Figure 2. Plot of $k_{HBrO_2}/f_{CeSO_4^{2+}}$ as a function of $f_{Ce(SO_4)_2}/f_{CeSO_4^{2+}}$.

The results of an earlier kinetic study[13] on the reaction of large excesses of cerium(III) with bromate ion in sulfuric acid solution have been questioned[4] as a result of computer simulations using eq 1–7. The present study suggests that results of the latter analysis must be viewed with serious reservations in that the estimated values for the rate constants k_{-5} and k_7 are poor estimates. The present results do not provide evidence that would give rise to reservations concerning the basic mechanism for the Belousov–Zhabotinskii oscillating reaction proposed by Noyes and co-workers. They do reaffirm, however, that computer modeling[4] in which a number of extraneous rate parameters have to be estimated is not a useful procedure for assessing the validity of direct kinetic measurements. If the experimental data are not correct, it is preferable to demonstrate this fact in the laboratory.

References and Notes

(1) Work performed under the auspices of the Division of Basic Energy Sciences of the Department of Energy.
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(11) J. C. Sullivan, R. C. Thompson, W. Mulac, and S. Gordon, to be submitted for publication. We also have studied the reaction BrO₂⁻ + OH → BrO₂ + OH⁻ in basic solution with use of preparation A. The results are very similar to those reported in ref 10 and add confidence to the integrity of the Ba(BrO₂)₂ sample used in the present study.
(12) It may be possible to obtain better values for the rate constants k_{-5} and k_7 by a numerical analysis of the kinetic data obtained in these experiments. We will furnish these data to interested parties upon request.
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Chloritopentaamminecobalt(III): Synthesis, Decomposition, and Oxidation–Reduction Reactions

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The synthesis and characterization of chloritopentaamminecobalt(III) nitrate are described. In acidic solution the complex decomposes by an internal oxidation–reduction process with the formation of chlorine dioxide and cobalt(II). At 25 °C and $I = 0.50$ M, k(extrapolated) $= 8.0 \times 10^{-6}$ s⁻¹, $\Delta H^{\ddagger} = 25._3 \pm 1._7$ kcal/mol, and $\Delta S^{\ddagger} = 3 \pm 5$ cal/(mol deg). The presence of pentaamminecobalt(III) rather than a proton greatly reduces the rate of oxidation of chlorite. The rate law for the cobalt(III) oxidation of the chlorito complex is $-d[\text{comp}]/dt = k_{comp}[\text{comp}][\text{Co(III)}]/[\text{H}^+]$, with $k_{comp} = 9.1$ s⁻¹, $\Delta H^{\ddagger} = 28._1 \pm 0._4$ kcal/mol, and $\Delta S^{\ddagger} = 40 \pm 1$ cal/(mol deg) at 25 °C and $I = 2.1$ M. For the Co^{III}–HClO₂ reaction, $-d[\text{HClO}_2]/dt = k_{HClO_2}[\text{HClO}_2][\text{Co(III)}]/[\text{H}^+]$, with $k_{HClO_2} = 2.4 \times 10^3$ s⁻¹, $\Delta H^{\ddagger} = 15._5 \pm 0._7$ kcal/mol, and $\Delta S^{\ddagger} = 9 \pm 3$ cal/(mol deg) at 25 °C and $I = 2.0$ M. The stoichiometry of the chromium(II) reduction of the chlorito complex is similar to and compared with that for the corresponding reduction of chlorous acid. Oxygen-18 tracer experiments demonstrate that the cobalt–oxygen bond originally present in the complex is largely retained in the $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ product during reduction with Fe²⁺, VO²⁺, and HSO₃⁻ but is substantially broken during oxidation with cobalt(III).

Introduction

The oxidation–reduction chemistry of oxyhalogen ions and acids is a rich field and has received considerable attention. The reactivity of these species would be expected to be modified upon coordination to substitution-inert metal cations. However, the lack of synthetic techniques for the preparation of such complexes has been a serious obstacle to experimental investigation. To the best of our knowledge, the comparative

chemistry of an oxyhalogen as a free ion and as a ligand has been examined only with chlorate ion and chloratopentaaquochromium(III).[1]

We have recently synthesized salts of chloritopentaamminecobalt(III). This complex ion is sufficiently stable in aqueous solution to allow studies of a variety of oxidation–reduction reactions. Several interesting conclusions have been drawn based on oxygen-18 tracer experiments. The decomposition of the chlorito complex is unusual in that an internal redox reaction producing cobalt(II) and chlorine dioxide occurs. We report the results of these investigations in this paper.

Experimental Section

Reagents. The preparation and standardization of chromium(II)[2] and cobalt(III)[3] solutions have been reported previously. Sodium chlorite was obtained from Matheson Coleman and Bell. Lithium perchlorate was prepared by the neutralization of lithium carbonate with perchloric acid and was recrystallized three times. Other reagents were commercial products of analytical reagent grade. Deionized water was distilled before use, first from acidic dichromate and then from alkaline permanganate.

Synthesis of Chloritopentaamminecobalt(III) Nitrate. In a typical preparation, 36.6 g of $Co(NO_3)_2 \cdot 6H_2O$, 90 g of NH_4NO_3, and 120 mL of 28% NH_3 were dissolved in 240 mL of water and cooled in an ice bath. An excess of ClO_2 was vigorously delivered by a stream of N_2 into the flask for ca. 30 min with constant stirring. The ClO_2 was generated by allowing *excess* $NaClO_2$ to disproportionate in $HClO_4$ solution.[4] The fine crystals which precipitated were collected by filtration, washed with methanol and acetone, and air-dried (yield 24 g, 57% based on initial cobalt(II)). The synthesis should be carried out in near darkness, as solutions of chloritopentaamminecobalt(III) are slowly bleached by room light.

The product was purified by dissolution in a slight excess of dilute nitric acid at room temperature, filtered, and precipitated by the addition of solid $NaNO_3$ at 0 °C. A saturated solution was prepared from the precipitate in dilute nitric acid at room temperature and allowed to stand overnight at 0 °C in the dark. The reddish crystals were collected by filtration, washed with methanol and acetone, and air-dried. Anal. Calcd for $[(NH_3)_5CoOClO](NO_3)_2$: H, 4.51; N, 29.22; Cl, 10.57. Found: H, 4.60; N, 29.05; Cl, 10.43.

The solid appears to be stable for months at room temperature when protected from light and may be safely heated or shocked. The visible absorption spectrum in acidic solution exhibits maxima at 515 nm (ϵ 87 M^{-1} cm^{-1}) and 358 nm (ϵ $(2.3_2 \pm 0.0_3) \times 10^3$ M^{-1} cm^{-1}). Weighed samples were treated with excess, standardized iron(II) solutions in 1 M perchloric acid, and the remaining iron(II) was determined by titration with standardized permanganate. A ratio of (mmol Fe(II) consumed)/(mmol complex) = 3.88 was found, corresponding to 97.0% purity based on chlorite in the complex. Ion-exchange separations of these reaction mixtures showed $(NH_3)_5CoOH_2^{3+}$ as the only detectable cobalt product.

Other salts can be prepared by metathesis, but the perchlorate salt is very soluble and difficult to isolate. Chloritopentaamminecobalt(III) exhibits ion-exchange behavior typical of dipositive pentaamminecobalt(III) species.

Decomposition Studies. Preliminary experiments showed that the chlorito complex slowly decomposes in acidic solution by an internal redox reaction with the formation of equal amounts of cobalt(II) and chlorine dioxide; trace amounts of aquopentaamminecobalt(III) were also observed. The yield of chlorine dioxide in the spent reaction solutions was measured spectrophotometrically at 358 nm (ϵ 1242 M^{-1} cm^{-1}).[5] The amount of the cobalt(II) product was determined by the Kitson method.[6] A very slow ion-exchange separation at 0 °C of a reaction mixture that had undergone ca. 50% decomposition gave no indication of the presence of $(NH_3)_4(H_2O)CoOClO^{2+}$.[7]

A jacketed, 100-mL glass syringe fitted with a capillary tip was used as the reaction vessel for the kinetic experiments. All reagents except the chlorito complex were initially present in the syringe at the desired temperature. The reaction was initiated by drawing 2–3 mL of a complex solution into the syringe with rapid mixing. Aliquots were removed periodically by injection into a small container at 0 °C; no empty space developed in the shrinking reaction vessel, and thus volatilization of the chlorine dioxide product was negligible. In most of the studies the chlorito complex and chlorine dioxide were

monitored spectrophotometrically at 358 nm; plots of ln $(A_t - A_\infty)$ vs. t were linear for a least 80% reaction. Cobalt(II) produced during the reaction was assayed in a few experiments by a modification of the Kitson method.[6] An aliquot of the reaction mixture was added to a solution containing concentrated HCl, and an excess of Na_2SO_3 was introduced to rapidly convert the chlorito complex to $(NH_3)_5CoOH_2^{3+}$ and Cl^- and the ClO_2 to Cl^-. The solution was then made to volume with the appropriate amounts of acetone and NH_4SCN. The absorbance was measured at 625 nm, and the [cobalt(II)] was calculated from a calibration plot that was linear in the range $(2–27) \times 10^{-5}$ M Co^{2+}. Plots of ln $([Co^{2+}]_\infty - [Co^{2+}]_t)$ vs. t were linear for at least 80% reaction.

All rate constants reported in this paper were determined by a least-squares adjustment of the kinetic data to the integrated form of the appropriate rate equation.

Kinetic Study of the Oxidation of Chloritopentaamminecobalt(III) and Chlorous Acid by Cobalt(III). The relatively slow cobalt(III) oxidation of the chlorito complex was studied with a Zeiss PMQ-II spectrophotometer equipped with a thermostated, rapid-mixing (ca. 1 s) sample compartment. The reaction was monitored at the 358-nm absorption maximum of the complex; absorbance corrections for loss of cobalt(III) and production of $(NH_3)_5CoOH_2^{3+}$ were very small. The reactions were usually studied with a large excess of the oxidant but in a few cases were studied under second-order conditions. The kinetic data were well correlated to at least 80% of complete reaction by the integrated form of the rate expression: $-d[(NH_3)_5CoOClO^{2+}]/dt = k[(NH_3)_5CoOClO^{2+}][Co(III)]$.

The cobalt(III) oxidation of chlorous acid is a rapid reaction and was studied by the stopped-flow technique. Chlorine dioxide is the sole oxidation product if excess chlorous acid is used. Sodium chlorite solutions containing lithium perchlorate were kept slightly basic in one syringe to prevent disproportionation; the other syringe contained the cobalt(III) and perchloric acid. The reaction was monitored at 358 nm, an absorption maximum for chlorine dioxide. Again, the integrated form of the rate expression, $d[ClO_2]/dt = k[HClO_2] \cdot [Co(III)]$, adequately correlated the kinetic data to ca. 70% of complete reaction.

A few experiments were performed with a ratio of $[Co(III)]_0/[HClO_2]_0 > 13$. A very rapid increase in absorbance followed by a much slower decrease was observed at 358 nm. The slow portion was attributed to the Co^{III}–ClO_2 reaction and was analyzed as a second-order process. The kinetic results were compared with those previously obtained in a direct study of this system[4] (vide infra).

Stoichiometry Study of the Chromium(II) Reduction of Chloritopentaamminecobalt(III) and Chlorous Acid. Both of these reactions are extremely rapid. A previous study of the stoichiometry of the chromium(II) reduction of the chlorine oxidants demonstrated that rapid-mixing procedures are necessary in order to obtain reproducible results.[2] Therefore, the rapid-mixing (ca. 2 ms) system of a Durrum stopped-flow instrument was used to generate the reaction solutions. One syringe contained either the chlorito complex (as the perchlorate after ion-exchange separation) or a sodium chlorite solution (in dilute base to eliminate disproportionation) and the other the desired chromium(II) solution; both solutions were thoroughly deoxygenated. The spent reaction mixtures were separated by ion-exchange chromatography at 3 °C. When excess chromium(II) was used, it was first converted to a polynuclear chromium(III) species by treatment with oxygen. Co^{2+}, $CrCl^{2+}$, Cr^{3+}, and $(NH_3)_5CoOH_2^{3+}$ were cleanly separated by this procedure; the yield of polynuclear chromium(III) was calculated by difference. $CrCl^{2+}$ and Cr^{3+} were assayed spectrophotometrically as CrO_4^{2-} after oxidation by H_2O_2 in base.[8] $(NH_3)_5CoOH_2^{3+}$ was assayed at 491 nm (ϵ 47.2 M^{-1} cm^{-1}).[9]

Oxygen-18 Tracer Experiments. $(NH_3)_5CoOClO^{2+}$ is rapidly reduced by Fe^{2+}, VO^{2+}, and HSO_3^- in acidic solution; the only detectable cobalt product is $(NH_3)_5CoOH_2^{3+}$, except for the HSO_3^- reduction where ca. 12% $(NH_3)_5CoOSO_3^+$ is formed. The source of the oxygen in the $(NH_3)_5CoOH_2^{3+}$ was determined by using a chlorito complex of normal isotopic abundance in solvent that was 2–8 times enriched in oxygen-18. An excess of the reducing agent was used to ensure complete reaction of the chlorito complex. The VO^{2+} (in 0.5 M $HClO_4$)[10a] and HSO_3^- (in $HC_2H_3O_2$–$C_2H_3O_2^-$ buffer)[10b] were in isotopic equilibrium with solvent. After complete reaction, the aquopentaamminecobalt(III) product was precipitated as the bromide salt, washed with methanol and acetone, and thoroughly dried under vacuum. Cl_2 produced in the VO^{2+} reaction was removed before precipitation. The solution spectrum of the precipitate was

Table I. Kinetic Results for the Decomposition of Chloritopentaamminecobalt(III) in Acidic Solution[a]

[H⁺], M	T, °C	k_{comp}, s⁻¹
0.50	50.0	2.65 × 10⁻⁴
0.50[b]	50.0	2.44 × 10⁻⁴
0.010	50.0	2.66 × 10⁻⁴
2 × 10⁻⁵ [c]	50.0	2.50 × 10⁻⁴
0.50	45.0	1.27 × 10⁻⁴
0.50	40.0	7.79 × 10⁻⁵
0.50	35.0	3.35 × 10⁻⁵

[a] $HClO_4$ was used as the acid. Ionic strength was maintained at 0.50 M with lithium perchlorate. $[(NH_3)_5CoOClO^{2+}]_0 = 2.40 \times 10^{-4}$ M except in the second experiment. [b] Rate monitored by production of cobalt(II). $[(NH_3)_5CoOClO^{2+}]_0 = 2.10 \times 10^{-3}$ M. [c] 0.025 M $HC_2H_3O_2$–$NaC_2H_3O_2$ buffer used.

Table II. Kinetic Results of the Cobalt(III) Oxidation of Chloritopentaamminecobalt(III)[a]

[HClO₄], M	T, °C	10³[Co-(III)]₀, M	k_2,[b] M⁻¹ s⁻¹	k_2[H⁺], s⁻¹
2.05	20.0	2.60	1.96 ± 0.02	4.02
2.11	20.0	6.03	1.90 ± 0.06	4.01
1.15	20.0	5.10	3.32 ± 0.04	3.81
0.553	20.0	5.04	7.24 ± 0.04	4.00
0.229	20.0	3.82	17.4 ± 0.1	3.99
0.224	20.0	0.382	17.4 ± 0.1	3.91
			av	3.96 ± 0.06
0.553	12.3	4.87	1.95 ± 0.01	1.08
0.553[c]	12.3	4.82	1.95 ± 0.04	1.08
0.270	4.9	4.87	1.01 ± 0.01	0.272

[a] $[(NH_3)_5CoOClO^{2+}]_0$ ca. 1.40 × 10⁻⁴ M. Ionic strength was maintained at 2.1 M with lithium perchlorate. [b] Uncertainties are average deviations of two to three replicate experiments. [c] Added $[NaNO_3] = 1.09 \times 10^{-3}$ M.

checked in blank experiments for each system and found to be in satisfactory agreement with that of $(NH_3)_5CoOH_2^{3+}$. Oxygen in the dried precipitate was converted to CO_2 by the $Hg(CN)_2$ method.[11] The CO_2 was separated by gas chromatography and the 46/(44 + 45) ratio was measured with a Nuclide dual collector mass spectrometer.

In a separate experiment, an excess of $(NH_3)_5CoOClO^{2+}$ was allowed to react with HSO_3^{*-} (in H_2O^*) in $HC_2H_3O_2$–$C_2H_3O_2^-$ buffer. The stoichiometry ratio $[HSO_3^-]_0/\Delta[(NH_3)_5CoClO^{2+}] = 2.04$ was determined in a blank experiment. After the residual chlorito complex had decomposed and the $(NH_3)_5CoSO_3^+$ had largely aquated, the sulfate product was precipitated as barium sulfate. The barium sulfate was ignited with graphite,[12] and the resulting CO_2 was analyzed by mass spectrometry.

The $(NH_3)_5CoOH_2^{3+}$ product of the $(NH_3)_5CoOClO^{2+}$–excess Co(III) reaction in enriched solvent was separated by ion exchange before precipitation.

Results

Survey of Oxidation–Reduction Reactions. In general, the oxidation of chloritopentaamminecobalt(III) appears to be much slower than the corresponding oxidation of chlorous acid. Thus, cobalt(III), cerium(IV), chromium(VI), bromate, chlorous acid, hypochlorous acid, and chlorine attack the chlorite bonded to the pentaamminecobalt(III) center at rates substantially lower than with chlorous acid.

The comparative reduction rates are more difficult to assess. Reagents such as chromium(II), oxovanadium(IV), iron(II), and iodide rapidly reduce both oxidants. However, the rate behavior of the latter three reducing agents with the chlorito complex is complicated, and to date we have been unsuccessful in attempts to unravel the rate laws.

Decomposition Studies. In acidic solution, at least 94% of the decomposition of the chlorito complex proceeds via the stoichiometry shown in eq 1. Only traces of $(NH_3)_5CoOH_2^{3+}$

$$(NH_3)_5CoOClO^{2+} + 5H^+ = 5NH_4^+ + Co^{2+} + ClO_2 \quad (1)$$
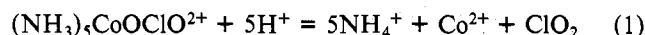
are observed as a product. No evidence was obtained for labilization of coordinated ammonia ligands prior to the internal redox reaction.

Values of the first-order rate constant, k_{comp}, at various acidities and temperatures are summarized in Table I. Within experimental error, the rate of production of cobalt(II) is equal to the rate of disappearance of the chlorito complex, and the decomposition rate is independent of the hydrogen ion concentration. The values of the activation parameters determined from the temperature dependence of k_{comp} are $\Delta H^* = 25._3 \pm 1._7$ kcal/mol and $\Delta S^* = 3 \pm 5$ cal/(mol deg).
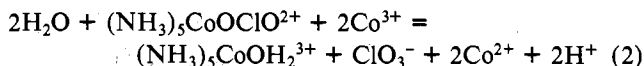
Oxidation of Chloritopentaamminecobalt(III) and Chlorous Acid by Cobalt(III). The stoichiometric ratios $\Delta[Co(III)]/[comp]_0 = 2.02 \pm 0.02$ and $[(NH_3)_5CoOH_2^{3+}]_\infty/[comp]_0 = 0.98 \pm 0.02$ were determined for the oxidation of the chlorito complex with a small excess of cobalt(III). Thus

the stoichiometry of this reaction can be summarized by eq 2. Values of the second-order rate constant, k_2, are summarized in Table II. Chlorine dioxide is a likely intermediate

$$2H_2O + (NH_3)_5CoOClO^{2+} + 2Co^{3+} = (NH_3)_5CoOH_2^{3+} + ClO_3^- + 2Co^{2+} + 2H^+ \quad (2)$$

marized in Table II. Chlorine dioxide is a likely intermediate in this reaction, but no evidence for its buildup was observed. The small concentration of nitrate ion introduced with the chlorito complex salt has no influence on the kinetic results.

The values of k_2[H⁺] at 20.0 °C are, within experimental error, constant over the range of hydrogen ion concentration studied and support the empirical rate expression:

$$-d[(NH_3)_5CoOClO^{2+}]/dt = k_2'[(NH_3)_5CoOClO^{2+}][Co(III)]/[H^+] \quad (3)$$

Values of $\Delta H^* = 28._1 \pm 0._4$ kcal/mol and $\Delta S^* = 40 \pm 1$ cal/(mol deg) were calculated from the temperature dependence of k_2'.

The ratio $[ClO_2]_\infty/[Co(III)]_0 = 0.97 \pm 0.04$ was determined for the rapid oxidation of excess chlorous acid with cobalt(III). Disproportionation of chlorous acid is negligible during the reaction.[5] Equation 4 summarizes the observed stoichiometry.

$$HClO_2 + Co^{3+} = ClO_2 + Co^{2+} + H^+ \quad (4)$$
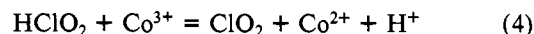
No spectral evidence for the formation of an intermediate such as $CoOClO^{2+}$ was found.[13]

Values of the second-order rate constant, k_4, are summarized in Table III. Again, within experimental error the values of k_4[H⁺] are constant, a result consistent with the empirical rate expression:

$$d[ClO_2]/dt = k_4'[HClO_2][Co(III)]/[H^+] \quad (5)$$

The calculated values of $\Delta H^* = 15._5 \pm 0._7$ kcal/mol and $\Delta S^* = 9 \pm 3$ cal/(mol deg) were determined from the temperature dependence of k_4' in 1.00 M $HClO_4$.

A limited set of experiments were conducted with $[Co(III)]_0/[HClO_2]_0 > 13$. A rapid increase in absorbance followed by a much slower decay was observed at 358 nm, an absorption maximum for chlorine dioxide. The maximum absorbance observed was approximately 85% of that calculated for the complete conversion of the chlorous acid to chlorine dioxide. The middle half of the decay curve obeyed pseudo-first-order kinetics; according to our interpretation, this region should correspond to the Co^{III}–ClO_2 reaction, a system that has previously been studied directly.[4] Over the conditions 25.0 °C, $[Co(III)]_0 = (2.29–4.58) \times 10^{-3}$ M, $[(NH_3)_5CoOClO^{2+}]_0 = 1.71 \times 10^{-4}$ M, $[HClO_4] = 0.52–1.13$ M, and $I = 2.1$ M ($LiClO_4$), the empirical rate law was equal to $(103 \pm 2$ s⁻¹$)[ClO_2][Co(III)]/[H^+]$, in satisfactory

Table III. Kinetic Results for the Cobalt(III) Oxidation of Chlorous Acid[a]

[HClO$_4$], M	T, °C	10^4[Co^{3+}]$_0$, M	10^4[HClO$_2$]$_0$, M	$10^{-3}k_4$,[b] M^{-1} s^{-1}	k_4[H$^+$], s^{-1}
1.00	25.5	1.82	12.2	2.44 ± 0.01	2.44 × 10^3
1.00	25.5	3.41	12.2	2.66 ± 0.03	2.66 × 10^3
1.00	25.5	3.63	7.34	2.64 ± 0.01	2.64 × 10^3
1.50	25.5	3.81	7.34	2.00 ± 0.01	3.00 × 10^3
0.70	25.5	4.20	7.34	3.83 ± 0.01	2.58 × 10^3
0.50	25.5	3.90	7.34	5.15 ± 0.03	2.32 × 10^3
0.35	25.5	4.13	7.34	7.54 ± 0.04	2.64 × 10^3
0.20	25.5	4.12	7.34	11.6 ± 0.2	2.68 × 10^3
				av	(2.62 ± 0.13) × 10^3
1.00	17.0	3.46	7.34	1.11 ± 0.01	1.11 × 10^3
1.00	17.0	3.83	12.2	1.08 ± 0.01	1.08 × 10^3
1.00	9.7	3.85	7.34	0.587 ± 0.002	5.87 × 10^2
1.00	9.7	3.73	12.2	0.558 ± 0.003	5.58 × 10^2

[a] Ionic strength was maintained at 2.0 M with lithium perchlorate. [b] Uncertainties are average deviations of duplicate experiments.

Table IV. Stoichiometry Results for the Chromium(II) Reduction of Chloritopentaamminecobalt(III) and Chlorous Acid at 25 °C

expt	oxidant[a]	[Cr^{2+}]$_0$, M	[H$^+$], M	[Cl$^-$]$_0$, M	mole % Cr(III) in prod[b]		
					CrCl^{2+}	Cr^{3+}	polynuclear[c]
1[d]	(NH$_3$)$_5$CoOClO^{2+}	0.0299	0.55		20.5	28.8	50.7
2[e]	(NH$_3$)$_5$CoOClO^{2+}	0.0540	0.55		24.8	29.0	46.2
3[e]	(NH$_3$)$_5$CoOClO^{2+}	0.0542	0.55	0.088	47.6	38.9	13.5
4[e]	(NH$_3$)$_5$CoOClO^{2+}	0.0534	1.9		24.6	35.6	39.8
5[f]	HClO$_2$	0.0440	0.55		20.8	45.4	33.8
6[f]	HClO$_2$	0.0440	0.55	0.088	37.5	50.6	11.9
7[f]	HClO$_2$	0.0440	1.9		22.1	53.4	24.5

[a] [Oxidant]$_0$ = 0.008 90 M. The chlorito complex was subjected to ion-exchange separation at 0 °C to avoid introduction of nitrate ions. [b] (H$_2$O)$_5$CrCl^{2+} ≡ CrCl^{2+}, (H$_2$O)$_6$Cr^{3+} ≡ Cr^{3+}, and polynuclear refers to the green higher charged (>3+) product; the identity of this product(s) was not established in this study. [c] Mole % calculated by difference. [d] Percent CrCl and Cr^{3+} ≡ (mmol product found × 100)/(mmol Cr^{2+} initial). [e] Percent CrCl^{2+} ≡ (mmol CrCl^{2+} found × 100)/(4 × mmol (NH$_3$)$_5$CoOClO^{2+} initial). Percent Cr^{3+} ≡ (mmol Cr^{3+} found − mmol (NH$_3$)$_5$CoOClO^{2+} initial) × 100)/(4 × mmol (NH$_3$)$_5$CoOClO^{2+} initial). [f] Percent CrCl^{2+} and Cr^{3+} ≡ (mmol product found × 100)/(4 × mmol HClO$_2$ initial).

agreement with the previously determined value 98 ± 2 s^{-1}.

Stoichiometry Study of the Chromium(II) Reduction of Chloritopentaamminecobalt(III) and Chlorous Acid. The percent yields of (H$_2$O)$_5$CrCl^{2+}, (H$_2$O)$_6$Cr^{3+}, and an uncharacterized polynuclear chromium(III) product are summarized in Table IV. In the first experiment, the stoichiometry ratio [Cr^{2+}]$_0$/Δ[(NH$_3$)$_5$CoOClO^{2+}] = 4.04 was determined; (NH$_3$)$_5$CoOH$_2^{3+}$ was the only cobalt product. This result indicates that the chlorite ligand is completely reduced prior to reduction of the cobalt(III) center. Complete reduction of the cobalt(III) center was observed in experiments 2–4, in which a [Cr^{2+}]$_0$/[(NH$_3$)$_5$CoClO^{2+}]$_0$ ratio >5 was used, but presumably this reduction occurred subsequently via the relatively slower (NH$_3$)$_5$CoOH$_2^{3+}$–Cr^{2+} reaction.[14] Since the latter reduction is known to produce (H$_2$O)$_6$Cr^{3+} as the chromium(III) product, the yields of this species have been corrected for this contribution in experiments 2–4.

The stoichiometry results for the Cr^{2+}–HClO$_2$ reaction are very similar to those determined previously.[2]

Both reactions show several similar characteristics. Nearly all the chlorine originally present in the oxidant appears in the coordination sphere of the (H$_2$O)$_5$CrCl^{2+} product. When chloride ion is present in the reaction solution, substantially more chlorochromium(III) and slightly more hexaaquochromium(III) are formed at the expense of the polynuclear species. Small increases in the yield of the hexaaquochromium(III) product are found with increasing acidity.

Oxygen-18 Tracer Results. A limited series of experiments were performed to determine the source of the oxygen in the (NH$_3$)$_5$CoOH$_2^{3+}$ product that was formed through oxidation or reduction of the chlorito complex. (NH$_3$)$_5$CoOClO^{2+} of normal isotopic abundance was allowed to react in oxygen-18-enriched solvent under conditions where the water and oxygen in the primary coordination sphere of the oxidant or reductant were in isotopic equilibrium with the solvent. The

Table V. Oxygen-18-Tracer Results for Reduction of Chloritopentaamminecobalt(III)[a]

species[b]	[H$^+$], M	atom % ^{18}O		n[c]
		solvent	(NH$_3$)$_5$-CoOH$_2^{3+}$	
Fe^{2+}	0.47	1.460	0.213	0.99
VO^{2+}	0.84	0.832	0.288	0.87
HSO$_3^-$	3 × 10^{-5}	0.398	0.236	0.84
Co^{3+}	1.43	0.578	0.449	0.34

[a] [(NH$_3$)$_5$CoOClO^{2+}]$_0$ = 0.020–0.055 M and is of normal isotopic abundance (taken as 0.204 atom % oxygen-18). [b] In each experiment a stoichiometric excess of the oxidant or reductant was present to ensure complete reaction of the chlorito complex. The species was in isotopic equilibrium with solvent. [c] n ≡ fraction of normal oxygen in the (NH$_3$)$_5$CoOH$_2^{3+}$ product.

experimental results are summarized in Table V. The three reducing agents tested show substantial retention of the cobalt–oxygen bond originally present in the chlorito complex; within experimental error, the retention is complete in the case of iron(II). In contrast, substantial bond breaking accompanies oxidation of the chlorito ligand with cobalt(III).

The source of the oxygen in the sulfate product of the (NH$_3$)$_5$CoOClO^{2+}–HSO$_3^-$ reaction was examined. A stoichiometric excess of the chlorito complex was used to ensure complete oxidation of the hydrogen sulfite ion at pH ca. 4.3. We found 0.66 oxygen atoms of normal isotopic composition per sulfate ion. The stoichiometry of this reaction can be written as (if the small amount of (NH$_3$)$_5$CoOSO$_3^+$ is omitted) in eq 6. Thus, 2.1$_6$ of the chlorite oxygens originally present

$$H_2O + 2HSO_3^- + (NH_3)_5CoOClO^{2+} = 2HSO_4^- + (NH_3)_5CoOH_2^{3+} + Cl^- \quad (6)$$

in the complex are found in the sulfate and aquopentaamminecobalt(III) products. The excess of transfer over the

maximum value of 2.00 indicates that the tracer results are subject to moderate experimental error.

Discussion

The synthetic procedure for chloritopentaamminecobalt(III) appears to require an inner-sphere attack of chlorine dioxide on pentaamminecobalt(II). The substantial yield indicates that this is the predominant reaction, a rather surprising result if one considers other possible reactions such as outer-sphere attack and oxidation of ammonia. The salts are quite stable in the absence of light, and solutions of the complex are sufficiently stable to allow a variety of chemical studies. The chlorite ligand is almost certainly bonded through an oxygen to the cobalt(III) center; the most convincing experimental confirmation is offered by the oxygen-18-tracer result with iron(II) as the reducing agent.

The internal oxidation–reduction decomposition of the chlorito complex is unusual. The rate of this process is within the range observed for the acid hydrolysis of simple pentaamminecobalt(III) complexes.[15] Loss of bound ammonia is usually a much slower process. In the present case it is conceivable that loss of an ammonia ligand precedes electron transfer, but if so, then the redox reaction of the resulting chloritoaquotetraamminecobalt(III) intermediate must be relatively rapid since this species was not detected by ion-exchange chromatography during the decomposition. The rate data in Table I give no evidence for an inverse hydrogen ion-dependent pathway in the decomposition of the chlorito complex. Such a path might be expected if a buildup of an aquo intermediate occurred.[16] It appears more likely that an electron is transferred to the cobalt(III) center from the coordinated chlorite in the pentaammine complex during the rate-determining step.[17]

Internal ligand to metal thermal electron transfer in a simple octahedral cobalt(III) amine complex has been reported for chloro(hydroxylamine)bis(ethylenediamine)cobalt(III)[16a] and aquo(hydroxylamine)bis(ethylenediamine)cobalt(III).[16b] The latter ion becomes increasingly unstable as the pH is raised and decomposes rapidly in neutral solution.[16b] The presence of the aquo ligand may play an important role in the decomposition. We find that reduction of the cobalt(III) center is not quantitative for this complex.[16b]

The relative rates of oxidation of the chlorito complex and chlorous acid with a common oxidant indicate a much lower reactivity for the coordinated chlorite in the cases tested. Electrostatic effects undoubtedly play a role with some of the oxidants but by no means account for all of the substantial rate reduction. The situation is similar to observations on the $Cr \cdot NpO_2^{4+}$, NpO_2^+ and $Cr \cdot PuO_2^{4+}$, PuO_2^+ pairs.[18] It has been suggested that the actinide–oxygen bond is lengthened in the complex, whereas this bond must ultimately be shortened in the NpO_2^{2+} or PuO_2^{2+} oxidation products.[18b] Bond lengthening in the chlorito complex in contrast to bond shortening in the chlorine dioxide product may be an important factor in the reduced reactivity of the complex toward oxidation.
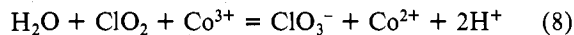
Cobalt(III) is the only oxidant for which quantitative data are available. The chlorito complex and chlorous acid exhibit comparable rate equations, and in both systems $CoOH^{2+}$ is most likely the reactive cobalt(III) species.[19] The distinction between outer- or inner-sphere mechanisms for reactions of $CoOH^{2+}$ is usually not straightforward. However, the kinetic data are indicative of an inner-sphere reaction for the chlorito complex and an outer-sphere pathway for chlorous acid.[19]

The rate constants for the cobalt(III) oxidation of the chlorito complex, chlorous acid, and chlorine dioxide at 25 °C are 9.1, 2400, and 108 s^{-1}, respectively. With excess chlorous acid, the oxidation of the chlorine dioxide product is sufficiently slow to result in essentially no competitive oxidation, as shown in eq 4. In contrast, the kinetic analysis for the

$(NH_3)_5CoOClO^{2+}$–Co^{III} reaction assumed a negligible accumulation of chlorine dioxide. If the stoichiometry associated with the rate-determining step is

$$H_2O + (NH_3)_5CoOClO^{2+} + Co^{3+} = (NH_3)_5CoOH_2^{3+} + ClO_2 + Co^{2+} \quad (7)$$
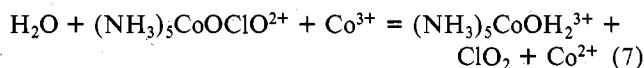
followed by the more rapid reaction

$$H_2O + ClO_2 + Co^{3+} = ClO_3^- + Co^{2+} + 2H^+ \quad (8)$$

a detailed kinetic analysis indicates that at maximum ClO_2 production, the chlorine dioxide concentration in a typical kinetic experiment would be approximately 8% of that of the prevailing chlorito complex.[20] This translates to a 4% contribution to the measured absorbance at that time; the experimental data are not sensitive enough to test this point. Reactions 7 and 8, with the former essentially rate determining, offer an attractive reaction scheme for this system. The oxygen-18-tracer experiment indicates that the cobalt–oxygen bond is substantially, but not completely, broken in reaction 7. This result is qualitatively consistent with the very low (in fact not detected) oxygen-exchange rate with solvent for chlorite[21] and chlorine dioxide.[22] Of course, the oxygen exchange of $(NH_3)_5CoOH_2^{3+}$ with solvent, for example, is also very slow,[23] but bond breaking must occur at one of the two sites in $(NH_3)_5CoOClO^{2+}$ in this reaction since $(NH_3)_5CoOClO_2^{3+}$ is not formed.

We have searched unsuccessfully for an oxidant that will convert the chlorito complex to chloratopentaamminecobalt(III). This nonetheless represents an attractive synthetic route for the presently unknown chlorato complex and efforts along this line are being pursued.

Quantitative data are not available for the reduction rates of the chlorito complex and chlorous acid with a common reagent. Our efforts to obtain such data for iron(II) and iodide ion have been frustrated by the complex kinetic profiles observed with the chlorito complex. If the comparative reduction rates[24] of the $Cr \cdot NpO_2^{4+}$, NpO_2^+ and $Cr \cdot PuO_2^{4+}$, PuO_2^+ pairs are applicable, then reduction of $(NH_3)_5CoOClO^{2+}$ may proceed more rapidly than with $HClO_2$. This feature cannot be profitably examined until rate expressions are determined.

The stoichiometry results for the chromium(II) reduction of coordinated and protonated chlorite are interesting, but the complexity of these reactions precludes a detailed interpretation. The chlorite ligand is apparently completely reduced prior to reduction of the cobalt(III) center. The Cr^{2+}–$HClO_2$ reaction has been proposed to proceed via inner-sphere reactions with the formation of chromium(III)–oxychlorine intermediates.[2] The similar stoichiometry for the chlorito complex suggests the formation of such intermediates also, with the possible difference that the intermediate(s) may be dinuclear and contain cobalt(III) and chromium(III) bridged by an oxychlorine species. This feature could account for the different yields of the hexaaquochromium(III) product with the two oxidants.

The tracer results for the hydrogen sulfite reduction of the chlorito complex indicate that all the chlorite oxygen is transferred to the $(NH_3)_5CoOH_2^{3+}$ (0.84) and SO_4^{2-} (1.32) products. A previous study revealed a defect from complete transfer of $HClO_2$ oxygen to HSO_3^- (1.25 found compared to 2.00 possible) in $HC_2H_3O_2$–$C_2H_3O_2^-$ buffer solutions.[10b] This defect was suggested to occur at the hypochlorite stage due to competition between transfer of oxygen and Cl^+ to sulfite (or hydrogen sulfite). The present results are not inconsistent with this suggestion, the difference being that the presumed hypochlorite intermedite may be coordinated to the cobalt(III), and the oxygen in question remains largely bonded to the cobalt center after reaction.

The synthesis of oxyhalogen complexes of substitution inert metal ions remains a difficult task. Chloratopentaaquochromium(III) and chloritopentaamminecobalt(III) have been prepared, but by admittedly fortuitous pathways in appropriate oxidation–reduction reactions. The iodate salt of iodatopentaamminechromium(III) has been isolated but rapidly forms the aquo complex in solution via breakage of the iodine(V)–oxygen bond.[25] Modifications of the synthesis described herein may allow the preparation of chlorito complexes of metal ions other than pentaamminecobalt(III). The chemistry of these complexes seems sufficiently interesting to merit further experimental effort.

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Chemical Reactivity of Ruthenium Complexes Supported on Y-Type Zeolites

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The detailed chemical reactivity of the [Ru^{II}(NH_3)$_5$N$_2$]$^{2+}$ ion supported on a Y-type zeolite has been probed by infrared and UV–visible spectroscopy. The air oxidation of the supported ruthenium complex produces a wine red species previously thought to be [Ru^{III}(NH_3)$_5$OH]$^{2+}$–Y. However, extensive spectral characterization of this material has revealed that the trimer, "ruthenium red", has been formed on the zeolite support: [(NH_3)$_5$Ru^{III}–O–Ru^{IV}(NH_3)$_4$–O–Ru^{III}(NH_3)$_5$]$^{6+}$–Y. Heat treatment of the [Ru(NH_3)$_5$N$_2$]$^{2+}$–Y species under vacuum produced a highly reactive ruthenium species, designated Ru^{ac}–Y, which chemically reacted with CO, NH_3, and NO. The reaction with NH_3 indicated that a Brønsted acid site interaction in the zeolite was involved. The reaction with CO could be interpreted as interaction with metal ion sites in the zeolite supercages. The absence of a CO–cation specific infrared band indicated that the oxidation state of the ruthenium in Ru^{ac}–Y is probably less than 2, i.e., small clusters such as Ru$_n^0$ or Ru$_n^+$. The reaction of the active species and NO produced a material containing coordinated nitrosyl. No reaction could be observed for molecular nitrogen, H_2S, or SO_2.

Introduction

Noble metals and their complexes supported on a variety of "inert" materials have been used as heterogeneous catalysts in a variety of reactions.[1,2] Ruthenium-containing catalysts have been found to be very versatile, their properties ranging from a pronounced selectivity for the reduction of nitrogen oxides to molecular nitrogen[3–8] to a high specific activity for the carbon monoxide–hydrogen methanation reaction.[9–12] Ruthenium complexes have also been used as homogeneous catalysts in the water gas shift reaction to produce hydrogen.[13] Thus the practical potential of ruthenium catalysts range from the control of nitrogen oxide emissions to the gasification of coal. At the present time, the mechanisms for the ruthenium catalysts are only partially understood, and detailed characterization data for the catalyst materials are still quite limited. The chemistry of ruthenium is unique among the platinum metals in that it exhibits a range of stable oxidation states (from 0 to +8), it forms an almost unlimited number of complex molecules, and it has a pronounced tendency to form multinuclear complexes where ruthenium atoms are bridged by a variety of atomic and molecular ligands. This versatility of chemical reactivity is both an advantage, in terms of the variety of chemical reactions which are possible, and a problem, in that most ruthenium reaction systems are complex, and the maintenance of a particular species or oxidation state can be quite difficult. An example of this behavior as applied to ruthenium catalysts is exhibited in the so-called "dual state" behavior where the catalytic activity of dispersed ruthenium metal is enhanced by exposure to oxygen.[14] The potential utility of supported, heterogeneous ruthenium catalysts and the rich ruthenium chemistry associated with such materials provides a challenge to the experimental chemist to specifically characterize the catalytic materials and

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