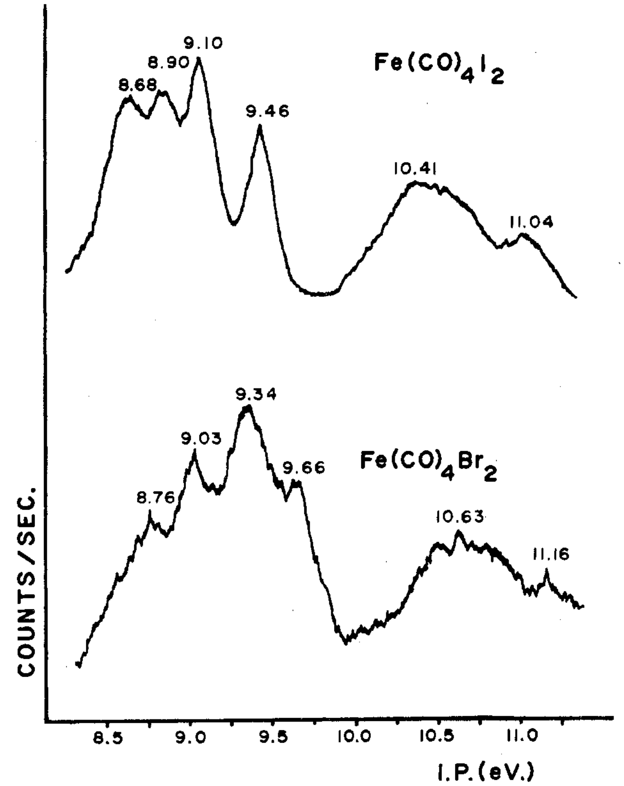

Figure 1. Ultraviolet photoelectron spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$.

Results and Discussion

Figure 1 shows the photoelectron spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ in the range of ca. 8–11 eV. The quality of the spectrum of the bromo derivative is somewhat less than that for the iodo analog because of the lower volatility of the former. No other bands attributable to these species occur below 14 eV; these higher energy and more poorly resolved bands are assigned as ionizations from Fe–C σ levels and molecular orbitals primarily localized on the CO ligands. The first broad band and most intense band at ca. 8.5–9.5 eV in both complexes are split into four components which are assigned as ionizations from the four X_π levels (a_1, a_2, b_1, and b_2 in C_{2v}). These bands are very similar in appearance to those in the methylene halides, CH_2Br_2 and CH_2I_2,[10] with respect to band shapes and relative intensities; the broadening in the iron carbonyl derivatives relative to the methylene halide spectra is attributed to the greater number of molecular vibrations associated with the transition metal complexes. These bands are at approximately the same energy as are those associated with the X_π levels in the pentacarbonyl halides of manganese and rhenium.[7] They are also similar in appearance to the low-energy bands in the dihalosilanes and -germanes.[11]

The next two highest energy bands are assigned to an overlapping combination of the metal d orbitals (d_{xy}, d_{xz}, and d_{yz} which have symmetries a_2, b_1, and b_2, respectively) and X_σ orbitals (a_1 and b_2 for halogens in the yz plane). A band at ca. 10 eV observed in the pentacarbonyl halides of manganese and rhenium is absent in these iron derivatives; this is further evidence for its assignment as the metal b_2 level[7] and not the X_σ level.[3] Unfortunately, it is not presently possible to make more definitive assignments. Still, there is no question that the ionizations arising from the d orbitals are at higher energy than those in the $Mn(CO)_5X$ complexes, which is what one would predict on the basis of increased metal charge and increased atomic number.

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Registry No. $Fe(CO)_4Br_2$, 18475-84-8; $Fe(CO)_4I_2$, 14911-55-8.

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Contribution from the Department of Chemistry,
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Convenient Synthesis of *trans*-Dichlorotetraamineruthenium(III) Cations

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Considerable effort has recently been devoted toward the discovery of synthetic methods for ruthenium(III) amine complexes.[1-5] The recently reported methods for diacidobis(ethylenediamine)ruthenium(III) complexes have unequivocally yielded cis compounds.[1-4] Our desire to study the photochemical and thermal substitution kinetics of *trans*-tetraamineruthenium(III) complexes has prompted us to examine a new synthetic route which we wish to report.

Although a previous attempt to prepare bis(ethylenediamine)ruthenium(III) complexes by the direct reaction of potassium aquopentachlororuthenate(III) with ethylenediamine was reported unsuccessful,[2] we repeated the method under various reaction conditions and have been successful in preparing *trans*-$[Ru(en)_2Cl_2]^+$. *trans*-$[Ru(cyclam)Cl_2]^+$ was similarly prepared by the direct reaction of $K_2[RuCl_5OH_2]$ with 1,4,8,11-tetraazacyclotetradecane (cyclam).

Experimental Section

***trans*-Dichlorobis(ethylenediamine)ruthenium(III) perchlorate (*trans*-$[Ru(en)_2Cl_2]ClO_4$)** was prepared by refluxing a mixture of $K_2[RuCl_5(OH_2)]$ (Johnson Mathey and Co., 3.8 g, 0.01 mol) and ethylenediamine (1.3 g, 0.02 mol) in methanol (300 ml) for 4 days. The reddish brown solution was then evaporated down to ca. 100 ml in a rotary evaporator and was cooled. The bright red solid which separated out was collected and washed with ethanol and ether. The perchlorate salt was prepared by dropwise addition of perchloric acid to a saturated solution of the solid, which was recrystallized from hot water. The pale orange crystals were collected and washed with ethanol and ether. They were dried under vacuum at 90°; yield 2.94 g (75%). Anal. Calcd for $C_4H_{16}N_4O_4Cl_3Ru$: C, 12.3; H, 4.0; N, 14.3; Cl, 27.3. Found: C, 12.5; H, 4.0; N, 14.6; Cl, 27.5.

***trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) chloride (*trans*-$[Ru(cyclam)Cl_2]Cl$)** was similarly prepared by refluxing a mixture of $K_2[RuCl_5(OH_2)]$ (3.8 g, 0.01 mol) and cyclam (2 g, 0.01 mol) in methanol (300 ml) for 3 days. The compound was recrystallized from 0.1 *M* hydrochloric acid (50 ml). The brown crystals were collected, washed with acetone and ether, and dried under vacuum at 100°; yield 3.0 g (75%). Anal. Calcd for $C_{10}H_{24}N_4Cl_3Ru$: C, 29.5; H, 5.9; N, 13.7; Cl, 26.1. Found: C, 29.8; H, 5.9; N, 13.7; Cl, 26.0.

Physical Measurements. Visible and ultraviolet absorption spectra

Table I. Visible and Ultraviolet Absorption Spectra (200–700 nm) of Some Tetraammineruthenium(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)$_2$Cl$_2$]ClO$_4$	343 (3850); 292 sh (800); 272 (900)
cis-[Ru(en)$_2$Cl$_2$]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*-dichlorotetraammineruthenium(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)$_2$Cl$_2$]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)$_2$Cl$_2$]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)$_2$Cl$_2$]ClO$_4$ is, therefore, consistent with a trans configuration. The well-characterized *cis*-[Ru(en)$_2$Cl$_2$]Cl·H$_2$O 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)$_2$Cl$_2$]Cl·H$_2$O.[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)$_2$Cl$_2$]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$_2$O$_2$, is substitution controlled[2] and it was suggested[1] that a similar process is also rate determining in the corresponding reaction of Co(NH$_3$)$_2$OH$^{2+}{}_{aq}$ 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$_2$O$_2$] = (1.70–9.59) × 10^{-4} *M*, [Co^{III}] = (0.71–1.18) × 10^{-3} *M*, and [H$^+$] = 0.05–0.1 *M* at 48°.

Kinetic Measurements. The disappearence of the cobalt(III)