

deactivation of the proposed intermediates.

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results obtained by other spectral techniques.

**Registry No.** *trans*- $\text{Ir}(\text{en})_2\text{Cl}_2^+$ , 25952-90-3; *trans*- $\text{Ir}(\text{en})_2\text{Br}_2^+$ , 25956-87-0; *trans*- $\text{Ir}(\text{en})_2\text{I}_2^+$ , 25952-91-4; *cis*- $\text{Ir}(\text{en})_2\text{Cl}_2^+$ , 31312-35-3; *cis*- $\text{Ir}(\text{en})_2\text{Br}_2^+$ , 45838-51-5; *cis*- $\text{Ir}(\text{en})_2\text{I}_2^+$ , 45838-65-1; *trans*- $\text{Ir}(\text{en})_2(\text{H}_2\text{O})\text{Cl}_2^+$ , 45838-63-9; *trans*- $\text{Ir}(\text{en})_2(\text{H}_2\text{O})\text{Br}_2^+$ , 73985-94-1; *trans*- $\text{Ir}(\text{en})_2(\text{H}_2\text{O})\text{I}_2^+$ , 73985-95-2; *cis*- $\text{Ir}(\text{en})_2(\text{H}_2\text{O})\text{Cl}_2^+$ , 74034-28-9; *cis*- $\text{Ir}(\text{en})_2(\text{H}_2\text{O})\text{Br}_2^+$ , 74034-29-0; *trans*- $\text{Ir}(\text{en})_2(\text{OH})\text{Cl}^+$ , 73985-96-3; *cis*- $\text{Ir}(\text{en})_2(\text{OH})\text{Cl}^+$ , 74034-30-3; *cis*- $\text{Ir}(\text{en})_2(\text{OH})_2^+$ , 73985-97-4.

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## Photolysis of *cis*- and *trans*-Dichlorobis(ethylenediamine)ruthenium(III) and *cis*- and *trans*-Aquochlorobis(ethylenediamine)ruthenium(III) Cations in Acidic Aqueous Solution: Photoinduced Isomerizations at Ruthenium(III) Centers

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The ligand field photolysis of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  ions causes chloride loss, aquation, and geometric isomerization, yielding mixtures of *cis*- and *trans*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ . Photolysis of *cis*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  generates 84% *cis*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  and 16% *trans*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  with  $\phi_{\text{total}} = 0.0030$ . Photolysis of *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  yields a 66/34 mixture of the *cis*/*trans* aquochloro ions with  $\phi_{\text{total}} = 0.0050$ . The *cis*- and *trans*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  ions are photoconverted to each other with similar quantum yields ( $\phi_{\text{cis}} = 0.038$ ,  $\phi_{\text{trans}} = 0.042$ ). An inefficient photoinduced reaction of *cis*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  generates a yellow species, presumably a hydroxyl-bridged Ru(III) dimer. The implications of these results, in terms of the available ligand field photolysis models, are discussed.

### Introduction

Early models<sup>1</sup> of the photochemical behavior of transition-metal complexes concentrated on the identification of the photolabilized ligand, without regard for the stereochemistry of the photoproduct. Only recently has any distortion other than the radial extension of the metal-ligand bond been considered in a theoretical model of ligand field (LF) photochemistry. Models for the stereochemical rearrangements of  $d^3$  and  $d^6$  complexes have now been presented by Vanquickenborne and Ceulemans<sup>2</sup> as part of their theoretical treatment of LF photochemistry. In this work, the chemical processes resulting from LF excitation are separated into three distinct steps: (1) ligand labilization, (2) intramolecular distortion of the remaining five-coordinate species, and (3) water attack of that five-coordinate species. The possibility that these steps may be concerted to some extent is recognized but is not incorporated into the model's calculations.

A controversial feature of both the  $d^3$  and  $d^6$  models is the requirement of a thermally equilibrated five-coordinate intermediate(s) which exists long enough to attain its stablest geometry (or a distribution between two stable forms). A consequence of this model is that, for a given combination of metal and five ligands, the same photoproduct (or mixture of photoproducts) must result. There is not yet sufficient stereochemical data to test this hypothesis, but most of the available studies have been consistent with the concept of a thermally equilibrated intermediate. For example, both *cis*-<sup>3</sup> and *trans*-<sup>4</sup>  $[\text{Rh}(\text{en})_2\text{Cl}]^+$  lose chloride upon ligand field photolysis, so the five-coordinate intermediate in both cases would be  $[\text{Rh}(\text{en})_2\text{Cl}]^{2+}$ . Consistent with the equilibration

of this species, *trans*- $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  is the only photoproduct observed upon photolysis of either of the dichloro ions. The analogous Co(III) complexes<sup>5,6</sup> generate an approximately 30/70 mixture of *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$  upon ligand field photolysis. Unfortunately, the number of such examples, where two different complexes of the same metal leave the same five ligands upon photoinduced ligand loss, is limited; stereochemical support for a thermally equilibrated five-coordinate intermediate in ligand field photochemistry is not yet established.

As part of our general interest in the stereochemical consequences of the ligand field photochemistry of transition-metal complexes, we have initiated a study of the photochemistry of Ru(III) complexes. Only a few examples of ruthenium(III)-amine complex photochemistry have been reported. Irradiation of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  and  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ , between 254 (CTTM) and 321 nm (LF), causes ligand loss and aquation (or anation in the presence of other nucleophiles).<sup>7</sup> Stereochemical information was not available from this study, but the photolysis of aqueous solutions of *cis*- $[\text{Ru}(\text{NH}_3)_4\text{X}_2]^+$  ( $\text{X} = \text{Br}, \text{I}$ ) was reported<sup>8</sup> to yield *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}]^{2+}$ , although the limits of possible *trans* photoproduct formation were not reported.

Thus, it has not been established whether stereochemical rearrangements, so common in  $d^3$  and  $d^6$  photochemistry, occur about the  $d^5$  Ru(III) center. In addition, it is not known whether the concept of a thermally equilibrated five-coordinate intermediate, generated upon photoinduced ligand loss, is valid. Toward that end we have studied the ligand field photolysis of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{ClX}]^{n+}$  ( $\text{X} = \text{Cl}, \text{H}_2\text{O}$ ). The thermal behavior of these ions in aqueous solution has been characterized,<sup>9,10</sup> and the thermal reactions (aquation and anation)

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are all stereoretentive. Photochemical study of these ions would provide information on the stereochemical consequence of the photolysis of these  $d^5$  ions, as well as being a test for the existence of a thermally equilibrated five-coordinate intermediate in the photochemical reaction. A preliminary study showed that both dichloro ions lose chloride ion upon photolysis, presumably generating  $\{[\text{Ru}(\text{en})_2\text{Cl}]^{2+}\}$ . If equilibration of such a species occurs, photolysis of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  should generate the same photoproducts (or photoproduct mixture); formation of different photoproducts would imply that the concept of a distinct  $\{[\text{Ru}(\text{en})_2\text{Cl}]^{2+}\}$  ion is not valid.

### Experimental Section

**Preparation of Compounds.** *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]\text{Cl}$ . The chloride salts of the dichloro ions were prepared by the methods of Broomhead and Kane-Maguire<sup>10,11</sup> and were recrystallized from HCl (1 M) before use. Visible absorption spectra and molar absorptivity coefficients agreed ( $\pm 3\%$ ) with published values, and elemental analyses (C, H, N) were within 0.3% of the calculated values.

*cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$ . An aqueous solution of the  $[\text{Ru}(\text{en})_2\text{Cl}_2]\text{Cl}$  salt of the appropriate geometry was heated—the *cis* ion was held at 50 °C for 40 min, while the *trans* was heated to 60 °C for 60 min. After being cooled to room temperature, the solution was placed on a Sephadex SP-C-25 cation-exchange column in the  $\text{H}^+$  form. The unreacted dichloro ion was eluted with 0.02 N  $\text{CH}_3\text{SO}_3\text{H}$ , and the desired aquochloro ion was eluted with 0.2 N  $\text{CH}_3\text{SO}_3\text{H}$ . These solutions were used without further treatment and, due to thermal reactions, were prepared just before each use.

**Photolyses.** Photolyses were performed with a 350- and 200-W high-pressure Hg short-arc lamp (Illumination Industries, Inc.). Quantum yields were determined by using an interference filter with a transmittance maximum at 345 nm (for *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ ) and 334 nm (*cis*- and *trans*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ ). Both filters have fwhh of 20 nm and correspond to the maximum of the lowest energy ligand field bands. Incident light intensities were measured with ferrioxalate actinometry and averaged  $5.3 \times 10^{-10}$  (200 W) and  $2.5 \times 10^{-9}$  einstein/s (350 W) over a rectangular ( $0.8 \times 2.0$  cm) cell face. Samples were held at 2–3 °C (to reduce thermal reactivity) in 10-cm (28-mL) cells. The solvent was 0.2 N methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ), except for the pH studies when 0.001 N  $\text{CH}_3\text{SO}_3\text{H}$  was used to allow more sensitive  $\Delta\text{pH}$  measurements. No differences in photoinduced spectral changes were observed in these two acidic solutions.

**Instrumentation.** Electronic spectra were recorded on a Beckman Acta M IV spectrophotometer in the absorbance mode. A Radiometer (Copenhagen) PHM 64 pH meter with a GK2320C combined electrode was used for pH measurements, and a F1012C1 Selectrode (Radiometer) and K701 calomel reference were used for chloride determination. A Haake FK constant-temperature bath was used to cool samples.

**Product Analysis.** Aqueous solutions containing mixtures of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  were analyzed after chloride anation to the dichloro ion. Concentrated HCl (1.0 mL, 12 N) was added to an aliquot (2.5 mL) of the aquochloro solution and allowed to sit for at least 40 min at room temperature. The half-life of this anation is about 4.5 min<sup>12</sup> under these conditions, so 40 min represents about 9 half-lives. The spectra of independently prepared solutions of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  (at identical concentrations) showed that these two ions had isobestic points at 360.8 and 325.9 nm, so the total concentration of  $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ , independent of isomeric composition, could be determined by absorbance measurements at these wavelengths.

For a two-component system (*cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ )

$$C_{\text{total}} = C_{\text{cis}} + C_{\text{trans}} \quad (1)$$

$$A_{\text{total}} = l(\epsilon_{\text{cis}}C_{\text{cis}} + \epsilon_{\text{trans}}C_{\text{trans}}) \quad (2)$$

where  $l$  is the cell length,  $C_x$  represents the concentration of  $x$ ,  $\epsilon_x$  is the molar absorptivity coefficient of species  $x$  at the wavelength studied, and  $A_{\text{total}}$  is the total absorbance at that wavelength. Substitution

of (1) into (2) gives (3) from which concentration of *cis*- $[\text{Ru}$

$$C_{\text{cis}} = \frac{A_{\text{total}} - l(\epsilon_{\text{trans}})(C_{\text{total}})}{l(\epsilon_{\text{cis}} - \epsilon_{\text{trans}})} \quad (3)$$

$(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  in a given solution could be calculated; the concentration of *trans* ion was then determined from (1). These analyses were done at 372, 342, and 312 nm.

In addition to analyzing for the *cis*-*trans* isomeric composition of a  $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  ion solution, it was necessary to determine the total concentration of  $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  in the presence of large excesses of *cis*- (or *trans*-)  $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ . The two aquochloro ions have isobestics at 361.5, 314.0, and 291.3 nm, and at these wavelengths

$$C_{\text{H}_2\text{OCl}} = \frac{A_{\text{final}} - A_{\text{initial}}}{\epsilon_{\text{H}_2\text{OCl}} - \epsilon_{\text{Cl}_2}}$$

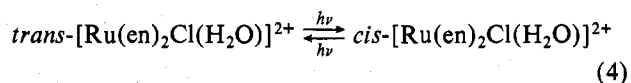
where  $A_{\text{initial}}$  and  $A_{\text{final}}$  represent the absorbance (at an isobestic wavelength) of the solution initially and after a photolysis period and  $\epsilon_{\text{H}_2\text{OCl}}$  and  $\epsilon_{\text{Cl}_2}$  represent the molar absorptivity coefficients of the aquochloro and dichloro ions, respectively, at that same wavelength.

### Results

**Thermal Reactions.** Both *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  have been reported<sup>9,10</sup> to undergo chloride aquation with retention of geometric configuration in acidic aqueous solution. The resulting *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  ions retain their isomeric identity in room-temperature aqueous solution, as chloride aquation of *cis*- or *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  yields the respective *cis*- or *trans*-diaquo ion. In addition, chloride anation of the aquochloro ions stereoretentively generates the appropriate dichloro ion. In short, there is no evidence for thermally induced *cis*-*trans* isomerization between any of these  $[\text{Ru}(\text{en})_2\text{ClX}]^{n+}$  ( $X = \text{Cl}, \text{H}_2\text{O}$ ) species.

For the photochemical studies, it was necessary to have the complete electronic spectra of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{ClX}]^{n+}$ , so some of the spectral data of Broomhead et al. had to be rechecked with our spectrophotometer. Allowing for minor instrumental differences, we found our data to be consistent with literature values,<sup>10,11</sup> except for the spectrum reported for *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$ . Rather than the one peak (310 nm) reported,<sup>10</sup> we observed two peaks (334 nm and 280 nm). Our preparation (Experimental Section) did not involve the  $\text{Ag}^+$ -induced aquation of *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  but rather the spontaneous aquation of the dichloro ion, followed by cation-exchange separation of the divalent cation product. Confirmation of the *trans* geometry was accomplished by the complete regeneration of *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  upon addition of hydrochloric acid.

**Photochemistry.** *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$ . Excitation of the low-energy ligand field band of either *cis*- or *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  causes no change in the concentration of free chloride ion in solution nor does it lead to pH increases which would imply amine labilization. Photoinduced spectral changes are apparent, however (Figure 1). The spectral changes and analytical data are consistent with the photoinduced isomerizations between the *cis*- and *trans*-aquochloro ions (eq 4).

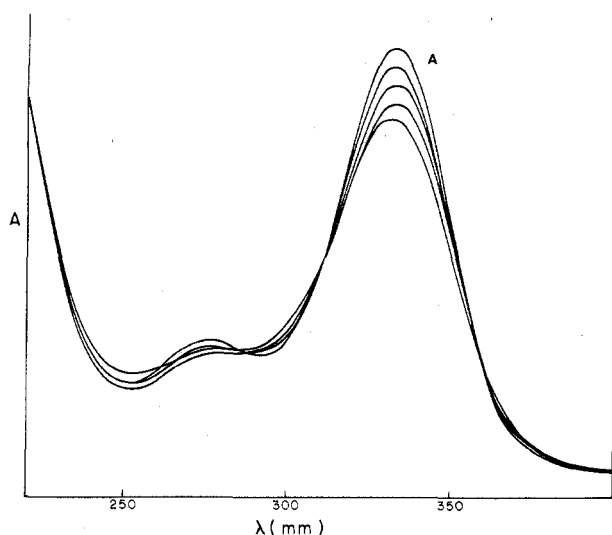


The amount of photoproduct formed was determined by anating the photoproduct (and starting material) with chloride ion and then analyzing the spectrum of the resulting *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  solution. Since the anation of  $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  is stereoretentive,<sup>9,10</sup> the composition of the solution generated upon chloride anation will be the same as the isomeric composition of the photolyzed solution. This indirect method was necessary as the electronic spectra of *cis*- and *trans*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$  are qualitatively similar, while the spectra of the dichloro ions are sufficiently distinct to

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**Figure 1.** Spectral changes induced upon photolysis of *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> in acidic aqueous solution. Initial spectrum is A; successive spectra represent photolysis times of 1000, 2000, 3200, and 5500 s.

**Table I**

compd	$\phi_{\text{total}}^a$	$\phi_{\text{isom}}$	$\phi_{\text{ret}}$	% cis photo-product
<i>trans</i> -[Ru(en) <sub>2</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>	0.042	0.042		
<i>cis</i> -[Ru(en) <sub>2</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>	0.038	0.038		
<i>trans</i> -[Ru(en) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>	0.0050	0.0033	0.0017	66 ± 2.5
<i>cis</i> -[Ru(en) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>	0.0030	0.0025	0.0005	84 ± 2.5

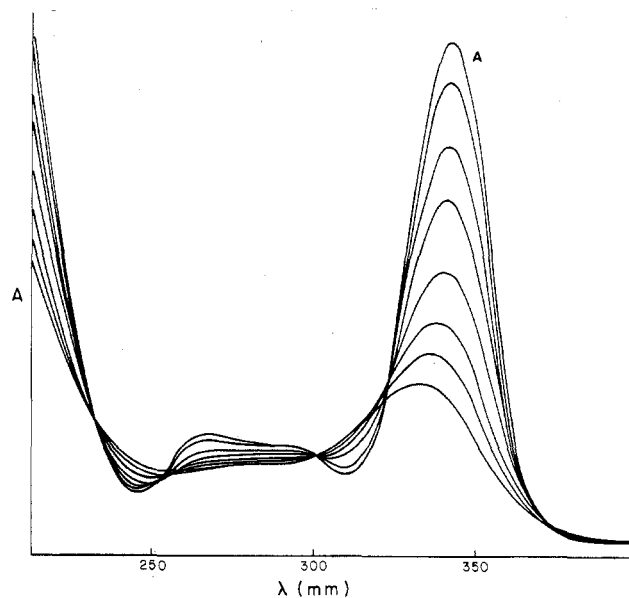
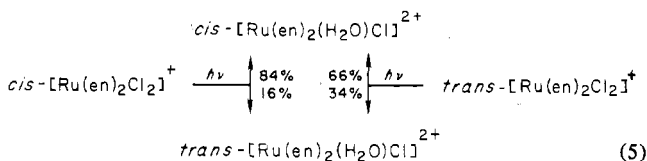
<sup>a</sup> Quantum yields are accurate to ±10%.

permit quantitative analysis of solution composition. (Numerous attempts to separate the *cis*- and *trans*-aquochloro ions by ion-exchange chromatography led to partial separations, but they were not clean enough to permit quantitative analysis.)

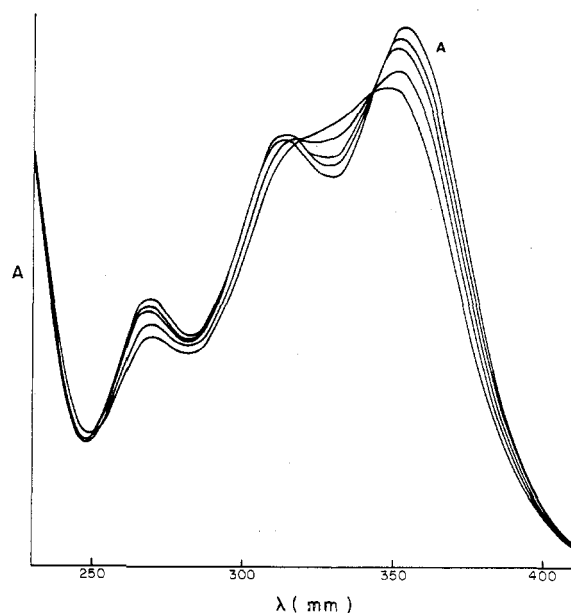
The quantum yields for isomerization for *trans*- and *cis*- and from *cis*- to *trans*-aquochloro ions are given in Table I.

*cis*- and *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. Ligand field excitation of an aqueous solution of either *cis*- or *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> causes (a) no increase in solution pH, (b) an increase in the concentration of free chloride in solution, and (c) pronounced changes in the electronic absorption spectra (Figure 2 and 3). The photoinduced spectral changes are complex, and isobestic points are not observed. The spectral changes and analytical data indicate that both dichloro ions undergo photoinduced aquation of coordinated chloride, but the similarity in the electronic spectra of *cis*- and *trans*-[Ru(en)<sub>2</sub>Cl(H<sub>2</sub>O)]<sup>2+</sup> makes direct determination of the photoproduct stereochemistry impossible.

Analysis was possible, however, as the divalent photoproducts could be quantitatively separated from the monovalent starting material by ion-exchange chromatography. After photoproduct separation, the isomeric composition of the aquochloro photoproducts could be determined by the chloride anation/spectral analysis technique described earlier. Table I also shows the quantum yields and isomeric composition of the aquochloro ions formed upon photolysis of *cis*- and *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (eq 5).



**Figure 2.** Spectral changes induced upon photolysis of *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in 0.2 M methanesulfonic acid solution. Initial spectrum is A; successive spectra represent photolysis times of 500, 1000, 1500, 2000, 2500, 3500, and 4500 s.



**Figure 3.** Spectral changes induced upon photolysis of *cis*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in 0.2 M methanesulfonic acid solution. Initial spectrum is A; successive spectra represent photolysis times of 400, 900, 1800, and 3000 s.

The isomeric composition of the aquochloro ions was initially determined by the primary photochemical reaction of the dichloro ions, but this composition could have been altered by secondary photolysis of the aquochloro ions (eq 4). Interference from secondary photolysis was reduced by limiting the photochemical conversion to the first 15% of the dichloro ion. Within that first 15%, isomeric composition of the photo-generated aquochloro ions was independent of photolysis time, so secondary photolysis need not be considered in these analyses.

In the absence of side reactions, prolonged irradiation of either of the aquochloro ions should lead to a photostationary state consisting of a mixture of the *cis*- and *trans*-aquochloro ions. A photostationary state does not develop, however, for there is a side reaction not indicated in eq 4. Prolonged photolysis of either *cis*- or *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> (or either

of the dichloro ions) leads to the development of a broad absorption band centered near 446 nm; the solution becomes increasingly yellow as this absorption grows.

Photochemical development of the yellow color was most efficient from *cis*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup>, but it also formed after extensive photolysis of *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup>, as well as the dichloro ions. Our attempts to isolate and unequivocally identify the yellow component have been unsuccessful. The yellow component is rapidly bleached when loaded onto a cation-exchange column in the H<sup>+</sup> form but could be separated with a Li<sup>+</sup> column. Photoinduced generation of the 446-nm band was accompanied by a decrease in solution pH.

## Discussion

The most obvious conclusion to be drawn from these results is that geometric isomerization occurs upon the ligand field photolysis of these ruthenium(III)-haloamine complexes. The photochemistry of *cis*- and *trans*-[Ru(en)<sub>2</sub>CIX]<sup>n+</sup> (X = Cl, H<sub>2</sub>O) is somewhat reminiscent of the reactions of the analogous Co(III) complexes,<sup>5</sup> as the aquochloro ions are converted to each other at relatively low efficiencies and the dichloro ions photolyze to a mixture of the aquochloro isomers. Amine labilization could not be detected in any of the complexes, and the aquochloro ions do not lose chloride ions, although isomerization may involve water exchange.

While identified as "ligand field photolysis", the assignment of the electronic character of the photoproduct excited states is not clear. These low-energy absorptions in ruthenium(III)-amine and -haloamine complexes occur at wavelengths characteristic of d-d transitions, but they are too intense to be pure, LaPorte-forbidden d-d transitions. A simplified molecular orbital analysis, originally used for Ru(II) complexes with electron-accepting nitrogen heterocycle ligands,<sup>13</sup> was adapted to halide donors and used to assign these low-energy electronic transitions as halide-to-metal charge transfers.<sup>14</sup> The number of bands, their approximate energies, and their relative intensities were accounted for by this technique.

This analysis uses one metal t<sub>2g</sub> orbital and one halide (π\*) orbital, and "NH<sub>3</sub> orbitals are not taken into account", so it cannot be used to account for the spectra of [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> (λ<sub>max</sub> 275 nm, ε 475) or [Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sup>3+</sup> (λ<sub>max</sub> 268 nm, ε 757). These ions do not have filled π\* ligand centered orbitals suitable for a LMCT excitation, yet they have bands in the same region as the haloamine complexes studied here. For the hexaammine, the transition has been identified<sup>7</sup> as an atypically intense ligand field band.

On the assumption of the normal red shift in the position of this band upon replacement of NH<sub>3</sub> by a lower ligand field strength chloride, the ligand field bands for the [Ru(en)<sub>2</sub>CIX]<sup>n+</sup> ions studied here should appear in approximately the region of the irradiated absorptions; the apparently accidental degeneracy with the halide-to-metal charge-transfer transitions confuses the interpretation of the photochemistry. Intensity of ligand field absorptions generally increases as the holohedral symmetry about the metal decreases. With the molar absorptivity coefficients for [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sup>2+</sup> at 475 and 757 M<sup>-1</sup> cm<sup>-1</sup>, respectively, the molar absorptivity coefficients for the ligand field bands for *cis*- and *trans*-[Ru(en)<sub>2</sub>CIX]<sup>n+</sup> (X = Cl, H<sub>2</sub>O) should be on the order of 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>. This is a significant component of the observed bands, so it is reasonable that these absorptions be considered as combinations of ligand field and charge-transfer bands.

Irradiation in this region should cause formation of both ligand field and charge-transfer excited states; the photo-

chemical consequences are characteristic of only ligand field excited states, however, and we could see no evidence of charge-transfer photochemistry. No Ru(II) products were observed, and the reactions were not affected by the presence or absence of oxygen in solution. The photoinertness of the LMCT states of [Ru(NH<sub>3</sub>)<sub>5</sub>X]<sup>n+</sup> (X = Cl, NH<sub>3</sub>) has also been noted.<sup>7</sup> We conclude that the photoinduced ligand labilization observed for these [Ru(en)<sub>2</sub>CIX]<sup>n+</sup> (X = Cl, H<sub>2</sub>O) ions results from ligand field excited states; whether these states are populated by direct absorption into d-d bands or by internal conversion from photoinert charge-transfer states is not known.

The similarity in the spectra of the *cis*- and *trans*-aquochloro isomers<sup>15</sup> initially hindered the detection of photoinduced isomerization, but chloride anation of the photoproducts revealed that stereochemical rearrangements had occurred. While *cis*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> is the predominant photoproduct upon irradiation of either dichloro ion, the two dichloro ions generated different isomeric mixtures of aquochloro ions upon photolysis (Table I). The isomeric mixtures reported are each the average of at least six separate determinations, and the scatter of experimental values was ±2.5%. We conclude that the difference in the isomeric composition produced upon photolysis of *cis*- and *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> is real.

Such a difference is not consistent with the models which include a thermally equilibrated five-coordinate excited-state intermediate.<sup>2</sup> Photoinduced chloride loss, observed from both dichloro ions, would lead to the {[Ru(en)<sub>2</sub>Cl]<sup>2+</sup>} ion. If this species existed long enough to distort to its stablest configuration, the eventual isomeric mixture of *cis*- and *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> would be independent of the initial structure of {[Ru(en)<sub>2</sub>Cl]<sup>2+</sup>}. However, the photoproduct composition is dependent on the structure of the starting material, implying that the transients generated upon photolysis of *cis*- and *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> are distinct.

On the assumption that one of the initial consequences of excited-state formation is the radial extension of at least one metal-ligand bond, these results imply that coordination of a solvent water must occur before any potential five-coordinate species can equilibrate to its stablest configuration. In addition, the substitution is not stereoretentive, so distortion away from the square pyramid (which would result from loss of one ligand from an octahedron) must occur before formation of the ruthenium-water bond. These considerations imply that the common theoretical device of separating photoinduced chemical processes into three sequential events (ligand loss, distortion, and water attack) does not realistically model the photochemistry of these Ru(III) complexes. The three steps must be concerted to a significant extent.

The obvious question is whether this reflects specific behavior of Ru(III) complexes or whether the lack of a thermally equilibrated five-coordinate intermediate (or of any common intermediate) has broader implications for other systems. Ru(III) complexes do differ from d<sup>3</sup> and d<sup>6</sup> complexes in that the d<sup>5</sup> electronic configuration lacks the symmetrically filled t<sub>2g</sub> (and t<sub>2g</sub> derived) metal orbitals. The effect of this asymmetric electron distribution on the mechanism of photoinduced ligand labilization is unknown.

This aspect of transition-metal photochemistry has not been thoroughly studied, and the available information concerning d<sup>3</sup> and d<sup>6</sup> complexes is inconclusive. For example, the concept

(15) The discrepancy between our spectrum of *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> and the published spectrum is difficult to explain. The previous preparation was briefly described as involving "reaction of *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]Cl·0.5H<sub>2</sub>O with the theoretical amount of silver *p*-toluenesulfonate". The ion used here was prepared by spontaneous aquation of *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, followed by ion-exchange separation of the divalent cation, presumably *trans*-[Ru(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup>. Chloride anation of this ion regenerated pure (≥99%) *trans*-[Ru(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, confirming our assignment.

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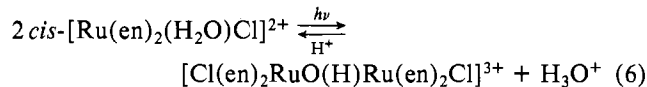
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of a thermally equilibrated five-coordinate species is supported by photolysis of  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,<sup>16</sup> *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ ,<sup>17</sup> and *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ .<sup>17</sup> Upon photoinduced ligand loss, these complexes would all produce  $\{[\text{Cr}(\text{NH}_3)_4\text{Cl}]^{2+}\}$  and all produce *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$  as the only detectable photoproduct. Similarly, both *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  (Cl<sup>-</sup> loss)<sup>18</sup> and *trans*- $[\text{Cr}(\text{en})_2\text{Cl}(\text{NCS})]^+$  (NCS<sup>-</sup> loss)<sup>19</sup> photolyze to *cis*- $[\text{Cr}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}$ , while both *trans*- $[\text{Cr}(\text{en})_2\text{XF}]^{n+}$  (X = NH<sub>3</sub><sup>20</sup> or NCS<sup>-21</sup>) lose X upon ligand field excitation, and *cis*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})]^{2+}$  is the dominant photoproduct in both cases.

For d<sup>6</sup> complexes, the situation is less clear, as in systems such as  $[\text{M}(\text{en})_2\text{Cl}_2]^+$  (M = Co<sup>5,6</sup> or Rh<sup>4</sup>) and  $[\text{Rh}(\text{NH}_3)_4\text{XY}]^{n+}$  (X = Cl, Br; Y = H<sub>2</sub>O, X)<sup>22</sup> the *cis* and *trans* isomers of the respective complexes photolyze to identical products or to identical product mixtures. The first exception to this trend was reported by Petersen and Jakse,<sup>3</sup> as *cis*- and *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$  both undergo photoinduced aquation of the chloride ligand with retention of the original geometry. Thus, if  $\{[\text{Rh}(\text{en})_2(\text{NH}_3)]^{3+}\}$  species actually are generated during these photolyses, they do not collapse to a common geometry. Petersen argues<sup>3</sup> that the lack of isomerization could be due to either the lack of a driving force between the two possible square-pyramidal structures for  $\{[\text{Rh}(\text{en})_2(\text{NH}_3)]^{3+}\}$  or that the kinetic barrier between them (through the TBP structure) is too high. Photolysis of *cis*-<sup>23</sup> and *trans*-<sup>24</sup>  $[\text{Ir}(\text{en})_2\text{Cl}_2]^+$  also causes stereoretentive chloride

loss and aquation. While kinetic barriers between possible  $\{[\text{Ir}(\text{en})_2\text{Cl}]^{2+}\}$  species could also be hypothesized, the stereoretentive photochemistry of  $[\text{Ir}(\text{en})_2\text{Cl}_2]^+$  and  $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$  isomers raises doubt about the existence of thermally equilibrated five-coordinate species even in d<sup>6</sup> photochemistry.

As for the inefficient side reaction which leads to a yellow species, we propose that the yellow compound is a Ru(III) dimer with a bridging hydroxyl group (eq 6). The relative



ease of production from the *cis*-aquochloro ion and the column catalyzed regeneration of the *cis*-aquochloro ion suggests the Ru center in the dimer has a *cis* configuration. Formation of the hydroxyl bridge would account for the pH decrease, as H<sub>3</sub>O<sup>+</sup> is also produced. Formation of a yellow color (λ at 450 nm) has been previously noted<sup>9</sup> in aged ("several days") solutions of *cis*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$  and *cis*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ ; it also appeared during attempts to measure the conductivity of solutions containing these ions. The yellow material formed photochemically was spectrally indistinguishable from thermally prepared samples, and while photochemical generation of the yellow species was much more rapid than the thermal path, the photochemical reaction was very inefficient and did not interfere with the study of the photoreactions discussed earlier.

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**Registry No.** *cis*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ , 38687-00-2; *trans*- $[\text{Ru}(\text{en})_2\text{Cl}_2]^+$ , 45839-20-1; *cis*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ , 31274-35-8; *trans*- $[\text{Ru}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$ , 55870-37-6;  $[\text{Cl}(\text{en})_2\text{RuO}(\text{H})\text{Ru}(\text{en})_2\text{Cl}]^{3+}$ , 73712-38-6.

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