methylene group, and the effect is therefore much less.

In summary we conclude that the data obtained for the reactions of Cr^{2+} with $Co(NH_3)_4(C_3H_2O_4)^+$ and $Co(C_3H_2O_4)_3^{3-}$ are best explained in terms of chelation of Cr^{2+} to a chelated malonate. Protonation of the $Co(C_3H_2O_4)_3^{3-}$ complex is believed to be largely responsible for the decrease in production of the chelated malonatochromium(III) species.

Acknowledgment. J.D.E. is grateful to the S.R.C. for a research studentship.

Registry No. $[Co(NH_3)_4(C_3H_2O_4)]ClO_4$, 54870-19-8; $Co(C_3H_2O_4)_3^{3-}$, 22174-09-0; $Cr(H_2O)_6^{2+}$, 20574-26-9; $Cr(H_2O)_4(C_3H_2O_4)^+$, 23153-91-5; $Cr(H_2O)_5(C_3H_3O_4)^{2+}$, 45095-55-4; $Cr(H_2O)_6^{3+}$, 14873-01-9; *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$, 18460-36-1; *cis*-$Co(NH_3)_4(H_2O)(C_3H_3O_4)^{2+}$, 54870-20-1; carbonatotetraamminecobalt(III) perchlorate, 37549-01-2.

References and Notes

(1) (a) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961); (b) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965); (c) C. Lavallee and E. Deutsch, *Inorg. Chem.*, **11**, 3133 (1972).
(2) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
(3) C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970).
(4) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc. A*, 1645 (1966).
(5) See, e.g., M. Gilroy, F. A. Sedor, and L. E. Bennett, *J. Chem. Soc., Chem. Commun.*, 181 (1972).
(6) H. Siebert and R. Scheidermaier, *Z. Anorg. Allg. Chem.*, **361**, 169 (1968).
(7) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).
(8) N. G. Kneten and S. T. Spees, *J. Inorg. Nucl. Chem.*, **33**, 2437 (1971).
(9) M. S. Al-Obadie and A. G. Sharpe, *J. Inorg. Nucl. Chem.*, **31**, 2963 (1969).
(10) Y. Sulfab and M. S. Al-Obadie, *J. Inorg. Nucl. Chem.*, **36**, 2067 (1974).
(11) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **260**, 65 (1949).
(12) D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).
(13) See, e.g., M. L. Hyde and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1586 (1974).
(14) J. Boesch, Dissertation No. 4579, Eidgenössische Technische Hochschule, Zürich, 1971.
(15) M. L. Tobe, "Inorganic Reaction Mechanisms", Nelson, 1972, p 87.
(16) R. H. Moore and R. K. Zeigler, Los Alamos Report LA 2367, and addenda, 1959.
(17) M. J. Frank and D. H. Huchital, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D.C., Sept 1971, No. INOR 42.
(18) M. V. Olson and C. E. Behnke, *Inorg. Chem.*, **13**, 1329 (1974).
(19) M. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).
(20) K. R. Butler and M. R. Snow, *Chem. Commun.*, 550 (1971).
(21) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **45**, 1755 (1972).
(22) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Wiley, New York, N.Y., 1966, p 882.
(23) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).
(24) D. H. Huchital, *Inorg. Chem.*, **9**, 486 (1970).
(25) See for example R. C. Mercier and M. R. Paris, *C. R. Hebd. Seances Acad. Sci.*, **347**, 598 (1966); J. L. Waller and S. M. Rosalie, *J. Inorg. Nucl. Chem.*, **28**, 132 (1963); and other data in *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).
(26) R. Van Eldik and J. A. van den Berg, *J. S. Afr. Chem. Inst.*, **22**, 175 (1969).
(27) L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 298 (1967); 2836 (1970).

Contribution from the Department of Chemistry,
Georgetown University, Washington, D.C. 20057

Kinetics of Reduction of $Co(NH_3)_5Cl^{2+}$ and *cis*- and *trans*-$Co(en)_2Cl_2^+$ by Ti(III)

MATO ORHANOVIC[1] and JOSEPH E. EARLEY*

Received November 27, 1974 AIC40806M

The variation of rate with [H^+] for reduction of three Co(III) oxidants by Ti(III) yields the following second-order rate constants (M^{-1} sec^{-1}, 25.2°) for reduction by $TiOH^{2+}$ and Ti^{3+}: $Co(NH_3)_5Cl^{2+}$, 0.48, <0.001; *cis*-$Co(en)_2Cl_2^+$, 0.75, 0.002; *trans*-$Co(en)_2Cl_2^+$, 2.8, 0.009. The influence of geometry of the oxidant is less than that expected on the basis of related systems.

Although Ti^{3+} is widely used analytically as an inorganic reductant, the rates of only a few of its redox reactions with Co(III) oxidants have been studied, perhaps partially because Ti^{3+} reduces ClO_4^-, the usual medium anion for such reactions. However, this reaction itself indicates that the electron-donor properties of Ti^{3+} are unusual and may be of special interest in understanding fundamental aspects of redox processes. We now report a study of Ti^{3+} reductions of three simple Co(III) oxidants.

Experimental Section

Preparation of Co(III) Complexes. $(Co(NH_3)_5Cl)Cl_2$[2] and *trans*- and *cis*-$(Co(en)_2Cl_2)Cl$[3] were prepared according to literature methods and recrystallized twice from 10^{-3} M HCl. Uv-visible spectra agreed with literature values.[4-6] $Co(NH_3)_5Cl(Tos)_2$ (Tos^- = *p*-toluenesulfonate anion) was prepared by dissolving the chloro salt in 40 times its weight of warm (80°) 0.1 M HTos, filtering, adding solid HTos to make the filtrate ~1 M in HTos, and cooling. The precipitate was recrystallized twice from 0.1 M HTos, washed with ethanol and ether, and dried at 100° for 2 hr.

Anal. Calcd: Co, 11.29; Cl, 6.79; C, 32.22; N, 13.42; S, 12.29; H, 5.60. Found: Co, 11.34; Cl, 6.68; C, 32.73; N, 13.50; S, 12.21; H, 5.72.

Preparation of Ti(III) Solutions. All manipulations of Ti(III) solutions were performed under anaerobic conditions using N_2 atmosphere. Ti(III) solutions were prepared in three different media: chloride, trifluoromethanesulfonate, and *p*-toluenesulfonate. For the two former media, titanium metal (Alfa Inorganics m3N+ sponge) was dissolved in 3 M acid by heating at 50–60° for 24–48 hr. The resulting stock solutions, 0.5–0.7 M in Ti(III), were filtered and stored at 1°. For *p*-toluenesulfonate media, titanium metal was first dissolved in a similar way in 2 M sulfuric acid, sulfate ion was precipitated with a 5% excess of barium *p*-toluenesulfonate, and the solution was centrifuged, filtered, and stored at 1°. Attempts were made to prepare a concentrated titanium(III) *p*-toluenesulfonate solution from sulfate solutions by using the Tos^- form of a strongly basic anion-exchange resin column (Fisher Rexyn 201) or of a weakly acidic cation-exchange resin column (Fisher Rexyn 102). However, Ti(III) reacted with both resins.

Diluted stock solutions of Ti(III) were standardized by oxidation to Ti(IV) with excess of chromium(VI), followed by addition of an excess of iron(II) and back-titration with chromium(VI) in ~1 M H_2SO_4 using *N*-phenylanthranilic acid as indicator. The concentration of H^+ was calculated by subtracting 3[Ti(III)] from the known concentration of the acid used to dissolve the Ti metal. The absence of Ti(IV) was checked spectrophotometrically in the 300-nm region.[7,8] For solutions in chloride media, Cl^- was determined by Volhard's method. The concentration of Cl^- agreed within 1% with the concentration of the acid used to dissolve the Ti metal.

Other Materials. Deionized water that had been doubly distilled through a quartz apparatus was used throughout. Baker reagent grade *p*-toluenesulfonic acid was recrystallized either from water at 80° or from water at 25° to avoid decomposition. Barium *p*-toluenesulfonate was prepared by neutralizing Baker reagent grade barium hydroxide with a 10% excess of *p*-toluenesulfonic acid in water at 60°. Cooling the concentrated solution to 0° converts the solution to a gel, but cooling to 25° yields crystalline $Ba(Tos)_2$. Trifluoromethanesulfonic acid from the 3M Co. and all other chemicals (Fisher and Baker reagent grade) were used without further purification. $LiCF_3SO_3$

was prepared by neutralizing trifluoromethanesulfonic acid with lithium carbonate.

Kinetic Measurements. Measurement of the kinetics of the reactions was accomplished by following a decrease in absorption at one of the Co(III) complexes' absorption maxima using a Gilford spectrophotometer equipped with a thermostatable 10-cm cell compartment and a fast-scanning recorder. Absorption changes were followed at 390 nm for *trans*-($Co(en)_2Cl_2$)Cl and at 385 nm for *cis*-($Co(en)_2Cl_2$)Cl. For $Co(NH_3)_5Cl^{2+}$, two wavelengths were used, 362 and 532 nm, with similar results.

For runs involving $Co(NH_3)_5Cl^{2+}$, all reaction mixture components except Ti(III) were placed in a two-necked 10-cm cell, sealed with serum rubber caps, prethermostated in a water bath and deoxygenated with O_2-free nitrogen. The reaction was initiated by injecting a thermostated Ti(III) solution in the cell using a syringe equipped with a platinum needle. Modifications of this procedure were employed for runs involving *trans*- and *cis*-($Co(en)_2Cl_2$)Cl. To cooled (1°) and deoxygenated solution components in the cell, solid trans or cis complex was added under a stream of nitrogen; the reaction mixture was then additionally deoxygenated at 1° prior to subsequent steps in the procedure. *cis*-($Co(en)_2Cl_2$)Cl aquates much more readily (half-life 47 min at 25°) than the two other Co(III) complexes. Additional deoxygenation at 1° and prethermostating at 25° were therefore shortened to 5 min each.

All runs were performed under pseudo-first-order conditions with an excess of titanium(III) high enough to make the reduction rate much faster than the aquation rate of Co(III). The ratio of the two rates for *trans*-($Co(en)_2Cl_2$)Cl was at least 25, except for two runs. For *cis*-($Co(en)_2Cl_2$)Cl the ratio ranged from 10 to 5, however. Specific rates presented below were calculated from the slopes of standard plots, which were linear to at least 3 half-lives of the reaction for ($Co(NH_3)_5Cl$)Cl and *trans*-($Co(en)_2Cl_2$)Cl. Plots for *cis*-($Co(en)_2Cl_2$)Cl were linear close to 2 half-lives showing slight deviation afterward. Analysis of the plots in a previously described manner[9,10] did not improve the plots nor did it change the rate constants significantly.

All reactions were studied in media of 1 *M* ionic strength.

Stoichiometry. Stoichiometry was checked for a number of runs by recording the uv–visible spectra of the reaction mixture after 7–10 half-lives of the reaction. Spectra were consistent with reduction of 1 mol of Co(III)/mol of Ti(III) oxidized.

Results

Reduction of $Co(NH_3)_5Cl^{2+}$. Preliminary investigation of the reduction of $Co(NH_3)_5Cl^{2+}$ by Ti(III) in 1 *M* *p*-toluenesulfonate medium showed that the medium influenced the course of the reaction. The use of unrecrystallized *p*-toluenesulfonic acid (Baker and Fisher reagent grade) gave erratic kinetic runs, while samples of recrystallized acid gave more reproducible runs with zero-order kinetics with respect to Co(III). Zero-order kinetics (even when various methods of recrystallization were used) seem unusual for this sort of reaction, and we assumed that tosylate ion, or an impurity, is involved in redox processes and sought more suitable media. Trifluoromethanesulfonate ion, the anion of a strong acid which is resistant to oxidation and reduction and has poor complexing ability,[11] was the next choice. The Ti(III) reduction of $Co(NH_3)_5Cl^{2+}$ in this medium was found to be first order in Co(III) and first order in Ti(III), with reaction rates much lower than those measured in *p*-toluenesulfonate media. It was found that the kinetics of the reaction in chloride medium were the same as those in trifluoromethanesulfonate. The rate law is given by

$$\text{rate} = k_2[Co(NH_3)_5Cl^{2+}][Ti(III)] \qquad (1)$$

at constant acid concentration in chloride or trifluoromethanesulfonate media.

Table I. Rate Constants for the Reaction between $Co(NH_3)_5Cl^{2+}$ and Ti(III) at 25.2° and 1.0 *M* Ionic Strength[a]

Medium	$[H^+]$, m*M*	10^4k_{obsd}, sec^{-1}	[Ti(III)], m*M*	10^2k_2, M^{-1} sec^{-1}
b	598	2.35	67.1	0.350
b	498	3.85	86.6	0.445
b	380	5.4	103	0.52
b	259	4.25	47.9	0.89
b	120	5.4	23.9	2.2
b	40	5.4	8.3	6.5
c	608	2.89	65.6	0.441
c	482	3.18	68.2	0.466
c	416	3.24	61.0	0.53
c	360	2.21	34.1	0.65
c	337	3.44	50.3	0.68
c	213	13.3	131	1.02
c	180	3.18	26.9	1.18
c	125	4.05	20.2	2.01
c	83.4	2.41	7.96	3.02
c	54.8	2.98	7.96	3.75
c	25.0	3.01	3.79	7.9
c	12.2	2.50	1.89	13.2
c	6.68	2.55	1.33	19.2
c	5.01	2.24	1.04	21.5
c	4.03	3.06	1.19	25.7
c	3.99	1.36	0.522	26.1
d	467	4.3	93.0	0.46
d	305	6.7	93.0	0.72
d	153	7.4	46.0	1.6
d	80	6.8	24.2	2.8

[a] $[Co(NH_3)_5Cl^{2+}] = 2.4 \times 10^{-3}–1.0 \times 10^{-4}$ *M*. [b] CF_3SO_3H + $Li(CF_3SO_3)$. [c] HCl + LiCl. [d] HCl + NaCl.

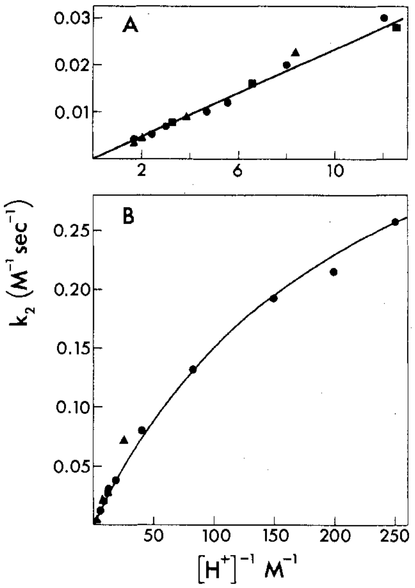


Figure 1. Dependence of k_2 on $[H^+]^{-1}$ for reaction between $Co(NH_3)_5Cl^{2+}$ and Ti(III) at 25.5° in 1 *M* ionic strength maintained with (▲) $Li(CF_3SO_3)$, (●) LiCl, and (■) NaCl.

The acid dependence of the mixed second-order rate constant k_2 was investigated at 25.5 ± 0.2° in both trifluoromethanesulfonate and chloride media. Ionic strength of 1 *M* was maintained with $LiCF_3SO_3$, LiCl, or NaCl. Data are presented in Table I. Specific rates increase with decrease in acidity and the nature of the dependence is shown in Figure 1. The linear dependence of k_2 on $[H^+]^{-1}$ at high acidities (part A of Figure 1) shows no intercept, within experimental error, and the overall acidity dependence is given by

$$k_2 = \frac{k_{-1}K_h[H^+]^{-1}}{1 + K_h[H^+]^{-1}} \qquad (2)$$

Expression 2 is consistent with one or more reaction paths involving deprotonation of a species prior to the electron-transfer step. Slope and intercept of the straight line obtained by plotting $1/k_2$ vs. $[H^+]$ were used to calculate the hydrolytic equilibrium constant $K_h = 4.6 \times 10^{-3}$ *M* and the electron-transfer rate constant $k_{-1} = 0.48$ M^{-1} sec^{-1}. In part B of Figure 1, experimental points are compared with the curve calculated from these values.

Table II. Rate Constants for the Reaction between *trans*-(Co(en)$_2$Cl$_2$)Cl and Ti(III) at 25.2° and 1 *M* Ionic Strength LiCl[a]

[H$^+$], m*M*	10^4k_{obsd}, sec^{-1}	[Ti(III)], m*M*	$10k_2$, M^{-1} sec^{-1}
921	3.12	12.5	0.250
706	4.33	17.8	0.278
497	9.0	23.3	0.38
301	9.1	15.7	0.58
100	11.1	7.32	1.51
49.7	10.5	3.66	2.87
24.9	10.3	2.01	5.1
13.0	15.4	2.01	7.7
9.98	16.3	2.01	8.1
7.69	19.3	2.01	9.6
6.58	22.6	2.01	11.3

[a] [Complex] = 1.3×10^{-3}–2.0×10^{-4} *M*.

Table III. Rate Constants for the Reaction between *cis*-(Co(en)$_2$Cl$_2$)Cl and Ti(III) at 25.0° and 1 *M* Ionic Strength LiCl[a]

[H$^+$], m*M*	10^3k_{obsd}, sec^{-1}	[Ti(III)], m*M*	10^2k_2, M^{-1} sec^{-1}
215	2.41	132	1.83
159	2.38	97.4	2.45
127	2.33	77.9	3.00
60.4	2.20	36.5	6.0
32.7	2.08	19.5	10.7
16.8	1.70	10.2	16.7
11.3	1.38	6.33	21.9
8.06	1.29	4.87	26.5
6.09	1.16	3.65	31.6

[a] [Co(III) complex] = 1.13×10^{-3}–2.0×10^{-4} *M*.

Reduction of *trans*- and *cis*-(Co(en)$_2$Cl$_2$)Cl. On the basis of the observation that Ti(III) reduces Co(NH$_3$)$_5$Cl^{2+} in chloride medium with similar rates to those in trifluoromethanesulfonate media, kinetics of the reduction of *trans*- and *cis*-(Co(en)$_2$Cl$_2$)Cl were studied in chloride media only, with 1 *M* ionic strength maintained with lithium chloride. Both reactions are first-order in Co(III) and first-order in Ti(III). The acid dependence of the mixed second-order rate constant is given in Table II for the trans isomer at 25.2 ± 0.1° and in Table III for the cis isomer at 25.0 ± 0.1°. The nature of the dependence is shown in Figures 2 and 3. The reactions of both substrates have acid-independent contributions to the overall rate, as seen from part A of Figures 2 and 3. These amount to 9×10^{-3} M^{-1} sec^{-1} for the trans and 2×10^{-3} M^{-1} sec^{-1} for the cis isomer. The rate of the reaction is given by

$$\text{rate} = [\text{Ti(III)}][\text{Co(III)}]\frac{k_0 + k_{-1}K_h[\text{H}^+]^{-1}}{1 + K_h[\text{H}^+]^{-1}} \qquad (3)$$

The hydrolytic equilibrium constant $K_h = 4.6 \times 10^{-3}$ *M* found for the reaction of Co(NH$_3$)$_5$Cl^{2+} with Ti(III) fits well, according to expression 3, to data given in Tables II and III for the reactions of *trans*- and *cis*-(Co(en)$_2$Cl$_2$)Cl, giving k_{-1} values 2.8 sec^{-1} and 0.75 M^{-1} sec^{-1}, respectively. In part B of Figures 2 and 3, experimental values of the mixed second-order rate constants are compared with the curve calculated from expression 3, using given k_0, k_{-1}, and K_h values.

Discussion

The ready oxidation of ClO$_4^-$ by titanium(III) is an inconvenience for studies of electron-transfer reactions of Ti(III) and prompts search for a noninterfering medium. Our observations that the reduction of Co(NH$_3$)$_5$Cl^{2+} by Ti(III) is much faster in certain tosylate media than in trifluoromethanesulfonate or chloride media and that the reaction follows zero-order kinetics in tosylate media only indicate interference by the tosylate media used. Although several different methods of recrystallization gave similar results, we cannot certainly conclude that the interference is due to the tosylate anion rather than a persistent impurity.[12]

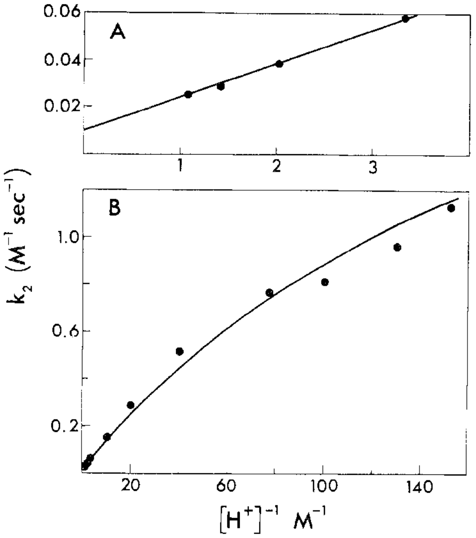


Figure 2. Dependence of k_2 on $[H^+]^{-1}$ for reaction between *trans*-(Co(en)$_2$Cl$_2$)Cl and Ti(III) at 25.2° in 1 *M* ionic strength (LiCl).

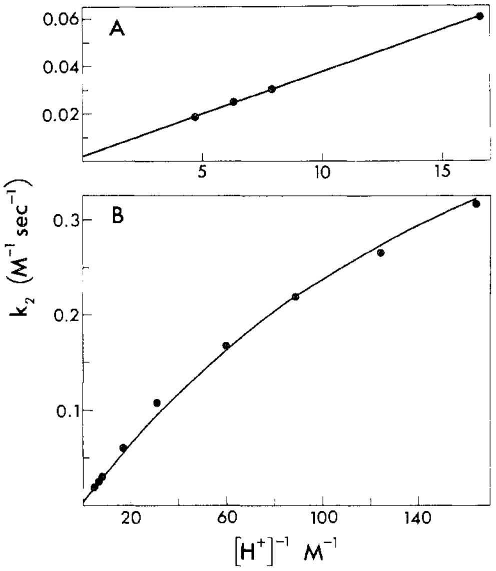


Figure 3. Variation of k_2 with $[H^+]^{-1}$ for reaction between *cis*-(Co(en)$_2$Cl$_2$)Cl and Ti(III) at 25.0° in 1 *M* ionic strength (LiCl).

The complex of Cr(III) with CF$_3$SO$_3^-$ has been shown to undergo aquation[11] more rapidly than the corresponding complex of NO$_3^-$ but less rapidly than the ClO$_4^-$–Cr^{III} species. On this basis it may be argued that complexing of CF$_3$SO$_3^-$ with "hard" acids like Cr(III), and presumably Ti(III), is small. These considerations, together with our observation that rates of Ti(III) reductions are the same in both CF$_3$SO$_3^-$and Cl$^-$ media, suggest that neither Cl$^-$ nor CF$_3$SO$_3^-$ influences these redox reactions through complexation. It is possible that, fortuitously, these two media give the same results, although one or both involve complexation, but we consider this to be unlikely. Duke and Quinney[13] calculated a stability constant (K = 2.2 at 40°) for a monochlorotitanium(III) complex, but this calculation was based on relatively small effects on rate of the Ti^{III}–ClO$_4^-$ reaction caused by [Cl$^-$] variations in solutions of which the ionic strength was not held constant. The value reported for K does not seem reliable.

The value of the protolytic equilibrium constant ($K_h = 4.6 \times 10^{-3}$ *M*) that is involved in the titanium(III) reduction of Co(NH$_3$)$_5$Cl^{2+} is also sufficient to fit the kinetic data observed for *trans*- and *cis*-$Co(en)_2Cl_2^+$. Pecsok and Fletcher[14] measured a value of $K = 6.9 \times 10^{-3}$ *M* for hydrolysis of Ti^{3+} in bromide media of 0.25–1.5 *M*. The closeness of this value to the K_h value measured here suggests that the acid-inverse term in rate laws 1–3 corresponds to the reaction of $TiOH^{2+}$ with the Co(III) complexes and that the acid-independent term in rate laws 2 and 3 corresponds to reaction of Ti^{3+}. $TiOH^{2+}$ reacts 311 times faster than Ti^{3+} with *trans*-$Co(en)_2Cl_2^+$ and 250 times faster with the cis isomer. $TiOH^{2+}$ is relatively more effective with $Co(NH_3)_5Cl^{2+}$, where the acid-independent path is not observed. One possible cause of this effect is that the higher charge of the latter oxidant favors the reductant of lower charge.

The relatively high rate of reaction of $TiOH^{2+}$ may be understood in terms of the nature of the Ti(IV) product. Ti(IV) would be expected to have an acidity like that of V(IV) and to exist as TiO^{2+} and related polymeric species. A short Ti–O distance in such a species would provide a barrier to reaction which would be reduced for a deprotonated reductant like $TiOH^{2+}$. The data presented here do not establish or disprove an inner-sphere mechanism for the reaction.

The rate of reaction of Ti(III) with $Co(NH_3)_5Cl^{2+}$ reported here is several orders of magnitude less than that of Fraser et al.,[15] who reported an acid dependence different from the one we observe. Their media contained ClO_4^- in high concentrations, and catalytic paths, perhaps involving radical intermediates, may have been important under the conditions they used.

Rosseinsky[16] has rationalized the observation that reaction of $Co^{III}L_4XY$ species with M^{2+} reductants showed decreased sensitivity to the nature of Y in the order ($Fe^{2+} > Ru^{2+} > V^{2+}$) on the basis of the order of reducing power ($Fe^{2+} < Ru^{2+} < V^{2+}$). Since electrode potential data indicate that $TiOH^{2+}$ is intermediate in reducing power between Ru^{2+} and V^{2+}, one would expect that the selectivity (with respect to variations in Y) of Ti(III) reductions should be more than that of V^{2+} reductions but less than that of Ru^{2+} reductions. The close similarity of redox rates between *cis*- and *trans*-dichloro Co(III) oxidants indicates an even lower selectivity than predicted on this basis. Among the many possible causes for such an effect (if it is real) is some Co^{III}–Ti^{III} overlap prior to the transition state.

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research under Grant AF 71-2003.

Registry No. $Co(NH_3)_5Cl^{2+}$, 14970-14-0; *trans*-$Co(en)_2Cl_2^+$, 14403-91-9; *cis*-$Co(en)_2Cl_2^+$, 14875-15-1; Ti(III), 22541-75-9.

References and Notes

(1) On leave from the Institute Ruder Boskovic, Zagreb, Yugoslavia.
(2) G. G. Schlessinger, *Inorg. Synth.*, **9**, 160 (1967).
(3) J. C. Bailar, Jr., *Inorg. Synth.*, **2**, 222 (1946).
(4) H. Taube, *J. Am. Chem. Soc.*, **82**, 524 (1960).
(5) C. H. Langford and W. R. Muir, *J. Phys. Chem.*, **71**, 2602 (1967).
(6) C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968).
(7) J. P. Birk and T. P. Logan, *Inorg. Chem.*, **12**, 580 (1973).
(8) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537, 2553 (1973).
(9) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).
(10) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969).
(11) A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).
(12) A few reactions carried out in ClO_4^--containing media were more rapid, but the addition of Cl^- reduced the rate. This seems to indicate ClO_4^- catalysis which is quenched by Cl^-, rather than Cl^- interference through complex formation. It appears that others have been able to purify tosylate media more completely, e.g., A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).
(13) F. R. Duke and P. R. Quinney, *J. Am. Chem. Soc.*, **76**, 3800 (1954).
(14) R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, **1**, 155 (1962).
(15) V. W. Cope, R. G. Miller, and R. T. M. Fraser, *J. Chem. Soc. A*, 301, 1967.
(16) D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun.*, 226 (1972).

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

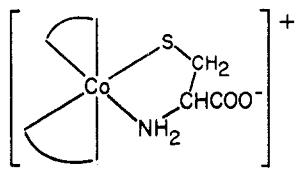
Oxidation of Coordinated Cysteine. Formation of Sulfinato- and Sulfenatocobalt(III) Complexes

CAMILLA P. SLOAN and JAMES H. KRUEGER*

Received December 17, 1974		AIC408345

Oxidation of (cysteinato)-*N*,*S*-bis(ethylenediamine)cobalt(III) perchlorate resulted in isolation of the corresponding sulfenato, $[Co(en)_2\{NH_2CH(COO)CH_2SO\}]ClO_4$, and sulfinato, $[Co(en)_2\{NH_2CH(COO)CH_2SO_2\}]ClO_4$, complexes. The products were characterized by elemental analysis and cation-exchange chromatography and by infrared, ^1H NMR, and uv-visible spectroscopy. The chemical and spectroscopic results are in accord with N and S bonding to cobalt in each complex. In the series thiolate, sulfenate, and sulfinate, an increase in the oxidation state of the coordinated sulfur ligand results in an increase in ligand field strength and an increase in deshielding of the methylene protons adjacent to sulfur.

Recently, Kothari and Busch[1] described a bis(ethylenediamine)cobalt(III) complex of cysteine for which it was shown that, of the three potential donor groups, it is the amine and thiolate functions that are coordinated. We have been interested in the oxidation of thiolate sulfur to the sulfinate stage in coordinated cysteine and it appeared that the above complex would be a useful choice for such a study. In particular, the nonlabile nature of a chelated cobalt(III) complex would maximize the chance that the sulfur function would remain coordinated during and after an oxidation reaction. The oxidation by hydrogen peroxide of a tris(cysteinato)cobaltate(III) complex, $Co(CyS)_3^{3-}$,[2] to the corresponding cysteinesulfinato complex, $Co(CySO_2)_3^{3-}$,[2] has been described, first by Schubert[3] and more recently by Gillard and coworkers,[4] and it seemed likely that I would undergo the same reaction.



I

A variety of sulfinato complexes have been prepared by oxidative addition, by SO_2 insertion into a metal–carbon bond, and by direct replacement of ligands by RSO_2^-.[5,6] Both