J. Am. Chem. Soc.*, **95**, 7898 (1973).

(22) M. Orhanovič and N. Sutin, *Inorg. Chem.*, **16**, 550 (1977).

Contribution from the Department of Inorganic & Structural Chemistry,
The University, Leeds LS2 9JT, England

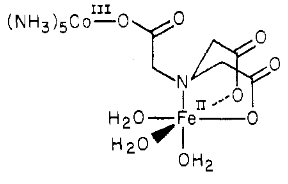
Mechanism of the Cr^{2+}, V^{2+}, and Ru(NH$_3$)$_6$$^{2+}$ Reduction of N-Bonded Glycinato- and β-Alaninatopentaamminecobalt(III) Complexes. Evidence for Paths Involving Precursor Complex Formation with Outer-Sphere Electron Transfer

CARMEL S. GLENNON, JULIAN D. EDWARDS, and A. GEOFFREY SYKES*

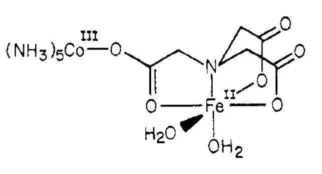
Received November 11, 1977

Rate constants ([H$^+$] = 0.07–1.00 M, 25 °C, I = 1.00 M (LiClO$_4$)) for the Cr^{2+} reduction of (glycinato-*N*)pentaamminecobalt(III), Co(NH$_3$)$_5$(NH$_2$CH$_2$CO$_2$H)$^{3+}$, give an [H$^+$] dependence, k_{obsd} (M^{-1} s^{-1}) = k_1 + k_2[H$^+$]$^{-1}$ (k_1 small). With V^{2+} as reductant the dependence is of the same form, k_{obsd} = k_3 + k_4[H$^+$]$^{-1}$, while with Ru(NH$_3$)$_6$$^{2+}$ no [H$^+$] dependence is observed, k_{obsd} = k_5, I = 1.00 M(LiCl). Ratios of rate constants k_1, k_3, and k_5 are consistent with a mechanism of outer-sphere electron transfer. The O-bonded complex Cr(H$_2$O)$_5$(O$_2$CCH$_2$NH$_3$)$^{3+}$ was identified as product of the Cr^{2+} reduction, and k_2 is believed to proceed with attachment of the reductant at the remote carboxylate. Corresponding reactions of (β-alaninato-*N*)pentaamminecobalt(III), Co(NH$_3$)$_5$(NH$_2$CH$_2$CH$_2$CO$_2$H)$^{3+}$, give rate dependences of the same form, and the product Cr(H$_3$O)$_5$(O$_2$CCH$_2$CH$_2$NH$_3$)$^{3+}$ was identified. The carboxylic acid group has dissociation pK_a values of 2.43 and 2.22 for the glycinato-*N* and β-alaninato-*N* complexes, respectively, and with the labile Cr^{2+} and V^{2+} reductants the remote (unprotonated) carboxylate serves to hold the reductant in the vicinity of the oxidant (paths k_2 and k_4). Since the metal atoms are linked by a flexible but saturated chain of atoms, electron transfer occurs as in an outer-sphere process. These studies provide the simplest and most clearly established case yet of reactions involving precursor complex formation but with outer-sphere electron transfer.

The possibility that precursor complex formation may not always be diagnostic of inner-sphere electron transfer has been recognized for some time. Cannon and Gardiner[1] in their study of the Fe^{2+} reduction of O-bonded (nitrilotriacetato)-pentaamminecobalt(III) obtained kinetic evidence for the formation of a precursor complex (I) but were unable to rule out formation of a second intermediate (II), in which inner-sphere electron transfer via the bridging carboxylate could occur.

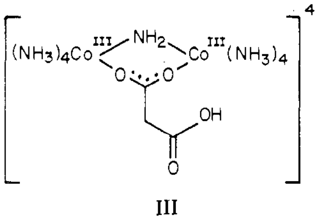


I

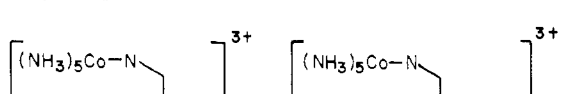


II

Substantial contributions from [H$^+$]$^{-1}$-dependent paths have been observed in the Cr^{2+} reduction of μ-malonato- and μ-dimethylmalonato-dicobalt(III) complexes of type III and are believed to correspond to acid dissociation with reductant attachment at the remote carboxylate.[2] Furthermore, outer-sphere electron transfer occurring independently of a connecting chain of atoms has been proposed by Taube and colleagues in studies on intramolecular electron transfer in the binuclear complex IV.[3]

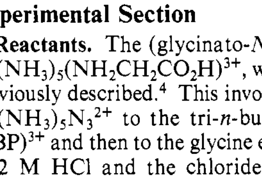


III

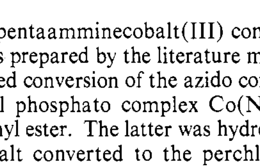


IV

This paper reports investigations into the mechanism of reduction of (glycinato-*N*)pentaamminecobalt(III), V, and (β-alaninato-*N*)pentaamminecobalt(III), VI, with Cr^{2+}, V^{2+}, and Ru(NH$_3$)$_6$$^{2+}$. The possibility that precursor complex formation occurs with Cr^{2+} and V^{2+} reductant at the remote carboxylate position is investigated.



V



VI

Experimental Section

Reactants. The (glycinato-*N*)pentaamminecobalt(III) complex, Co(NH$_3$)$_5$(NH$_2$CH$_2$CO$_2$H)$^{3+}$, was prepared by the literature method previously described.[4] This involved conversion of the azido complex Co(NH$_3$)$_5$N$_3$$^{2+}$ to the tri-*n*-butyl phosphato complex Co(NH$_3$)$_5$(TBP)$^{3+}$ and then to the glycine ethyl ester. The latter was hydrolyzed in 2 M HCl and the chloride salt converted to the perchlorate, [Co(NH$_3$)$_5$(NH$_2$CH$_2$CO$_2$H)](ClO$_4$)$_3$. No loss in weight was observed when the sample was left over P$_2$O$_5$ in vacuo for 4 days. An identical procedure was used for the preparation of the β-alaninato-*N* analogue, Co(NH$_3$)$_5$(NH$_2$CH$_2$CH$_2$CO$_2$H)$^{3+}$. Completion of the ester hydrolysis

0020-1669/78/1317-1654$01.00/0 © 1978 American Chemical Society