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# Stereochemical Consequences of the Ligand Field Photolyses of Dihalo- and Aquohalotetraamminerhodium(III) Complexes in Aqueous Solution

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Ligand field excitation of the *cis*-disubstituted tetraamminerhodium(III) complexes *cis*-$Rh(NH_3)_4XY^{n+}$ ($X^- = Cl^-$ or $Br^-$, $Y = X^-$ or $H_2O$) in aqueous solution leads in each case to the corresponding *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$ ion as the predominant product. Quantum yields are high, falling in the range 0.24–0.50 mol/einstein, and there is no indication of stable intermediates formed under conditions of continuous photolysis. Hence, at least for the dihalo complexes $Rh(NH_3)_4X_2^+$, photoaquation of a ligand and cis to trans isomerization are concomitant. In contrast, photoaquation of halide from the *trans*-$Rh(NH_3)_4X_2^+$ ions is stereoretentive. These results are interpreted in terms of the dissociation of halide from a ligand field excited state of $Rh(NH_3)_4X_2^+$ to give a pentacoordinate intermediate $Rh(NH_3)_4X^{2+}$, having a square-pyramidal configuration and displaying an energetic preference for the isomer with $X^-$ in the apical position. In addition it is argued that the square-pyramidal intermediate undergoing isomerization is in an excited electronic state and that deactivation to the singlet ground electronic state of the same coordination leads to immediate trapping by $H_2O$ without further isomerization. The latter point draws some support from the thermochemical studies of the nitrous acid decomposition of the azido complex *cis*-$Rh(NH_3)_4(N_3)Cl^+$ which proceeds with retention of configuration to give *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$. Also described are the syntheses of the dithionate salts of the mixed-ligand complexes *cis*- and *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and *cis*- and *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$.

## Introduction

Irradiation of the ligand field (LF) absorption bands of haloamine–rhodium(III) complexes in aqueous solution has been shown to result in the reasonably facile labilization of one coordinated ligand (e.g., eq 1 and 2).[2-5] These photo-

$$Rh(NH_3)_5Br^{2+} + H_2O \xrightarrow[h\nu\ (365\ nm),\ \Phi_{Br^-} = 0.02]{a} Rh(NH_3)_5H_2O^{3+} + Br^-$$
$$\xrightarrow[h\nu\ (365\ nm),\ \Phi_{NH_3} = 0.18]{b} trans\text{-}Rh(NH_3)_4(H_2O)Br^{2+} + NH_3 \qquad (1)$$

$$trans\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow[\Phi_{Cl^-} = 0.17]{h\nu\ (358\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} \qquad (2)$$

labilizations can be traced to the reactivities of the lowest energy excited states (es), triplet states from which weak emission has also been observed.[5] Although theoretical considerations[6] suggest that the ligands labilized will be those occupying sites along the weak-field axis (e.g., $Br^-$ or *trans*-$NH_3$ in $Rh(NH_3)_5Br^{2+}$), the actual stereochemical origin of the $NH_3$ photolabilized from $Rh(NH_3)_5Br^{2+}$ (eq 1) has not been identified. While one might have argued for stereochemical retention from the results of the LF photolysis of *trans*-dihalo complexes,[3] there were suggestions of stereoisomerizations in the earlier photochemical studies of *cis*-bis(ethylenediamine) complexes.[7] Such stereolability was confirmed in a preliminary communication[8] from this laboratory where it was demonstrated that the photolabilization of $Cl^-$ from *cis*-$Rh(NH_3)_4Cl_2^+$ occurs concomitantly with photoisomerization to give *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ (eq 3).

$$cis\text{-}Rh(NH_3)_4Cl_2^+ + H_2O \xrightarrow[\Phi_{Cl^-} = 0.34]{h\nu\ (365\ nm)} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^- \qquad (3)$$

This observation, in contrast to the stereoretention indicated in eq 2, has stimulated theoretical modeling of excited state and (proposed) transient intermediate stereochemical properties by Vanquickenborne.[9] A related treatment has been offered by Petersen[10] to account for the stereochemical consequences of the LF photolyses of the *cis*- and *trans*-$Rh(en)_2ClX^{n+}$ ($X = Cl^-$ or $NH_3$) ions. Here we describe quantitative photochemical studies of the cis tetraammine complexes *cis*-$Rh(NH_3)_4X_2^+$ and *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ ($X = Cl^-$ or $Br^-$). Notably, unlike the other cases where the photochemistries of *cis*-dihalorhodium(III) complexes have now been investigated,[7,10-12] the tetraammine complexes described here do not have polydentate ligands which may either prevent or force (via proposed secondary reactions)[13] such photoisomerizations.

## Experimental Section

**Materials.** The tetraamminerhodium(III) complexes *cis*-$[Rh(NH_3)_4Cl_2]Cl\cdot{}^1/_2H_2O$,[14] *cis*-$[Rh(NH_3)_4Br_2]Br\cdot{}^1/_2H_2O$,[14] *trans*-$[Rh(NH_3)_4Cl_2]Cl$,[15] and *trans*-$[Rh(NH_3)_4Br_2]Br$[15] were all prepared and recrystallized by published procedures. The haloaquotetraammines *cis*- or *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$ ($X^- = Cl^-$ or $Br^-$) were prepared by the stereoretentive thermal aquation of one halide from the corresponding dihalo complexes[16] and isolated as follows:

*cis*-**$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$.** A 500-mg portion of *cis*-$[Rh(NH_3)_4Cl_2]Cl\cdot{}^1/_2H_2O$ (1.75 mmol) was dissolved in 20 mL of hot water. To this was added a solution of 410 mg of silver(I) oxide (1.77 mmol) dissolved in 20 mL of 0.2 M perchloric acid. The mixture was gently boiled for 3 h while protected against light, then evaporated to 3 mL, and finally diluted to 7 mL and filtered through a fine sintered-glass filter. To the filtrate was added a warm solution of 0.7 g of sodium dithionate dihydrate in 7 mL of water and 7 mL of 95% ethanol. The solution was allowed to cool overnight to room temperature and further in ice. The crude product was filtered off and washed with 1 mL of ice water and then with 2 mL of 95% ethanol: crude yield 470 mg (70%). The product was recrystallized from 2 mL of hot water by slowly cooling to room temperature. The pale yellow crystals (elongated prisms) were filtered off and washed with 95% ethanol: yield 340 mg (50%). The product was recrystallized once more: yield 245 mg (36%). Anal.[17] Calcd for *cis*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$: H, 3.67; N, 14.56; Cl, 9.22; S, 16.67. Found: H, 3.82; N, 14.64; Cl, 9.27; S, 16.59.

*cis*-**$[Rh(NH_3)_4(H_2O)Br]S_2O_6$.** This compound was prepared in a similar manner to its chloro analogue from 740 mg of *cis*-$[Rh(NH_3)_4Br_2]Br\cdot{}^1/_2H_2O$ (1.76 mmol): crude yield 465 mg (62%). The product was crystalline (light orange elongated prisms) but was recrystallized twice to give an overall yield of 340 mg (45%). Anal.[17] Calcd for *cis*-$[Rh(NH_3)_4H_2OBr]S_2O_6$: H, 3.29; N, 13.06; Br, 18.62; S, 14.94. Found: H, 3.45; N, 13.10; Br, 18.86; S, 14.91.

*trans*-**$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$.** The trans isomer was synthesized by the same method as the cis isomer starting with 485 mg of *trans*-$[Rh(NH_3)_4Cl_2]Cl$ (1.75 mmol) in 55 mL of hot water. No protection against light is, however, necessary for synthesis of complexes in the trans series: crude yield 355 mg (53%). The yield after two recrystallizations was 220 mg (33%). The compound was obtained as shiny, brownish orange flakelike crystals. Anal.[17] Calcd for *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$: H, 3.67; N, 14.56; Cl, 9.22; S, 16.67. Found: H, 3.77; N, 14.60; Cl, 9.29; S, 16.71.

*trans*-**$[Rh(NH_3)_4(H_2O)Br]S_2O_6$.** Again the same method was used, starting with 720 mg of *trans*-$[Rh(NH_3)_4Br_2]Br$ (1.75 mmol) in 40

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**Table I.** Electronic Spectra of Complexes in Dilute Aqueous Solutions

| complex ion | $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) |
|---|---|
| *cis*-Rh(NH$_3$)$_4$Cl$_2^+$ | 360 (126),[a] 295 (108)[a] |
| *trans*-Rh(NH$_3$)$_4$Cl$_2^+$ | 415 (74),[b] 293 (85)[b] |
| *cis*-Rh(NH$_3$)$_4$Br$_2^+$ | 377 (170),[a] ~275 sh (~940)[a] |
| *trans*-Rh(NH$_3$)$_4$Br$_2^+$ | 441 (111),[b] ~280 sh (~2700)[b] |
| *cis*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | 348 (112), 283 (95) |
| *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | 389 (55), 284 (114) |
| *cis*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | 363 (125) |
| *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | 466 sh (38), 406 (62), 255 (~560) |
| *cis*-Rh(NH$_3$)$_4$(N$_3$)Cl$^+$ | 355 (~390), 257 (~6700), ~206 sh (~17 000) |

[a] Reference 14. [b] Reference 15.

mL of hot water. However, the ethanol was added after the precipitation of the desired product had begun, and the solution was only cooled to room temperature: crude yield 525 mg (70%). The yield after two recrystallizations was 315 mg (42%). The product consisted of large, transparent red-brown prismatic crystals. Anal.[17] Calcd for *trans*-[Rh(NH$_3$)$_4$(H$_2$O)Br]S$_2$O$_6$: H, 3.29; N, 13.06; Br, 18.62; S, 14.94. Found: H, 3.83; N, 13.20; Br, 18.67; S, 15.15.

***cis*-[Rh(NH$_3$)$_4$(N$_3$)Cl]$_2$S$_2$O$_6$.** A 500-mg sample of *cis*-[Rh(NH$_3$)$_4$(H$_2$O)Cl]S$_2$O$_6$ (1.30 mmol) and 90 mg of sodium azide (1.38 mmol) were dissolved in 10 mL of water. The solution was heated to 90 °C for 30 min, protected against light. Solid sodium dithionate dihydrate (0.50 g) was dissolved in the warm solution, which then was filtered and allowed to cool to room temperature. After 2 h of cooling in ice, the resulting precipitate was filtered off and washed with 0.5 mL of ice water and then with 1 mL of methanol: crude yield 100 mg (23%). The bright yellow product was recrystallized from 3 mL of 90 °C water: yield 70 mg (16%). After one more recrystallization, the product appeared as a shiny yellow microcrystallinic powder: yield 50 mg (12%). Cation-exchange chromatography showed monopositive-ion behavior for more than 95% of this material. However, the nitrous acid decomposition experiments indicate that the isolated solid apparently contains only 70 mol % of [*cis*-Rh(NH$_3$)$_4$(N$_3$)Cl]$_2$S$_2$O$_6$ and 30 mol % of [*cis*-Rh(NH$_3$)$_4$Cl$_2$]$_2$S$_2$O$_6$ (see Results). [The dichloro species is apparently formed from chloride labilized from the *cis*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ starting complex when heated in solution.] These two species apparently have similar solubility properties such that the mixture's spectral properties are unchanged on recrystallization. The elemental analysis was consistent with this interpretation. Anal.[17] Calcd for the 30/70 mol % ratio of [Rh(NH$_3$)$_4$Cl$_2$]$_2$S$_2$O$_6$/[Rh(NH$_3$)$_4$(N$_3$)Cl]$_2$S$_2$O$_6$: H, 3.7; N, 26.2; Cl, 14.1; S, 9.8. Found: H, 4.0; N, 25.0; Cl, 14.1; S, 9.9. The IR spectrum (KBr pellet) showed a typical coordinated azide stretching band at 2035 cm$^{-1}$.

**Photolyses.** Photolyses were carried out by the same methods and with the photolysis apparatus previously described.[18] Temperature control was better than ±1 °C. Light intensities were determined by ferrioxalate actinometry. The quantum yields were evaluated from spectral changes (monitored on a Cary Model 118C spectrophotometer) and from pH changes (glass-electrode measurements) by numerical procedures also previously described.[18]

Photolytic ammonia aquation was a major reaction path only in the photolysis of *cis*-Rh(NH$_3$)$_4$Br$_2^+$. The bromide aquation quantum yield was in this case also evaluated after ion-exchange separation of the *trans*-Rh(NH$_3$)$_4$H$_2$OBr$^{2+}$ product from the photolyzed solution.

All photolyses were performed in dilute aqueous solutions with a pH of 3–4, adjusted with perchloric acid.

**Ion Exchange.** Bio-Rad AG 50W-X4, 200–400 mesh, hydrogen ion form, ion-exchange resin (length of column ~7 cm, diameter ~1 cm) was used in each of the ion-exchange separations described. After application of the solution containing the reaction mixture on the resin and elution of anions with water, monopositive complex ions were eluted with 0.5 M perchloric acid, and dipositive complex ions, with 2.0 M perchloric acid.

**Spectra.** Electronic absorption spectra of relevant complexes were recorded in dilute perchloric acid solutions over the region 600–200 nm on a Cary Model 118C spectrophotometer. Further recrystallization of the compounds did not change the spectra. Data for absorption maxima or shoulders (sh) are given in Table I. The electronic spectrum of the *cis*-Rh(NH$_3$)$_4$(N$_3$)Cl$^+$ ion was estimated from the spectrum of the isolated mixture described above, corrected for the presence of 30 mol % of [*cis*-Rh(NH$_3$)$_4$Cl$_2$]$_2$S$_2$O$_6$.

## Results

Quantum yields for the 365-nm photolyses of *cis*-Rh(NH$_3$)$_4$X$_2^+$ and *cis*-Rh(NH$_3$)$_4$(H$_2$O)X$^{2+}$ (X = Cl$^-$ or Br$^-$) are listed in Table II. Ammine aquation quantum yields are based on solution pH changes[18] while halide photoaquation and cis to trans photoisomerization quantum yields are based upon the combination of spectral analysis and ion-exchange chromatography procedures.

***cis*-Rh(NH$_3$)$_4$Cl$_2^+$.** LF photolysis of the *cis*-dichloro ion leads cleanly to a final spectrum [$\lambda_{max}$ ($\epsilon$) 389 (51 M$^{-1}$ cm$^{-1}$), 284 nm (111)] virtually identical with that of *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$. Good isosbestic points are maintained at 291 and 268 nm throughout the photolysis, indicating that there is no spectrally significant buildup of intermediates and that secondary photolysis of the product does not lead to measurable spectral changes. The latter point was confirmed by direct photolysis of the *trans*-aquochloro species synthesized thermally. Spectral and pH changes after long photolyses of aqueous *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ were minute or immeasurable; thus the quantum yields listed in Table II for this ion represent upper limits for halide and ammine labilization based upon experimental uncertainties. The $\Phi_{Cl^-}$ and $\Phi_{isom}$ values [$\Phi_{isom} = \Phi_{Cl^-} = 0.34 \pm 0.03$ mol/einstein] listed for *cis*-Rh(NH$_3$)$_4$Cl$_2^+$ are based on spectral changes. The solution pH (initially pH 4.0) increased slightly over long photolysis, indicating a $\Phi_{NH_3}$ (0.007 ± 0.002) about $^1/_{50}$th the other photoreactions.

***cis*-Rh(NH$_3$)$_4$Br$_2^+$.** LF photolysis of this ion leads to both halide and ammine aquation, hence complicating analysis of the reaction via spectral techniques. The $\Phi_{NH_3}$ value (0.064 ± 0.005) was determined from pH changes (initial pH 3–4), but the NH$_3$ aquation product was not identified. The spectrum of the reaction solution during photolysis displayed an isosbestic point at 448 nm for a period corresponding to about 50% reaction, and the spectrum of the product solution after exhaustive photolysis was similar to that of *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$. However, this ion was identified as the product of Br$^-$ photoaquation from the spectra of ion-ex-

**Table II.** Photoreaction Quantum Yields for Disubstituted Tetraamine Complexes[a]

| complex | principal product[b] | $\Phi_{X^-}$[c] | $\Phi_{NH_3}$[d] | $\Phi_{isom}$[e] |
|---|---|---|---|---|
| *cis*-Rh(NH$_3$)$_4$Cl$_2^+$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | 0.34 | 0.007 | 0.34 |
| *cis*-Rh(NH$_3$)$_4$Br$_2^+$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | 0.24 | 0.06 | 0.24 |
| *cis*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | <0.01 | <0.001 | 0.46 |
| *cis*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | <0.01 | ~0.006 | 0.50 |
| *trans*-Rh(NH$_3$)$_4$Cl$_2^+$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | 0.13[f] | <0.002[f] | *g* |
| *trans*-Rh(NH$_3$)$_4$Br$_2^+$ | *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | 0.10[h] | 0.002[h] | *g* |
| *trans*-Rh(NH$_3$)$_4$(H$_2$O)Cl$^{2+}$ | *i* | <0.01 | <0.001 | *g* |
| *trans*-Rh(NH$_3$)$_4$(H$_2$O)Br$^{2+}$ | *i* | <0.01 | ~0.003 | *g* |

[a] Photoreaction resulting from 365-nm irradiation in dilute aqueous solutions, pH 3–5, 25 °C. Quantum yields expressed in moles/einstein and reported for three or more determinations. [b] Evaluated from reaction product spectra. [c] Quantum yield for halide aquation. [d] Quantum yield for ammine aquation evaluated from solution pH changes. [e] Quantum yield for cis $\rightleftarrows$ trans isomerization evaluated from analysis of product solution. [f] Reference 3, $\lambda_{irr}$ 407 nm. [g] Not detectable. [h] $\lambda_{irr}$ 405 nm. [i] Not determined; negligible photoreaction observable.

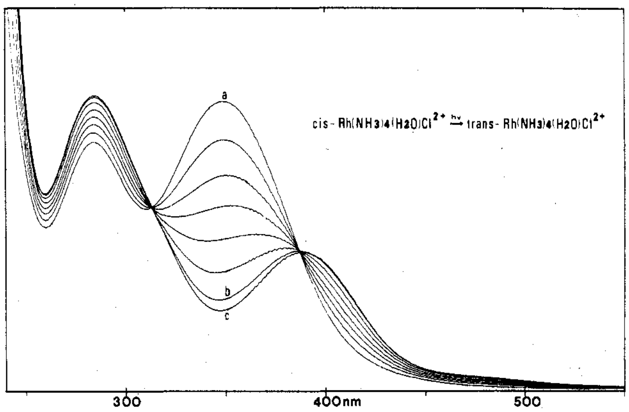


**Figure 1.** Electronic spectra recorded periodically during the LF photolysis of a pH 4 aqueous solution initially containing *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ ($3.2 \times 10^{-3}$ M). Spectrum a is the starting solution while spectra b and c are those of the reaction solution after 705-s and 30-min irradiation, respectively. The final spectrum c has $\lambda_{max}$ 389 ($\epsilon$ 53 $M^{-1}$ $cm^{-1}$) and 283 nm (114) in comparison to the spectrum of *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ with $\lambda_{max}$ 389 (55) and 284 nm (114).

change-separated fractions. When product solutions of partial photolyses (8–35% reaction) were subjected to ion-exchange chromatography, the dipositive product fraction had a spectrum identical with that of *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ (the ratio $\epsilon_{406}/\epsilon_{466} = 1.64 \pm 0.03$ as compared to the value 1.63 for authentic *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$, Table I). The quantum yield for formation of this product calculated from the ion-exchanged aliquots had the value 0.24 ± 0.04 mol/einstein (six experiments). Calculation of $\Phi_{Br^-}$ from the spectral changes of the product solutions during photolysis based upon the assumption that *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ is the sole product gave the value 0.24 ± 0.01 mol/einstein (seven experiments). The agreement between the quantum yields obtained spectrally from product solutions and from ion-exchange experiments is fortuitous and suggests that the extinction coefficients of the primary ammine aquation product(s) must be similar to those of the starting material at the monitoring wavelength (377 nm).

The photochemistry of aqueous *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ synthesized thermally was also examined in order to evaluate secondary photoreactions in the *cis*-$Rh(NH_3)_4Br_2^+$ photolyses. In similarity to the chloro analogue, spectral changes were minor after long photolyses. However, small but measurable pH increases indicated a low quantum yield of ammine photoaquation (Table II).

*cis*-$\mathbf{Rh(NH_3)_4(H_2O)Cl^{2+}}$. LF photolysis of this ion in aqueous solution leads cleanly and efficiently ($\Phi = 0.46 \pm 0.01$) to the *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ ion as evidenced in the photoproduct solution spectrum [$\lambda_{max}$ ($\epsilon$) 389 (54 $M^{-1}$ $cm^{-1}$), 284 nm (116)]. Isosbestic points at 313 and 387 nm were maintained throughout the photolysis (Figure 1) and the values of $\Phi_{Cl^-}$ and $\Phi_{NH_3}$ listed represent only generous upper limits estimated from the experimental uncertainties.

*cis*-$\mathbf{Rh(NH_3)_4(H_2O)Br^{2+}}$. LF photolysis of this ion in aqueous solution leads efficiently ($\Phi = 0.50 \pm 0.04$) to a product with a spectrum [($\lambda_{max}$ ($\epsilon$) 406 (62 $M^{-1}$ $cm^{-1}$), 466 sh (40)] virtually identical with that of *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ (Table I). An isosbestic point corresponding to more than 50% reaction persisted at 409 nm during photolyses. However, in contrast to the *cis*-aquochloro analogue, small but measurable pH increases were noted, indicating some ammine photoaquation ($\Phi_{NH_3} = 0.006 \pm 0.004$). Bromide photoaquation, if any, was very minor and only an upper limit for $\Phi_{Br^-}$ can be estimated from spectral changes.

*trans*-$\mathbf{Rh(NH_3)_4Br_2^+}$. Photolysis (405 nm) of the *trans*-$Rh(NH_3)_4Br_2^+$ ion in dilute aqueous solution leads cleanly to the *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ ion as evidenced by the final product spectrum after long photolysis. Isosbestic points during the photolysis were noted at 354, 408, and 474 nm. The quantum yield for $Br^-$ aquation (0.098 mol/einstein) was smaller than for the cis isomer, and ammonia aquation as determined from pH changes was at most a minor photoreaction pathway ($\Phi_{NH_3} \simeq 0.002$).

**$HNO_2$ Decomposition of** *cis*-$\mathbf{Rh(NH_3)_4(N_3)Cl^+}$. Products of the nitrous acid decomposition of the azido complex *cis*-$Rh(NH_3)_4(N_3)Cl^+$ were analyzed as follows: A 5.0-mg sample of the [*cis*-$Rh(NH_3)_4(N_3)Cl]_2S_2O_6$ synthesis product (0.015 mmol) was dissolved in 5 mL of 0.5 M perchloric acid and mixed with 5.0 mg of $NaNO_2$ (0.073 mmol) dissolved in 1 mL of water. The yellow color of the solution bleached immediately with simultaneous gas evolution. The reaction mixture was left 0.5 h in the dark and then separated by ion-exchange chromatography. The *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ ion, thus, separated, represented 70 ± 2% of the theoretical yield, assuming a pure material. No other dispositive ions were observed, but a unipositive ion fraction was identified spectrally as *cis*-$Rh(NH_3)_4Cl_2^+$ in an amount representing 30 ± 2 mol % of the original product mixture (see Experimental Section). No evidence for any complex ions belonging to the trans tetraammine series was found. *cis*-$Rh(NH_3)_4(N_3)Br^+$ decomposition with nitrous acid gave closely analogous results, the most important point being the absence of any stereoisomerization as the result of this procedure.

**Thermal Aquation of** *cis*-$\mathbf{Rh(NH_3)_4Cl_2^+}$. The stereochemistry of chloride aquation from *cis*-$Rh(NH_3)_4Cl_2^+$ was studied as follows: When an aqueous solution containing [*cis*-$Rh(NH_3)_4Cl_2]Cl$ (0.0296 mmol) and $AgClO_4$ (0.060 mmol) in dilute $HClO_4$ was heated at boiling (in the dark) for 1 h, the resulting solution spectrum after filtration was consistent with a mixture of *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$. Sufficient NaCl was then added to give a concentration of ~1 M and the solution was reheated at boiling for 15 min. The electronic spectrum of the product solution indicated nearly quantitative re-formation of *cis*-$Rh(NH_3)_4Cl_2^+$ with the optical density of the 360-nm maximum corresponding to an extinction coefficient of 124 $M^{-1}$ $cm^{-1}$ (see Table I). The higher energy band at 295 nm proved about 3% too intense, and since the intensity of this absorption increased with continued heating, some $NH_3$ aquation under these conditions is suspected. However, there was no evidence from this experiment for the formation of any trans products, indicating that the thermal substitution occurs with a high degree of stereoretention.

## Discussion

The ensuing discussion will focus on two aspects of the results: first, the cis to trans photoisomerization of the disubstituted Rh(III) tetraammines, apparently concomitant with ligand photosubstitution, and second, the nature of the ligand labilized or apparently labilized as the result of ligand field excitation. The LF photochemistry of *cis*-dihalorhodium(III) complexes in aqueous solution has now been reported for a number of species where the remaining four coordination sites are occupied by nitrogen-donor ligands. With the exception of the *cis*-$Rh(NH_3)_4X_2^+$ complexes (I) reported here,[8] the nitrogen-donor ligands of the systems examined are multidentate, the other complexes being[19] *cis*-$Rh(en)_2X_2^+$ (II),[7,10,11] *cis*-$Rh(phen)_2X_2^+$ (III),[7] *cis*-$Rh(bpy)_2X_2^+$ (IV),[7] *cis*-$Rh(cyclam)X_2^+$ (V),[11] $Rh(tren)Cl_2^+$ (VI),[12a] *cis*-α-$Rh(trien)Cl_2^+$ (VII),[12b] and *cis*-β-$Rh(trien)Cl_2^+$ (VIII).[12b] Schematic representations of these species are shown in Figure 2. Among these dihalo ions, LF photolysis gives *cis*-haloaquo products for V and VI and probably for III and IV, each of these being constrained to the cis configuration by thermodynamic considerations and/or the rigidity of the

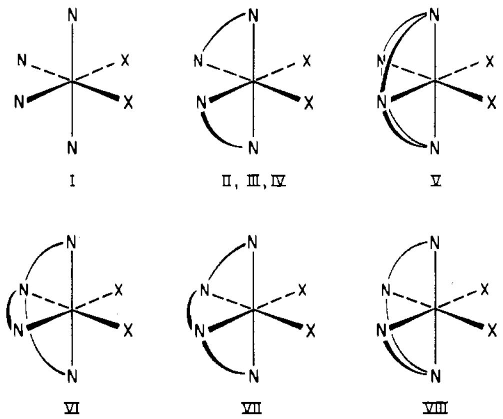
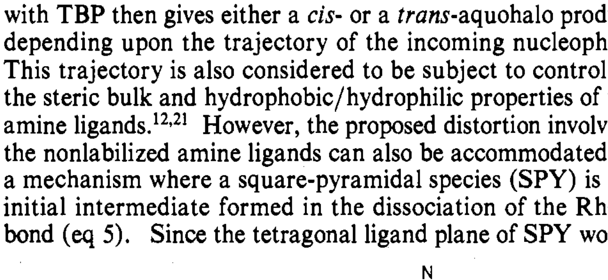


**Figure 2.** Schematic representations of various *cis*-dihalotetraamminerhodium(III) complexes. (Only one optical isomer is shown in each case.)

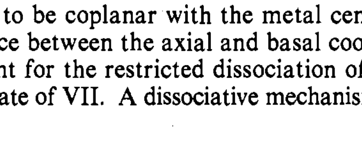
amine ligand(s). Notably, photostereomobility is observed for I, II, VII, and VIII, the first three giving cis to trans isomerization concomitant with chloride photoaquation and the last giving a mixture of *cis*- and *trans*-aquochloro photoproducts. This behavior is in contrast to thermal aquations of haloamine–Rh(III) complexes, which have been demonstrated to occur with full stereochemical retention.[16]

A remarkable result is that while VII parallels I and II in displaying photoisomerization concomitant with halide photoaquation, the photoaquation quantum yields for this complex are several orders of magnitude smaller than for the photoaquations from I, II, V, or VIII.[12] This observation and others relating to the photoreactions of complexes VI, VII, and VIII have been interpreted[12] in terms of a requirement that halide dissociation from the excited complex is simultaneous with a distortion mode involving the nonlabilized amines which is of high energy for complex VII with a trien ligand in the $\alpha$ configuration[20] (Figure 2). In addition it was proposed that this simultaneous distortion terminates at a trigonal-bipyramidal intermediate (TBP), eq 4. Reaction of solvent water



(4)

with TBP then gives either a *cis*- or a *trans*-aquohalo product depending upon the trajectory of the incoming nucleophile. This trajectory is also considered to be subject to control by the steric bulk and hydrophobic/hydrophilic properties of the amine ligands.[12,21] However, the proposed distortion involving the nonlabilized amine ligands can also be accommodated by a mechanism where a square-pyramidal species (SPY) is the initial intermediate formed in the dissociation of the Rh–X bond (eq 5). Since the tetragonal ligand plane of SPY would



(5)

not be expected to be coplanar with the metal center,[22] the increased distance between the axial and basal coordination sites may account for the restricted dissociation of $X^-$ from the LF excited state of VII. A dissociative mechanism leading from the excited state to a SPY intermediate is supported by theoretical calculations comparing the relative energies of the proposed SPY and TBP configurations in the triplet electronic states.[9] In addition, the latter mechanism is more consistent with the observation that the homologous iridium(III) complexes *cis*- or *trans*-$Ir(en)_2Cl_2^+$ undergo little photoisomerization concomitant with halide photoaquation.[23,24] These points are discussed below.

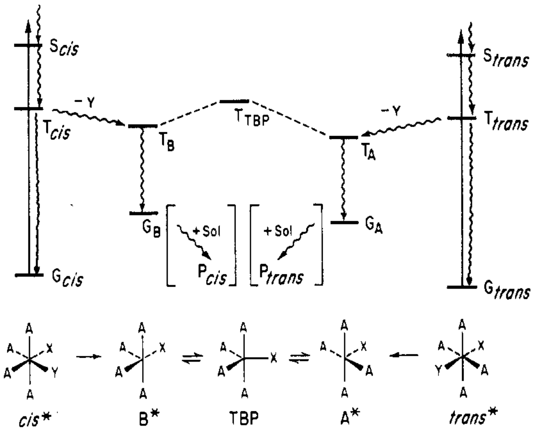


**Figure 3.** Qualitative energy diagram for the photolysis of *cis*- or *trans*-$Rh(NH_3)_4XY^{n+}$ ($X^-$ = $Cl^-$ or $Br^-$, Y = $X^-$ or $H_2O$). G is the ground state, T is the first triplet state, and S is the first singlet excited state of the respective coordination environments (note that the ground state of TBP is a triplet). $P_{cis}$ and $P_{trans}$ are the photosolvation products *cis*- and *trans*-$Rh(NH_3)_4(sol)X^{2+}$, respectively.

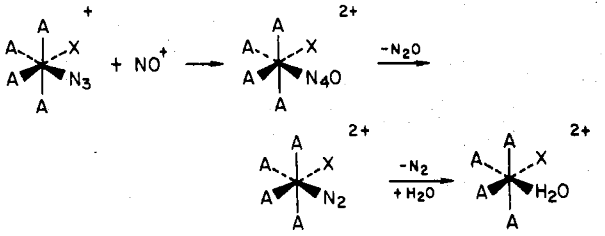
In view of the more quantitative theoretical treatments[9,10] of the photostereochemistry of *cis*-$Rh(NH_3)_4Cl_2^+$ and *cis*-$Rh(en)_2Cl_2^+$ (with which we are in general agreement), the discussion here will follow a more qualitative trend. A qualitative model is described in Figure 3 for the photoreactions of the disubstituted complexes $Rh(NH_3)_4XY^{n+}$ (X = $Cl^-$ or $Br^-$, Y = $X^-$ or $H_2O$). The key features of this model are the following: (1) For either cis or trans hexacoordinate complex, initial excitation to the singlet LF states is followed by internal conversion/intersystem crossing to give the lowest energy LF triplet state $T_{cis}$ or $T_{trans}$, respectively, from which most ligand labilization occurs. (2) This state, having considerable electron density in orbitals antibonding with respect to M–L bonds, dissociates Y to give a pentacoordinate SPY species $Rh(NH_3)_4X^{2+}$ with X in the basal (B) or apical (A) sites and still in a triplet electronic state ($T_A$ or $T_B$, respectively). (3) Available to $T_A$ and $T_B$ are two alternatives: basal–apical rearrangements via the TBP intermediate configuration or deactivation to the lower energy singlet ground states $G_A$ and $G_B$, respectively, having electronic configurations analogous to the $(t_{2g})^6$ ground states of octahedral complexes. (4) Basal–apical rearrangement of the triplet states is relatively facile given the triplet nature of the lowest energy TBP intermediate and the relative closeness in energy of the $T_B$, $T_{TBP}$, and $T_A$ triplets (see below). (5) Deactivation of $T_B$ to $G_B$ or $T_A$ to $G_A$ is not followed by any further rearrangement (since this would require thermal reactivation to the TBP intermediate), but $G_B$ and $G_A$ react rapidly with the nucleophilic solvent to give the hexacoordinate products $P_{cis}$ and $P_{trans}$, respectively.

Point 1 has been discussed elsewhere[4,5] and is discussed below. Point 2 is crucial to the general mechanism of the photoisomerization of $d^6$ complexes. Calculations based on angular overlap methods find both $T_A$ and $T_B$ to be lower in energy than $T_{TBP}$, with $T_B$ higher than $T_A$ ($X^-$ = $Cl^-$ or $Br^-$), but all the states within a range smaller than 5000 $cm^{-1}$.[9] Similarly, a qualitative evaluation of d-orbital energies drawn from crystal field calculations[25] (assuming five identical ligands) leads to the conclusion that a $d^6$ SPY triplet (CFSE

$-14.6Dq$) is more stable than the lowest energy $d^6$ TBP triplet (CFSE $-12.5Dq$). Furthermore, the CFSE for the SPY lowest energy $d^6$ singlet is $-20.4Dq$, suggesting that, despite the added electron pairing energy, the SPY singlets are the lowest energy five-coordinate intermediates, in accord with Figure 3 and point 5.[27-29] These simplistic CFSE calculations also illustrate that the SPY → TBP barriers are functions of the field strengths of the remaining five ligands. Hence a greater LF strength (e.g., chelating amine rather than $NH_3$ or an amine instead of the halide) might inhibit isomerization among the pentacoordinate triplets regardless of the relative stabilities of the SPY species $T_A$ and $T_B$.

With regards to points 3 and 4, the observation of only trans products from the photolysis of *cis*- or *trans*-$Rh(NH_3)_4X_2^+$ in aqueous solution can be rationalized in two ways: Either the triplets are sufficiently long-lived to establish equilibrium favoring the lowest energy $T_A$ species *or* the $T_B$ species is sufficiently long-lived to rearrange to $T_A$ but $T_A$ very rapidly deactivates to $G_A$. According to Vanquickenborne, who assumes the former case,[9] the major difference between $T_A$ and $T_B$ lies in the energy of the singularly occupied "$d_{z^2}$" orbital (approximating the symmetry as $C_{4v}$ in both cases). Qualitatively, the site preference of $X^-$ for the apical position can be understood in terms of this orbital's $\sigma^*$ character with regard to the M–L apical bond. Since the halide is a weaker $\sigma$ donor than $NH_3$,[6c] the energy of this $\sigma^*$ orbital is lower in $T_A$ than $T_B$.

The nitrous acid decompositions of the azido complexes *cis*-$Rh(NH_3)_4(N_3)X^+$ were studied with the goal of testing point 5. This reaction presumably leads to the dinitrogen complex[30] IX (eq 6) which is very labile and gives in this case the *cis*-aquohalo product.



(6)

IX

A = $NH_3$

While the mechanism of the last step in the sequence is not known, it is generally argued[30a,31] that this should be dissociative or dissociative interchange for the Co(III) analogue. A dissociative step should lead to the SPY intermediate $G_B$, but the exact configuration of the complex during an $I_d$ process is rather poorly defined. At any rate, the failure of the nitrous acid decomposition to lead to any cis → trans isomerization of the coordination sphere indicates one of two conclusions, either of which support point 5. If $G_B$ is formed by dissociation of $N_2$, then this intermediate is trapped by the nucleophilic solvent at a rate much faster than it undergoes isomerization. On the other hand, if an $I_d$ mechanism is prevalent, this would be further indication of the very electrophilic character of the $G_B$ intermediate, since this species can then be considered to be trapping an outer-sphere ligand even as the $N_2$ is leaving.

The results with the iridium(III)–haloamine complexes mentioned above can best be interpreted in terms of Figure 3. In most respects the photochemistry of the iridium(III) haloamines mimics that of the Rh(III) homologues;[23,24] however, an exception is the photostereochemistry of *cis*-$Ir(en)_2Cl_2^+$ which photoaquates $Cl^-$, but primarily with retention of configuration (eq 7).

$$cis\text{-}Ir(en)_2Cl_2^+ + H_2O \xrightarrow{h\nu} \underset{>90\%\ \text{cis}}{Ir(en)_2(H_2O)Cl^{2+}} + Cl^- \qquad (7)$$

The rhodium(III) homologue shows ~100% photoisomerization concomitant with photoaquation of $Cl^-$.[10] If labilization from the LF excited state leads simultaneously to a TBP intermediate as proposed in eq 4, then considerably more isomerization might be expected, especially in view of the observation that LF photolysis of *trans*-$Ir(en)_2Cl_2^+$ leads to photoaquation of $Cl^-$ with full retention of configuration.[23] The model described in Figure 3 explains these observations by emphasizing that the SPY intermediate $T_B$ first generated by dissociation of $Cl^-$ has two options, isomerization to $T_A$ *or* deactivation to $G_B$, which ultimately leads to cis products. Since SPY → TBP activation energy for the triplet states is a function of the LF strength (i.e., $Dq$) $T_B \rightarrow T_A$ isomerization would be expected to be slower for the Ir(III) complexes than for the Rh(III) homologues. In addition, deactivation of the triplet state ($T_B \rightarrow G_B$) should be more rapid for Ir(III) owing to the larger spin–orbit coupling constant of this ion.[4] Thus the combined slower isomerization and the faster deactivation of $T_B$ serve to explain the relative reluctance of *cis*-$Ir(en)_2Cl_2^+$ to undergo photoisomerization.

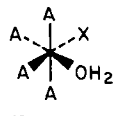
The remainder of the discussion will focus on the nature of the ligand labilized or apparently labilized in the LF photolyses of *cis*-$Rh(NH_3)_4X_2^+$ and *cis*-$Rh(NH_3)_4XY^{n+}$. When *cis*- or *trans*-$Rh(NH_3)_4Cl_2^+$ is irradiated in aqueous solution, $Cl^-$ is labilized with a moderate quantum yield while $NH_3$ aquation is at most a minor pathway (Table II). This behavior parallels closely that of the pentaamminerhodium(III) species $Rh(NH_3)_5Cl^{2+}$.[2,5] The story for the dibromo complexes is similar with $Br^-$ photoaquation predominating, although the cis ion does undergo significantly more $NH_3$ aquation (about 20% of the total photosubstitution) than the trans or the dichloro analogues. In contrast, the predominant photoreaction pathway for $Rh(NH_3)_5Br^{2+}$ is ammine aquation to give *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$.[2,5] The stereochemical origin of the labilized $NH_3$ is not known. The qualitative theoretical treatments[6] generally argue for labilization of the $NH_3$ trans to the $Br^-$, but it is clear from the present study that *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ would be the likely product regardless of which $NH_3$ is labilized.

The photolability of the aquohalotetraammines is less certain. The *trans*-$Rh(NH_3)_4(H_2O)X^{2+}$ ions, like $Rh(NH_3)_5H_2O^{3+}$, appear essentially inert to LF excitation when observed spectrally. Since the latter has been shown by isotopic labeling experiments to be very photoactive but undergoes only photoexchange of coordinated and solvent $H_2O$,[30b] it is likely the *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$ ions are similarly photoactive. The facile photoisomerization of *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ could be explained by an intramolecular mechanism; however, given that halide photoaquation accompanies photoisomerization of the cis-dihalo complexes, the more likely prospect would be a process such as eq 8. The photolytic lability of coordinated $H_2O$ is

$$cis\text{-}Rh(NH_3)_4(H_2O)X^{2+} \xrightarrow{h\nu} Rh(NH_3)_4X^{2+} + H_2O \rightarrow trans\text{-}Rh(NH_3)_4(H_2O)X^{2+} \qquad (8)$$

confirmed by preliminary experiments[32] in nonaqueous media such as formamide. Photolysis of *cis*-$Rh(NH_3)_4(H_2O)X^{2+}$ in formamide solution leads to the efficient formation of *trans*-$Rh(NH_3)_4(\text{formamide})X^{2+}$ ($X^- = Cl^-$ or $Br^-$), notably involving photoisomerization concomitant with the photolabilization of the coordinated $H_2O$.

The *cis*-aquohalotetraammines X provide rare examples where the quantitative LF photochemistry has been studied



X, A = $NH_3$

for a hexacoordinate complex displaying three distinct LF axes (i.e., $NH_3$–$NH_3$, $NH_3$–$H_2O$, and $NH_3$–X). It has been proposed[33] that in such a case, ligand labilization will occur principally from the axis of weakest crystal field strength. According to this criterion, the ligand labilized should be from the $NH_3$–X axis, in contrast to the apparent behavior of these ions in aqueous solution and the observed photochemistry in formamide solution.

Labilization of $H_2O$ from X is perhaps better rationalized by Vanquickenborne's treatment.[6c] For simplification, this method views X and the *cis*-dihalo complexes as having an approximate $D_{4h}$ holohedral symmetry with the $NH_3$–$NH_3$ axis defined as the *z* axis. This leads to the d-orbital splitting diagram

| | energy |
|---|---|
| – $d_{z^2}$ | $2\bar{\sigma}_{ax} + \bar{\sigma}_{eq}$ |
| – $d_{x^2-y^2}$ | $3\bar{\sigma}_{eq}$ |
| – $d_{xy}$ | $4\bar{\pi}_{eq}$ |
| – – $d_{xz}, d_{yz}$ | $2\bar{\pi}_{ax} + 2\bar{\pi}_{eq}$ |

where the d-orbital energies are derived from the additive angular overlap parameters $\bar{\sigma}_{ax}$, $\bar{\sigma}_{eq}$, $\bar{\pi}_{ax}$, and $\bar{\pi}_{eq}$ which are the average parameters for the axial and equatorial ligands. The lowest energy LF state (if one ignores configuration interaction) can be represented in terms of the one-electron transition giving a $(d_{xz})^2(d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1(d_{z^2})^0$ configuration. According to this approximation, the excitation is confined to the *xy* plane involving electronic promotion from an orbital $\pi$ antibonding with respect to the equatorial ligands to one $\sigma$ antibonding with respect to the same ligands with an overall change in each M–$L_{eq}$ bond's strength equal to $+\pi_{eq} - 0.75\sigma_{eq}$.

Which equatorial ligand undergoes aquation depends on several factors, one being the strengths of the various M–L bonds in the ground state. Since the M–$L_{eq}$ bond strength changes resulting from excitation are simply proportional to the spectrochemical field strength of each individual $L_{eq}$,[6c] the magnitude of these changes in X follows the order M–$NH_3$(eq) > M–$OH_2$ > M–X. However, since the ground-state lability of the Rh(III)–$OH_2$ bond is considerably greater than that of the Rh(III)–$NH_3$ bonds,[34] the presumed accelerated $NH_3$ substitution is still apparently too slow to compete with the similarly accelerated labilization of $H_2O$.[35] A similar rationalization can be utilized to explain the predominance of $Cl^-$ aquation in the LF photolyses of aqueous $Rh(NH_3)_5Cl^{2+}$ and *cis*-$Rh(NH_3)_4Cl_2^+$, although in both cases small quantum yields of $NH_3$ aquation were also noted (Table II and ref 5). For the bromo complexes there is a behavioral crossover between the $Rh(NH_3)_5Br^{2+}$ and *cis*-$Rh(NH_3)_4Br_2^+$ LF photochemistries in aqueous solution, the former ion showing predominantly $NH_3$ photoaquation (Table II). There is nothing inherent in the calculations[6c] of bond-strength changes induced by LF excitation that predicts this crossover; however, the explanation may again lie in an analogy drawn from ground-state substitution kinetics. In thermal substitution reactions, the presence of a $\pi$-donor anion in an adjacent (cis) coordination site generally enhances the substitution rates of anionic leaving groups. This enhancement is about 1 order of magnitude for Rh(III)–haloamine complexes but several orders of magnitude for Co(III) analogues.[28] Notably, the probable thermal substitution mechanisms for these Rh(III) complexes is associative or associative interchange while that for the Co(III) complexes is dissociative or dissociative interchange.[29] In comparison, the LF photosubstitution reactions of $d^6$ complexes are generally viewed[6] as dissociative in nature and in this context might be expected to respond to the perturbations in the coordination sphere parallel to those in the Co(III) thermal substitutions.

The key point to be drawn from this discussion is that in comparing the possible reactive pathways from a LF excited state (es), one must consider not only perturbations of the metal–ligand bonding resulting from the excitation but also the activation energies of the various reaction channels from the es. Although often small, the activation energy determines the rate along such a channel, and hence that reaction's ability to compete with other es reactions and radiative and nonradiative deactivation. Systemic perturbations such as changing the nonlabilized ligands or the reaction medium may change the relative magnitudes of these activation energies even if the electronic distributions in the excited states are little perturbed.

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**Registry No.** *cis*-$Rh(NH_3)_4Cl_2^+$, 57195-16-1; *cis*-$Rh(NH_3)_4Br_2^+$, 57172-77-7; *cis*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, 71424-38-9; *cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$, 71382-14-4; *trans*-$Rh(NH_3)_4Cl_2^+$, 38781-29-2; *trans*-$Rh(NH_3)_4Br_2^+$, 61697-82-3; *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$, 38781-25-8; *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$, 71424-39-0; *cis*-$Rh(NH_3)_4(N_3)Cl^+$, 71382-15-5; *cis*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$, 71424-40-3; *cis*-$[Rh(NH_3)_4(H_2O)Br]S_2O_6$, 71382-16-6; *trans*-$[Rh(NH_3)_4(H_2O)Cl]S_2O_6$, 71382-17-7; *trans*-$[Rh(NH_3)_4(H_2O)Br]S_2O_6$, 71424-41-4; *cis*-$[Rh(NH_3)_4(N_3)Cl]_2S_2O_6$, 71382-18-8; *cis*-$[Rh(NH_3)_4Cl_2]Cl$, 71382-19-9; *cis*-$[Rh(NH_3)_4Br_2]Br$, 71382-20-2; *trans*-$[Rh(NH_3)_4Cl_2]Cl$, 37488-14-5; *trans*-$[Rh(NH_3)_4Br_2]Br$, 37488-15-6.

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(19) Abbreviations used: en = ethylenediamine, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine, cyclam = 1,4,8,11-tetraazacyclotetradecane, tren = $\beta,\beta',\beta''$-triaminotriethylamine, trien = triethylenetetraamine.

(20) (a) While this is a plausible explanation, there is an alternative one. Since $\Phi_{Cl}$ is a ratio of rate constants for the reactive, radiative, and nonradiative deactivation pathways, quantum yield perturbations in response to changes in the ligand configuration may be the result of increases or decreases in the nonradiative deactivation rates.[5,20b] (b) Ford, P. C. *Inorg. Chem.* **1975**, *14*, 1440.

(21) A question which was not addressed in this proposal[12] is the point that, since the lowest energy TBP intermediate is in a triplet electronic state

and the products are singlets, the proposed reaction path involving nucleophilic $H_2O$ attack on TBP would necessitate the crossing of triplet and singlet surfaces.

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(26) A referee questioned whether the energetics of this system allow generation of a SPY intermediate in an electronic excited state (i.e., in $T_A$ or $T_B$). While available information is insufficient to answer this with certainty, the following rationale can be offered in support of this premise. Consider the case of cis → trans photoisomerization. The question of primary concern is whether $T_B$ can be generated from $T_{cis}$, i.e., whether $T_B \leq T_{cis}$ in energy. The energy of $T_{cis}$ ($E_1$) can be estimated from the lowest triplet energies of other chloroammine–Rh(III) complexes[27] as $\sim$18 000 $cm^{-1}$ ($\sim$52 kcal, defining the relative energy of $G_{cis}$ as 0). The energy of $T_B$ ($E_2$) is equal to the dissociation energy $E_D$ for eq i (since this

$$cis\text{-}Rh(NH_3)_4Cl_2^+(aq) \rightarrow basal\text{-}Rh(NH_3)_4Cl^{2+}(aq) + Cl^-(aq) \qquad \text{(i)}$$

represents the energy differences between $G_{cis}$ and $G_B$) plus the excitation energy ($E_3$) from $G_B$ to $T_B$. Vanquickenborne's calculation[9] suggests $E_3$ to be $<5000$ $cm^{-1}$; therefore, for the condition $E_1 > E_2 = E_3 + E_D$ to hold, $E_D$ should be $\lesssim 13000$ ($\sim$37 kcal). $E_D$ is an unknown quantity. The activation energy $E_a$ for the aquation of halides from Rh(III) complexes falls in the 9000 $cm^{-1}$ range,[28] but these reactions are probably interchange associative in character.[29] However, analogous Co(III) substitution reactions are largely dissociative in character, with $E_a$ values of $\sim$8000 $cm^{-1}$ noted for aquations of Co(III)–chloroamine complexes. Thus, we do not consider an $E_a$ value less than or equal to 13 000 $cm^{-1}$ to be unreasonable.

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(35) In this context it should be noted that the recent emission studies[5] have allowed the calculation of reaction rates from LF excited states of Rh(III) complexes. For example $Cl^-$ aquation from excited $Rh(NH_3)_5Cl^{2+}$ in ambient aqueous solution ($k = 1.4 \times 10^7$ $s^{-1}$) is $\sim$14 orders of magnitude faster than from the ground state ($k = 5.8 \times 10^{-8}$ $s^{-1}$). $NH_3$ aquation from the same excited state is somewhat slower ($k = 1.5 \times 10^6$ $s^{-1}$) but represents rate accelerations of comparable or greater magnitude over the thermal analogue.

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# "Intersystem Crossing" Yields in Ruthenium(II) and Osmium(II) Photosensitizers

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Originally the efficiencies, $\phi'$'s, of populating the sensitizing charge-transfer excited states of Ru(II) and Os(II) photosensitizers were claimed to be unity. Recent experimental results have raised questions concerning this claim. This paper reexamines the question of the $\phi'$'s of these photosensitizers. With both photochemical and spectroscopic data, the early claim of unity $\phi'$'s is supported.

## Introduction

Since the introduction of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, as a luminescent photosensitizer,[1] it and related metal complexes have provided a wealth of new and potentially useful photochemical systems and reactions.[2–11] One of the key advantages of these metal complexes is the very high efficiency of populating the emitting–sensitizing state following excitation in upper levels. Originally, on the basis of the invariance of the luminescent yield with wavelength, Demas and Crosby[12] claimed that the efficiency of populating the excited state, $\phi'$, was unity.

This claim of a unity $\phi'$ for $[Ru(bpy)_3]^{2+}$ and other complexes having charge-transfer (CT) sensitizing states has recently come into question.[11] On the basis of flash photolysis work, a $\phi'$ of $\sim$0.5 was suggested for $[Ru(bpy)_3]^{2+}$. Similarly, excited-state electron-transfer reactions to $Fe^{3+}$ [6] and energy-transfer studies to Cr(III) complexes seemed to indicate that $\phi'$ for $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) might be 0.5–0.6 times as large as that of $[Ru(bpy)_3]^{2+}$.[13] Although the flash-photolytic work has probably been shown to be in error because of an incorrect assumption concerning the $^*[Ru(bpy)_3]^{2+}$ excited-state absorption,[5,9,13] there still seem to be conflicting claims and uncertainties concerning the correctness of $\phi'$ for Ru(II) and Os(II) sensitizers.

In view of the pivotal role of $[Ru(bpy)_3]^{2+}$ and related Ru(II) and Os(II) complexes in inorganic photochemistry, we felt it essential to address the question of the $\phi'$'s of these complexes. We believe that there is strong evidence to show that $\phi'$ is much greater than these claims would suggest. Indeed, we find no compelling reason to believe that $\phi'$ is less than unity. Our evidence is based on existing and new spectroscopic and photochemical data.

## Experimental Section

**Complexes.** Tris(2,2′-bipyridine)ruthenium(II) chloride was from G. Frederick Smith Chemical Co. and was recrystallized twice from water. The $[Ru(phen)_3]Cl_2$ was made by reduction of $RuCl_3$ with oxalate in the presence of phen. $[Ru(phen)_3]I_2$, isolated by precipitation with NaI, was recrystallized from water. $[Ru(phen)_3]Cl_2$ was formed by reaction of the iodide salt with $Ag_2O$ followed by neutralization with HCl. $Ru(bpy)_2(CN)_2$ and $Ru(phen)_2(CN)_2$ were obtained by reaction of $Ru(L)_2(C_2O_4)_2$ with aqueous NaCN; purification was by dissolving the complex in methanol and passing it through silica gel and alumina columns.

**Wavelength Dependence of the Quantum Yield.** Relative luminescence yields vs. excitation wavelength were obtained by using an optically dense quantum-counter comparator.[14] A schematic representation of this system is shown in Figure 1. Two 1 cm thick cylindrical quantum-counter cells were mounted side by side on a kinematic mount in the excitation path. Samples were rear-viewed by an IR-sensitive photomultiplier tube. One quantum-counter cell contained an optically dense solution of the metal complex, and the other cell contained a 5 g/L Rhodamine B (RhB) reference quantum counter in methanol. At each excitation wavelength, a series of phototube current readings were taken for the unknown ($X$'s). The quantum-counter mount was then moved to position the RhB counter in the excitation beam, and a second series of current readings ($S$'s)

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