Table I. Visible and Ultraviolet Absorption Spectra (200–700 nm) of Some Tetraamineruthenium(III) Complexes in 1 *M* Hydrochloric Acid

Compd	λ_{max}, nm[a]
trans-$[Ru(cyclam)Cl_2]Cl$	357 (2260); 312 (1250)
trans-$[Ru(en)_2Cl_2]ClO_4$	343 (3850); 292 sh (800); 272 (900)
cis-$[Ru(en)_2Cl_2]Cl$[b]	354 (1750); 314 (1420); 269 (900)

[a] Molar absorptivities in cm^{-1} l. mol^{-1} are given in parentheses; sh = shoulder. [b] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

were measured with a Unicam SP8000 spectrophotometer. Infrared spectra were measured in Nujol mulls on a Perkin-Elmer 337 spectrophotometer (400–4000 cm^{-1}) or on a Jesco IR-F far-infrared spectrophotometer (200–700 cm^{-1}). Magnetic susceptibilities of solid samples were measured at room temperature by the standard Gouy method.

Results and Discussion

The reaction of $K_2[RuCl_5(OH_2)]$ and ethylenediamine (or cyclam) is slow at the boiling point of methanol. There was no apparent reaction even after refluxing the mixture for 24 hr and this probably led previous workers[2] to draw the wrong conclusion that this direct method failed. It seems, however, that this method is rather general for the preparation of *trans*-dichlorotetraamineruthenium(III) cations.

The isomeric purity of the complexes was checked in two different ways. These complexes were first absorbed on a Dowex 50W-X8 (20–50 mesh) cation-exchange resin in the acid form and they were then eluted with hydrochloric acid of different strength. In every case only a single band was developed on the column, which could be eluted out. The second method was by comparing the ultraviolet spectra of these complexes (reported later) which had been repeatedly recrystallized. It was noticed that these spectra were not affected after several recrystallizations of the complexes.

The visible and ultraviolet absorption spectra of the two new compounds together with that of *cis*-$[Ru(en)_2Cl_2]Cl$ in dilute hydrochloric acid are collected in Table I. Although these compounds are highly colored, there is no distinct absorption peak in the visible region. The tails of the first ultraviolet bands ca. 350 nm are broadened indicating that some low-energy components are buried under the tails. They cannot, however, be resolved confidently into bands. The observed magnetic moments (μ_{295} = 2.23 and 2.10 BM for the $(en)_2$ and cyclam complexes, respectively) are in full agreement with a spin-paired d^5 electronic configuration of a Ru^{3+} ion.

The assignment of a trans configuration to these two complexes is made on the basis of infrared spectroscopy. It was pointed[6] out that the most consistent variations between cis and trans isomers of diacidobis(ethylenediamine) complexes were in the CH_2 rocking 870–900 cm^{-1} region where splitting occurred for the cis but not for the trans isomer. For the well-characterized *trans*-$[Co(en)_2Cl_2]ClO_4$ a band at 888 cm^{-1} and a shoulder at 881 cm^{-1} were observed.[6] The appearance of a band at 890 cm^{-1} and a shoulder at 881 cm^{-1} in this region for the new $[Ru(en)_2Cl_2]ClO_4$ is, therefore, consistent with a trans configuration. The well-characterized *cis*-$[Ru(en)_2Cl_2]Cl\cdot H_2O$ gave a doublet at 886 and 867 cm^{-1}.[2] The assignment of a trans configuration to this new complex is further supported by the presence of only one Ru–Cl stretching band at 328 cm^{-1} while two bands at 311 and 273 cm^{-1} were observed for the corresponding *cis*-$[Ru(en)_2Cl_2]Cl\cdot H_2O$.[2] For cyclam complexes, it was found true that in the 800–910 cm^{-1} region trans complexes gave two bands near 900 cm^{-1} and one band near 810 cm^{-1} while cis isomers had at least five bands spread rather evenly in this region.[7,8] The appearance of bands at 898, 888, and 805 cm^{-1} in this region of the infrared spectrum of the new $[Ru(cyclam)Cl_2]Cl$ has been taken to indicate a trans configuration. The far-infrared spectrum of $[Ru(cyclam)Cl_2]Cl$, like those of other cyclam complexes,[8] is much more complex than those of the corresponding bis(ethylenediamine) complexes[9] and we wish to postpone the discussion of far-infrared spectra of cyclam complexes to a separate paper.[8]

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Registry No. *trans*-$[Ru(en)_2Cl_2]ClO_4$, 56172-97-5; *trans*-$[Ru(cyclam)Cl_2]Cl$, 56172-98-6; $K_2[RuCl_5(OH_2)]$, 14404-33-2; ethylenediamine, 107-15-3.

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Substitution-Controlled Reduction of *cis*-Diammineaquocobalt(III) Species by Hydrogen Peroxide in Acid Perchlorate Solution

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In a recent paper from our laboratory[1] we pointed out similarities in the mechanisms of base-catalyzed complexation and redox reactions of aquo- and *cis*-diammineaquocobalt(III) species, despite great differences in their substitutional labilities.[1,2] Previous investigations have shown that the reduction of $CoOH^{2+}{}_{aq}$ by a number of species, including Br^- and H_2O_2, is substitution controlled[2] and it was suggested[1] that a similar process is also rate determining in the corresponding reaction of $Co(NH_3)_2OH^{2+}{}_{aq}$ with Br^-.

In this paper we report on the stoichiometry and kinetics of the reduction of *cis*-diammineaquocobalt(III) species by hydrogen peroxide in acid perchlorate solution.

Experimental Section

Reagents. The preparation and standardization of solutions of perchloric acid and *cis*-diamminetetraaquocobalt(III) and sodium perchlorate were as described previously.[1] Hydrogen peroxide solutions (prepared by dilution of 30% w/v stabilizer-free hydrogen peroxide) were standardized either by titration with cerium(IV) using ferroin as indicator or by estimation as the titanium(IV) complex (ϵ_{414} 731).[3] Thiourea was recrystallized from 20% v/v aqueous ethanol. All other chemicals were of reagent grade and doubly distilled water was used throughout.

Stoichiometry Measurements. The stoichiometry of the reaction was determined by spectrophotometric measurements of excess hydrogen peroxide (as the titanium(IV) complex[3]) remaining after reaction with known concentrations of the cobalt(III) oxidant. The reactant conditions used were $[H_2O_2] = (1.70–9.59) \times 10^{-4}$ *M*, $[Co^{III}] = (0.71–1.18) \times 10^{-3}$ *M*, and $[H^+] = 0.05–0.1$ *M* at 48°.

Kinetic Measurements. The disappearence of the cobalt(III)

Table I. Kinetic Data for Reaction of *cis*-Diammineaquocobalt(III) Species with Hydrogen Peroxide in Acid Perchlorate Media[a]

Temp, °C	$[H^+]$	$[H_2O_2]$	$10^4 k_{obsd}$[b]	$10^4 k_{calcd}$[b,c]
28.5	0.046	0.059	1.3	1.0
		0.196	3.4	3.3
		0.393	5.8	6.7
		0.589	8.3	10
	0.138	0.098	0.62	0.56
		0.196	1.1	1.1
		0.393	2.0	2.2
		0.982	5.2	5.6
	0.254	0.196	0.58	0.60
		0.589	1.7	1.8
		0.982	2.8	3.0
		1.375	3.5	4.2
	0.508	0.196	0.31	0.30
		0.589	0.84	0.91
		0.982	1.3	1.5
		1.96	2.7	3.0
38.5	0.092	0.099	4.8	3.9
		0.197	8.8	7.8
		0.395	17	16
	0.138	0.059	1.5	1.6
		0.127	3.7	3.4
		0.196	5.3	5.2
		0.393	11	11
	0.254	0.198	3.3	2.9
		0.398	5.8	5.8
		0.592	9.1	8.6
		0.790	12	12
	0.508	0.099	0.86	0.71
		0.198	1.86	1.4
		0.395	2.9	2.9
	0.762	0.395	1.9	1.9
		0.592	2.9	2.9
		0.790	3.8	3.8
		0.987	4.4	4.8
48.5	0.216	0.147	11	11
		0.245	19	18
	0.423	0.147	5.3	5.4
		0.245	8.4	9.0
		0.344	12	13
		0.491	19	19
	0.846	0.196	3.8	3.6
		0.589	9.5	11
		0.982	15	18

[a] All concentrations are *M*. [b] Units are sec^{-1}. [c] Calculated from a nonlinear least-squares fit of data (see text).

complex in the presence of excess hydrogen peroxide was monitored over the wavelength range 370–537 nm in a Beckman DK1 ratio-recording spectrophotometer equipped with a temperature-controlled cell housing. Most of the measurements were made at 537 nm where the absorbance of $Co(NH_3)_2{}^{3+}{}_{aq}$ is a maximum in the visible region.[1] The concentration ranges used were $[Co^{III}] = (1\text{–}3) \times 10^{-3}$ *M*, $[Co^{II}] = (8\text{–}160) \times 10^{-4}$ *M*, $[H_2O_2] = 0.059\text{–}1.96$ *M*, and $[H^+] = 0.046\text{–}0.98$ *M* at ionic strength 2.0 *M* ($NaClO_4$, $HClO_4$). Reactions were conducted in the presence of a sufficient excess of H_2O_2 to ensure first-order conditions. Studies were made over the temperature range 28.5–48.5° with a maximum uncertainty of ±0.2° throughout the range. The solutions to be mixed were thermostated at the desired temperature and transferred to the thermostated cell within 60 sec of mixing. Absorbance changes were followed for at least 5 half-lives and final absorbances were obtained for each run. Duplicate rate measurements under fixed experimental conditions had a maximum relative error of ±8%.

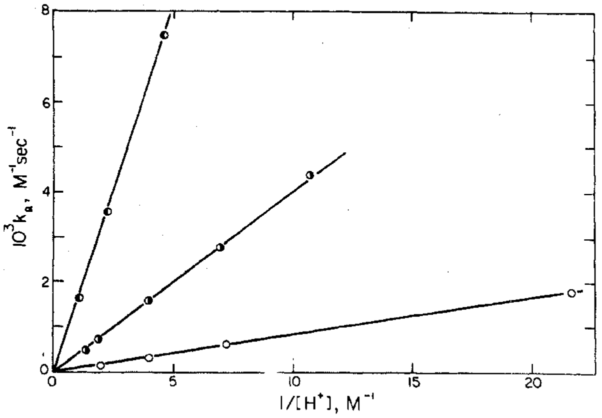

Figure 1. Plot of k_R vs. $1/[H^+]$ for reactions of *cis*-$Co(NH_3)_2{}^{3+}{}_{aq}$ with hydrogen peroxide at the following temperatures: ○, 28.5°; ⦶, 38.5°; ⊙, 48.5°. The ionic strength is 2.0 *M* throughout.

Table II. Empirical Rate Parameters for Reactions of *cis*-Diammineaquocobalt(III) in $NaClO_4$-$HClO_4$ Media

Reactant	Temp, °C	$10^4 A$[a]	$\Delta H^\ddagger{}_A$[b]	$\Delta S^\ddagger{}_A$[c]	Ref
Cl^-[d]	28.0	1.5 ± 0.03	28 ± 1	22 ± 4	1
Br^-[e]	28.0	1.7 ± 0.2	29 ± 1	21 ± 4	1
H_2O_2[e,f]	28.5	0.7 ± 0.1			g
	38.5	3.9 ± 0.2	28 ± 1	16 ± 2	g
	48.5	15.9 ± 0.5			g

[a] Obtained from $-d[Co^{III}]/dt$ or $d[product]/dt = A[X][Co^{III}]/[H^+]$, where $X = Cl^-$, Br^-, or H_2O_2. Units are sec^{-1}. Errors quoted are one standard deviation. [b] Units are kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1}. [d] Kinetic parameters refer to complex formation. [e] Kinetic parameters refer to oxidation. [f] The value for *A* in the reaction with H_2O_2 has been divided by 2 to conform to the unit stoichiometry of the Cl^- and Br^- reactions.[1,4] [g] This work.

Results and Discussion

The stoichiometric measurements established (within an experimental uncertainty of 5%) that reaction 1 occurred over

$$2Co(NH_3)_2{}^{3+}{}_{aq} + 2H^+{}_{aq} + H_2O_{2\,aq} \rightarrow 2Co^{II}{}_{aq} + 4NH_4{}^+{}_{aq} + O_2 \quad (1)$$

the experimental concentration ranges. Spectral scans of the reacting solutions gave no evidence for intermediate peroxo complex formation. Plots of $\ln (A_t - A_\infty)$ vs. time, where A_t and A_∞ are measured absorbances after time *t* and after many half-lives, respectively, were linear for at least 75% of reaction, establishing a first-order dependence of the rate on [Co(III)]. Pseudo-first-order rate constants k_{obsd} obtained over the experimental concentration and temperature ranges are collected in Table I. At fixed acidity, temperature, and ionic strength, k_{obsd} was found to be independent of initial $[Co^{III}]$, $[Co^{II}]$, monitoring wavelength, and the presence of oxygen. Plots of k_{obsd} vs. $[H_2O_2]$ at fixed acidity, ionic strength, and temperature were accurately linear, establishing a rate law of the form

$$-d[Co^{III}]/dt = k_R [Co^{III}][H_2O_2] \quad (2)$$

where k_R is an experimental second-order rate constant for reduction. This parameter had values of $(1.05, 0.86, 0.82, \text{and } 0.65) \times 10^{-3}$ M^{-1} sec^{-1} at ionic strengths of 0.50, 0.90, 1.50, and 3.00 *M*, respectively, at $[H^+] = 0.508$ *M* and at 38.5°.

Plots of k_R vs. $1/[H^+]$ at the three experimental temperatures and ionic strength 2.0 *M* were found to be linear (Figure 1), with no intercept at $1/[H^+] = 0$ within experimental error. This establishes that the empirical rate law is given by eq 2, with $k_R = A/[H^+]$, where *A* is an empirical parameter with units of sec^{-1}. Estimates for *A* at 28.5, 38.5, and 48.5° and the corresponding activation parameters obtained using a nonlinear least-squares[1] fit of the kinetic data are collected in Table II, together with analogous data for reaction with Cl^- and Br^-.[1]

The empirical rate law and the activation parameters for *A* in this system are very similar to those for oxidation of Br^- and for complex formation with Cl^- (Table II), suggesting the inner-sphere mechanism of eq 3–6 for H_2O_2 oxidation.[1,2]

$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq}} \overset{\text{fast}}{\rightleftharpoons} \mathrm{Co(NH_3)_2OH^{2+}{}_{aq} + H^+{}_{aq}} \quad K_\mathrm{h} \tag{3}$$

$$\mathrm{Co(NH_3)_2OH^{2+}{}_{aq} + H_2O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}} \tag{4}$$

$$\mathrm{Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}} \xrightarrow[\mathrm{H^+}]{k_2} \mathrm{Co^{II}{}_{aq} + H_2O_2{\cdot}^+ + 2NH_4{}^+{}_{aq}} \tag{5}$$

$$\mathrm{Co^{III}{}_{aq} + H_2O_2{\cdot}^+} \xrightarrow{\text{fast}} \mathrm{Co^{II}{}_{aq} + 2H^+{}_{aq} + O_2} \tag{6}$$

Reactions 4 and 5 are rate-determining and $\mathrm{H_2O_2{\cdot}^+}$ is a radical species.[4] If it is assumed that $K_\mathrm{h}/[\mathrm{H^+}] \lesssim 0.1$ at the lowest experimental acidity and if the inner-sphere peroxo complex $\mathrm{Co(NH_3)_2(OH)H_2O_2{}^{2+}{}_{aq}}$[5] and $\mathrm{H_2O_2{\cdot}^+}$ are both in a steady state, then it follows that $K_\mathrm{h} \lesssim 5 \times 10^{-3}$ *M* and that

$$k_\mathrm{obsd} = \frac{2k_1k_2K_\mathrm{h}/[\mathrm{H^+}]}{k_{-1} + k_2}[\mathrm{H_2O_2}] \tag{7}$$

A substitution-controlled mechanism corresponds to the situation where $k_2 >> k_{-1}$ in eq 7, in which case $A = 2k_1K_\mathrm{h}$ in eq 2, with step 4 forward as the rate-determining step.[1] Substitution of the above upper limit for K_h into the expression for A leads to $k_1 \gtrsim 7 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$ at 28.5° and ionic strength 2.0 *M*. Although an acid-independent term cannot be detected, within experimental error, in the empirical rate law for reduction of the aquodiammine by $\mathrm{H_2O_2}$, an upper limit of $k_0 \lesssim 7 \times 10^{-7}\ M^{-1}\ \mathrm{sec}^{-1}$ at 28.5° is obtained in step 8 if it is assumed that this step makes less than a 10% contribution to the overall rate of reduction at the highest experimental acidity. Comparison of these estimates for k_0 and k_1 indicates

$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq} + H_2O_2} \xrightarrow[\mathrm{H^+}]{k_0} \mathrm{Co^{II} + H_2O_2{\cdot}^+ + 2NH_4{}^+{}_{aq}} \tag{8}$$

that the presence of inner-sphere $\mathrm{OH^-}$ in $\mathrm{Co(NH_3)_2{}^{3+}{}_{aq}}$ leads to a ca. 10^4-fold increase in the lability of the remaining water molecules. Similar effects on substitutional lability have been noted in reactions at other aquocobalt(III) centers.[1,2]

Reaction 9 is kinetically indistinguishable from step 4.

$$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq} + HO_2{}^-{}_{aq}} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \mathrm{Co(NH_3)_2HO_2{}^-{}_{aq}} \tag{9}$$

However, the acid dissociation constant of $\mathrm{H_2O_2}$ is $K_\mathrm{a} \approx 2 \times 10^{-12}$ *M* at ionic strength 2.0 *M*,[6] and since kinetic indistinguishability leads to $k_1K_\mathrm{h} = k_1'K_\mathrm{a}$,[4] then $k_1' \approx 4 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ at 28.5° if reaction 9 is rate determining. Although not entirely ruled out, this alternative rate-determining process seems very unlikely when compared to the data for other reactions of hydrogen peroxide[7] and with the results of Table II.

The narrow range of *A* values and activation parameters for reactions of *cis*-$\mathrm{Co(NH_3)_2OH^{2+}{}_{aq}}$ with $\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{H_2O_2}$ strongly suggests that all these processes are controlled by substitution at the $\mathrm{Co^{III}}$ center. The acid-independent term observed in the empirical rate law for $\mathrm{Br^-}$ oxidation[1] is nonexistent, within experimental error, for reaction with $\mathrm{H_2O_2}$ and $\mathrm{Cl^-}$ and the origin of this term remains unclear. It is worth noting that wide and uncertain variations in acid-independent kinetic terms are also a feature of inner-sphere aquocobalt(III) reactions.[2]

Extension of this work to reductants such as $\mathrm{SCN^-}$ and thiourea, which have been found to undergo substitution-controlled oxidation by $\mathrm{CoOH^{2+}{}_{aq}}$,[2] was found to be impractical because the slow rates of cobalt(III) oxidation of these substrates are similar to those for substrate reaction with the acid perchlorate medium at $[\mathrm{H^+}] \gtrsim 0.1$ *M*: kinetic data obtained spectrophotometrically at $[\mathrm{H^+}] \gtrsim 0.1$ *M* were too irreproducible to establish the acid dependence of the respective reductions with any certainty with both $\mathrm{SCN^-}$ and thiourea as reductants, although a kinetic inverse acid dependence is indicated by initial rate data. The data obtained with $[\mathrm{H^+}] = 0.10$ *M* at ionic strength 2 *M* and 25.0° in the reaction with $\mathrm{SCN^-}$ (k_obsd = 1.3, 2.8, 3.4$_5$, and 5.1 × 10^{-3} sec^{-1} at $[\mathrm{SCN^-}]$ = 0.10, 0.20, 0.30, and 0.40 *M*, respectively) were sufficiently reproducible to allow comparison with the corresponding data for $\mathrm{Br^-}$, $\mathrm{Cl^-}$, and $\mathrm{H_2O_2}$ oxidations by $\mathrm{Co^{III}(NH_3)_{2aq}}$ (ref 1 and this work) under similar experimental conditions. This comparison suggests a substitution-controlled mechanism of oxidation of $\mathrm{SCN^-}$ by $\mathrm{Co^{III}(NH_3)_{2aq}}$ species.

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Registry No. *cis*-$\mathrm{Co(NH_3)_2{}^{3+}{}_{aq}}$, 51262-50-1; $\mathrm{H_2O_2}$, 7722-84-1.

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Correspondence

Nitrogen- and Oxygen-Bonded Nitrosyl. Metal Complexes of the Nitroprusside Ion

AIC50089B

Sir:

The nitrogen atom in (carbon-bound) metal cyanide complexes retains significant Lewis basicity, and as a consequence the cyanide ion is frequently found in a linear-bridged configuration.[1] Similarly, within the past few years the Lewis basicity of oxygen in metal carbonyl complexes has been amply demonstrated.[2] Surprisingly, a bridged configuration for the isoelectronic nitrosyl ligand has never been confirmed, and there are to our knowledge only two claims for such species. Solution infrared studies supported a bridging interaction between π-$\mathrm{CpCr(NO)_2Cl}$ and organolanthanides, although no solid species could be obtained,[3] and recently a solid compound

Table I. Infrared Frequencies for $\mathrm{MFe(CN)_5NO}$[a]

M	ν_CN, cm^{-1}	ν_NO, cm^{-1}
$\mathrm{Na^+}$	[2157][b]	1942
$\mathrm{Mn^{2+}}$	2172	1949
$\mathrm{Fe^{2+}}$	2179	1945.5
$\mathrm{Co^{2+}}$	2185	1947
$\mathrm{Ni^{2+}}$	2192	1951
$\mathrm{Cu^{2+}}$ form I	2204, 2193 sh	1952
form II	2199	1961
$\mathrm{Zn^{2+}}$	2184	1950

[a] Spectra obtained using a Beckman IR-20A spectrometer, with frequency calibration in the cyanide and nitrosyl stretching regions effected using the 2349 cm^{-1} absorption of $\mathrm{CO_2}$ and the 1601.8-cm^{-1} absorption of a polystyrene film. Although for consistency the data reported are specifically for the samples in KBr pellets, the spectra in Nujol mulls are not significantly different. [b] See text for the significance of this value.