complex (Figure 2). The T_{1g} rotatory strength, however, is substantially greater for the *l*-chxn complex. Since the effects of the ligand conformation and asymmetric atoms have been removed, the difference must be due to some other property of the *l*-chxn chelate rings such as the displacement of ligating atoms from octahedral positions.

For both sets of bis(diamine)(dicarboxylato)cobalt(III) complexes, the T_{1g} rotatory strength decreases sharply, $CO_3{}^{2-} > ox^{2-} > mal^{2-}$, with increasing size of the dicarboxylato chelate ring. This trend may be analyzed in terms of the distortion of ligand–metal–ligand bond angles observed in other complexes from the octahedral value (90°): *ca.* 70° for carbonate ion,[33] *ca.* 84° for oxalate ion,[34] and *ca.* 96° for malonate ion.[35] By emphasizing distortions from octahedral geometry rather than the number of atoms in each chelate ring, we see that the net T_{1g} rotatory strength decreases with increasing O–Co–O bond angle in the complexes [Co(diamine)₂(dicarboxylate)]⁺ where diamine = en or *l*-chxn.

It is of interest to compare these results with those obtained for other systems of C_2 symmetry involving dicarboxylato chelate rings of different sizes. For the complexes [Co(ox)₂en]⁻ and [Co(mal)₂en]⁻ it was found[12] that while the T_{1g} component peaks for the malonato complex were more intense than for the oxalato complex, the net T_{1g} rota-

tory strength was clearly greater in the latter case. The relative intensities of the individual component peaks depend greatly on the peak separation and the resulting mutual cancelation of peaks of alternating signs. For the complexes [Co(ox)₂gly]²⁻ and [Co(mal)₂gly]²⁻ it was again found[36] that the complex with the larger chelate rings (mal²⁻) gave a smaller net T_{1g} rotatory strength. Likewise, *s-cis*-[Co(trien)-CO₃]⁺ [37] gives a greater T_{1g} rotatory strength than its analog with a larger chelate ring, *s-cis*-[Co(trien)ox]⁺.[38] In all of these systems, the changes in CD intensities on changing ring size are substantial. A notable exception is the series[10] *s-cis*-[Co(EDDA)L]⁻ where $L^{2-} = CO_3{}^{2-}, ox^{2-}, mal^{2-}$. The CD curves for these three complexes are quite similar in both shape and intensity.

Registry No. [Co(en)₂(ox)]Cl, 17439-00-8; (+)$_D$-[Co(en)₂ox][H-(+)$_D$-tart], 40031-95-6; (+)$_D$-[Co(en)₂ox]I, 40028-98-6; (−)$_D$-[Co(en)₂ox]Br, 31126-57-5; K[Co(EDTA)], 14240-00-7; K[(+)-Co(EDTA)], 40029-01-4; K[(−)-Co(EDTA)], 23594-44-7; [Co(en)₂mal]I, 40029-03-6; (−)-[Co(en)₂mal]I, 40029-04-7; (+)-[Co(en)₂mal]I, 40029-05-8; *trans*-[Co(*l*-chxn)₂Cl₂]Cl, 15693-93-3; (−)-[Co(*l*-chxn)₂CO₃]Cl, 40029-07-0; (−)-[Co(*l*-chxn)₂mal]I, 40029-08-1; (−)-[Co(*l*-chxn)₂ox]-Br, 40029-09-2; [Co(*l*-chxn)₂ox]Cl, 40029-10-5; (+)-[Co(*l*-chxn)₂ox]Cl, 40029-11-6; [Co(en)₂CO₃]Cl, 15842-50-9; [Co(NH₃)₄CO₃]NO₃, 15040-52-5.

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Photoaquation of Some Complexes of Rhodium(III)[1]

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Photoaquation reactions of complexes of the type Rh(AA)₂X₂⁺ and RhA₄X₂⁺, where X is Cl, Br, or I, AA is en, bipy, or phen, and A is py or NH₃, have been studied. Photoaquation of halide was observed for all the complexes while photoaquation of amine could be observed only for complexes with pyridine. The yield of halide increased in the order Cl < Br < I no matter what the amine or the geometry of the complex. The quantum yields were independent of wavelength in the region of d–d transitions and decreased somewhat in the uv region.

Introduction

Photochemical reactions of several complexes of Rh(III) have been reported, although few quantitative studies have been done.[3–10] Attention has been directed to the possibilities for improved synthetic procedures for Rh(III) complexes such as Rh(AA)₂XY⁺ *via* the photoaquation of Rh(AA)₂X₂⁺, where AA is en,[3,11] bipy,[4] or phen,[4] and X and Y are halide or pseudohalide.

Complexes of Rh(III) which contain three or four pyridine molecules have been reported to undergo photoaquation of the pyridine.[5–8] The photochemistry of Rh(NH₃)₅X²⁺ depends on the nature of X. When X is I, photoaquation of the NH₃ trans to the I is observed,[9] whereas when X is Cl, the photoaquation of Cl⁻ is observed,[10] and when X is Br, photoaquation of both Br⁻ and NH₃ is observed.[9]

The low-temperature luminescent behavior of some Rh(III) complexes has been studied, and the luminescence of glassy

(1) Presented in part at the Caribbean Coordination Chemistry Conference, Mona, Jamaica, Dec 1970.
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(11) Abbreviations used in this work: ethylenediamine, en; pyridine, py; 2,2-bipyridyl, bipy; 1,10-phenanthroline, phen; AA, a diamine; A, an amine.

solutions of the complexes $Rh(py)_4X_2^+$ and $Rh(AA)_2X_2^+$, where AA is bipy or phen and X is Cl, Br, or I, has been assigned to a spin-forbidden d-d process.[12,13]

It seemed of interest to compare the yields of the various photoproducts from aqueous solutions of some Rh(III) complexes as a function of the nature of the ligand, the geometry of the complex, and the wavelength of irradiation. This work reports quantum yields for photoaquation reactions of the complexes $Rh(AA)_2X_2^+$ and $RhA_4X_2^+$, where AA is en, bipy, or phen, A is py or NH_3, and X is Cl, Br, or I.

Experimental Section

Physical Measurements. Absorption spectra in the visible–ultraviolet region were obtained with a Perkin-Elmer 202 spectrophotometer. Measurements of absorbance for determination of concentration were made with a Hitachi Perkin-Elmer 139 spectrophotometer. Determinations of the molar conductance for 1.00×10^{-3} M aqueous solutions were made with a Beckman RC 16 B2 bridge and a dip-type cell with a cell constant of 1.022 cm^{-1}. X-Ray powder diffraction photographs were taken with nickel-filtered Cu radiation (λ 1.5418 A) and a Philips Debye-Scherrer 5.73-cm camera.

Materials. Chemicals used in the preparation of complexes were reagent grade 2,2-bipyridyl, reagent grade 1,10-phenanthroline, and ethylenediamine from Aldrich Chemical Co., $RhCl_3 \cdot 3H_2O$ from Ventron Chemical Co., $RhBr_3$ from K and K Laboratories, and pyridine, which was refluxed 2 hr over BaO and distilled (bp 113–114°). Solvents were glacial acetic acid, reagent grade thiophene-free benzene, and water distilled from an all-glass still.

The complexes were all prepared and purified by methods from the literature and characterized by their X-ray powder patterns, molar conductance, and visible-uv spectra, as summarized below.

cis-[Rh(bipy)$_2$Cl$_2$]Cl·2H$_2$O.[14] *d* spacings (A): 12.88 vs, 8.84 vs, 6.88 m, 6.52 w, 6.06 w, 5.82 w, 5.24 m, 4.93 m, 4.78 w, 4.23 m, 3.87 s, and 3.78 s; $\Lambda_M(H_2O, 0.001 M) = 102$ ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 384 (ϵ 110), 312 (ϵ 3.5 × 10^4), 302 (ϵ 3.0 × 10^4). [Lit.[15] *d* spacings (A): 12.9 vs, 8.93 vs, 6.85 m, 6.51 w, 6.06 w, 5.82 s, 5.24 m, 4.93 m, 4.79 w, 4.23 m, 3.91 s, 3.78 s; vis-uv (H$_2$O) (nm): 384 (ϵ 110), 311 (ϵ 2.5 × 10^4), 302 (ϵ 2.43 × 10^4).]

cis-[Rh(bipy)$_2$Br$_2$]Br·2H$_2$O.[14] *d* spacings (A): 13.09 vs, 8.93 vs, 7.16 m, 6.21 w, 5.53 m, 5.11 m, 4.92 m, 4.39 m, 3.98 s, 3.83 s; $\Lambda_M(H_2O, 0.001 M) = 102$ ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 396 (ϵ 170), 312 (ϵ 2.8 × 10^4), 302 (ϵ 2.5 × 10^4). [Lit.[15] *d* spacings (A): 12.9 vs, 8.93 vs, 7.07 m, 6.15 w, 5.78 m, 5.27 m, 4.26 m, 3.93 s, 3.83 s; vis-uv (H$_2$O) (nm): 394 (ϵ 190), 312 (ϵ 2.63 × 10^4), 301 (ϵ 2.60 × 10^4).]

cis-[Rh(bipy)$_2$I$_2$]I.[14] *d* spacings (A): 7.22 s, 7.02 vs, 6.13 m, 5.53 w, 5.15 w, 4.87 w, 4.07 vs, 3.79 w, 3.41 s, 3.24 w, 2.75 s; Λ_M(H$_2$O, 0.001 M) = 103.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 406 (ϵ 8.0 × 10^2), 312 (ϵ 2.4 × 10^4), 302 (ϵ 2.4 × 10^4), 242 (ϵ 6.0 × 10^4). [Lit.[14] vis-uv (H$_2$O) (nm): 402 (ϵ 1.4 × 10^3), 312 (ϵ 2.4 × 10^4), 301 (ϵ 2.25 × 10^4), 238 (ϵ 7.0 × 10^4).]

cis-[Rh(phen)$_2$Cl$_2$]Cl·H$_2$O.[14] *d* spacings (A): 14.55 s, 11.32 s, 9.49 s, 8.55 s, 7.58 w, 6.73 vs, 6.27 w, 5.93 s, 5.46 m, 5.12 w, 4.76 w, 4.45 m, 4.26 m, 3.88 m, 3.72 w, 3.56 s, 3.14 s, 2.83 w; Λ_M(H$_2$O, 0.001 M) = 98 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 385 (ϵ 110), 353 (ϵ 2.2 × 10^3), 338 (ϵ 2.4 × 10^3), 321 (ϵ 4.2 × 10^3), 300 (ϵ 1.7 × 10^3), 273 (ϵ 5.3 × 10^4). [Lit.[15] *d* spacings (A): 14.64 s, 11.18 s, 9.40 s, 8.42 s, 7.49 w, 6.75 vs, 6.27 w, 5.94 s, 5.47 m, 5.15 w, 4.72 w, 4.43 m, 4.21 m, 3.84 m, 3.72 w, 3.54 s, 3.14 s, 2.93 w; vis-uv (H$_2$O) (nm): 385 (ϵ 110), 352 (ϵ 2.7 × 10^3), 336 (ϵ 2.9 × 10^3), 300 (ϵ 1.5 × 10^3), 318 (ϵ 4.75 × 10^3), 273 (ϵ 6.5 × 10^4).]

cis-[Rh(phen)$_2$Br$_2$]Br.[16] *d* spacings (A): 14.71 s, 11.25 s, 9.60 s, 8.71 s, 7.58 w, 6.88 vs, 6.04 w, 5.56 s, 4.50 m, 4.29 m, 3.91 m, 3.75 w, 3.60 m, 3.45 w, 3.40 w, 3.19 s, 2.89 w; Λ_M(H$_2$O, 0.001 M) = 95.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 395 (ϵ 220), 353 (ϵ 2.6 × 10^3), 337 (ϵ 2.8 × 10^3), 320 (ϵ 4.5 × 10^3), 300 (ϵ 1.6 × 10^4), 275 (ϵ 5.2 × 10^4). [Lit.[15] *d* spacings (A): 14.66 s, 11.24 s, 9.40 s, 8.50 s, 7.46 w, 6.75 vs, 6.27 w, 5.94 s, 5.47 m, 5.12 w, 4.74 w, 4.43 m, 4.25 m, 3.86 w, 3.72 w, 3.54 s, 2.93 w; vis-uv (H$_2$O) (nm):

396 (ϵ 235), 353 (ϵ 3.2 × 10^3), 337 (ϵ 3.0 × 10^3), 320 (ϵ 4.5 × 10^3), 300 (ϵ 1.6 × 10^4), 273 (ϵ 6.5 × 10^4).]

cis-[Rh(phen)$_2$I$_2$]I.[13] *d* spacings (A): 13.19 s, 11.26 s, 9.81 s, 8.39 s, 7.83 w, 7.49 s, 7.17 w, 6.73 m, 5.79 s, 5.29 m, 4.69 m, 4.50 w, 4.12 m, 3.98 m, 3.58 s, 3.33 s, 3.14 w, 2.99 w; Λ_M(H$_2$O, 0.001 M) = 98 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 408 (ϵ 420), 353 (ϵ 2.6 × 10^3), 337 (ϵ 2.8 × 10^3), 320 (ϵ 4.5 × 10^3), 300 (ϵ 1.5 × 10^4), 275 (ϵ 5.6 × 10^4). [Lit.[13] vis-uv (H$_2$O) (nm): 409, 353, 337, 320, 300, 275.]

cis-[Rh(en)$_2$Cl$_2$]NO$_3$.[17] *d* spacings (A): 11.41 s, 9.11 w, 7.93 m, 6.80 vs, 6.21 w, 5.86 vs, 5.23 m, 4.88 s, 4.64 w, 4.48 m, 3.79 m, 3.63 m, 3.35 m, 3.18 m; Λ_M(H$_2$O, 0.001 M) = 91 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 352 (ϵ 150), 295 (ϵ 178). [Lit.[17] vis-uv (H$_2$O) (nm): 352 (ϵ 155), 295 (ϵ 180).]

trans-[Rh(en)$_2$Cl$_2$]NO$_3$.[17] *d* spacings (A): 6.70 s, 5.90 s, 5.21 s, 4.86 m, 3.64 m, 3.35 s, 3.18 m, 2.78 w, 2.60 m, 2.48 w; Λ_M = 102.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 410 (ϵ 76), 290 (ϵ 130). [Lit.[17] vis-uv (H$_2$O) (nm): 406 (ϵ 75), 286 (ϵ 130).]

trans-[Rh(en)$_2$Br$_2$]Br.[17] *d* spacings (A): 7.04 s, 6.72 s, 6.34 s, 5.90 s, 4.67 w, 4.28 vs, 4.07 w, 3.91 w, 3.59 vs, 3.35 w, 3.02 w; Λ_M(H$_2$O, 0.001 M) = 108.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 430 (ϵ 100), 279 (ϵ 2.4 × 10^3). [Lit.[17] vis-uv (H$_2$O) (nm): 425 (ϵ 100), 276 (ϵ 1.8 × 10^3).]

trans-[Rh(en)$_2$I$_2$]I.[17] *d* spacings (A): 6.86 m, 5.98 m, 4.92 vs, 3.75 s, 3.46 m, 3.25 s, 3.09 w, 2.96 w, 2.85 m, 2.74 w, 2.58 w, 2.48 w; Λ_M(H$_2$O, 0.001 M) = 103.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 466 (ϵ 230), 342 (ϵ 1.0 × 10^4), 271 (ϵ 2.3 × 10^4), 227 (ϵ 1.9 × 10^4). [Lit.[17] vis-uv (H$_2$O) (nm): 462 (ϵ 260), 341 (ϵ 1.0 × 10^4), 269 (ϵ 3.0 × 10^4), 222 (ϵ 2.0 × 10^4).]

trans-[Rh(py)$_4$Cl$_2$]Cl·5H$_2$O.[18] *d* spacings (A): 12.92 s, 7.49 s, 6.91 w, 6.53 s, 6.14 s, 5.57 m, 4.94 s, 4.50 w, 4.14 w, 4.03 m, 3.70 s, 3.27 m, 3.22 w; Λ_M(H$_2$O, 0.001 M) = 90 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 410 (ϵ 74), 268 (ϵ 7.3 × 10^3), 263 (ϵ 1.4 × 10^4), 256 (ϵ 2.1 × 10^4), 228 (ϵ 2.6 × 10^4). [Lit.[19] vis-uv (H$_2$O) (nm): 411 (ϵ 70), 268 (ϵ 7.7 × 10^3), 261.5 (ϵ 1.1 × 10^4), 255 (ϵ 1.2 × 10^4), 228 (ϵ 3.3 × 10^4).]

trans-[Rh(py)$_4$Br$_2$]Br·5H$_2$O.[18] *d* spacings (A): 12.73 s, 8.72 s, 7.96 w, 7.22 w, 6.78 w, 6.30 s, 5.82 w, 5.30 m, 4.98 m, 4.19 w, 3.70 s, 3.47 m, 2.92 w; Λ_M(H$_2$O, 0.001 M) = 102.5 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 443 (ϵ 130), 315 (ϵ 1.9 × 10^3), 270 (ϵ 1.9 × 10^4), 262 (ϵ 3.0 × 10^4), 257 (ϵ 3.4 × 10^4), 252 (ϵ 2.7 × 10^4). [Lit.[20] vis-uv (H$_2$O) (nm): 443 (ϵ 133), 315 (ϵ 2015), 270 (ϵ 1.96 × 10^4), 262 (ϵ 3.14 × 10^4), 258 (ϵ 3.44 × 10^4), 251 (ϵ 2.77 × 10^4).]

trans-[Rh(NH$_3$)$_4$Cl$_2$]NO$_3$·H$_2$O.[17] *d* spacings (A): 7.47 s, 6.15 s, 5.79 m, 5.26 m, 4.58 s, 4.27 m, 3.71 m, 3.21 m, 2.76 w, 2.67 w; Λ_M(H$_2$O, 0.001 M) = 107 ohm^{-1} cm^2 mol^{-1}; vis-uv (H$_2$O) (nm): 412 (ϵ 66), 290 (ϵ 120). [Lit.[17] vis-uv (H$_2$O) (nm): 412 (ϵ 66).]

Photolyses. Photolyses at 254 and 350 nm were carried out in the Rayonet RPR-100 reactor equipped with Rayonet lamps of the corresponding wavelengths and with the MGM-100 merry-go-round accessory to provide equal intensity for all samples. The 254-nm lamps have a narrow bandwidth but the 350-nm lamps have a bandwidth of about 80 nm, which means values of quantum yields reported for that wavelength region are less accurate. This results in part from the difficulty of determining the correct value for the fraction of incident light absorbed by the sample over the entire 80-nm region.

Two or more quartz test tubes (inner diameter 1.32 cm) for use at 254 nm or Pyrex test tubes (inner diameter 1.58 cm) for use at 350 nm were each filled with 5 ml of the aqueous sample solution and stoppered with rubber syringe caps. A stream of N$_2$ was bubbled through the solution by means of syringe needles inserted through the cap. One such sample was kept in the dark for use as a reference and the remaining solutions were photolyzed for suitable periods of time such that the maximum extent of reaction was 20%.

Some photolyses were carried out at other wavelengths isolated from a medium-pressure Hg-arc lamp by means of filter solutions, prepared by methods from the literature.[21] The wavelengths, filters, solutions, and path lengths used were as follows: 313 nm, 0.089 M aqueous NiSO$_4$ (10 cm), 2.5 × 10^{-4} M aqueous K$_2$CrO$_4$ (10 cm), 0.0245 M aqueous potassium biphthalate (1 cm), and Corning glass filter 7-54 (0.3 cm); 334 nm, 0.192 M aqueous NiSO$_4$ (10 cm), Corning glass filter 7-51 (0.5 cm), and 1.28 g of naphthalene in 100

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ml of isooctane (1 cm); 365 nm, 0.192 *M* aqueous CuSO$_4$ (10 cm), Corning glass filter 7-37 (0.5 cm), and 0.01 g of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate in 100 ml of H$_2$O (1 cm); 436 nm, 0.44 g of CuSO$_4$·5H$_2$O in 100 ml of 2.7 *M* aqueous NH$_3$ (10 cm), and 1.087 *M* aqueous NaNO$_2$ (10 cm). A slit limiting the light beam to about the width of the reaction cell was placed just in front of the cell, a 1-cm quartz spectrophotometer cell. The cell was filled with 3 ml of solution and stoppered with a rubber syringe cap; nitrogen bubbled through the sample before photolysis was started. A sample was kept in the dark as a reference.

The intensity of the incident light was measured by means of the ferric oxalate actinometer[22] and/or the Reineckate actinometer.[23] As an additional check on the light intensity in the Rayonet photoreactor, the photolysis of one complex was determined relative to the actinometer system; then that complex was used as a standard and photolyzed at the same time as all the other complexes with the same halide ligand present. A different standard complex was used for each of the halides to facilitate rapid analysis of the products from both the sample and the standard.

The concentration of amine released during photolysis was measured by a modification of the method of Fritz.[24] The limit of detection of free amine was 5×10^{-6} *M* or less. The photolyzed solution was extracted with an equal volume of benzene, and the resulting benzene solution was titrated with 0.0012 *M* HClO$_4$ in glacial actic acid with 0.1% Methyl Violet in chlorobenzene as indicator. The distribution ratios of amine in benzene and water were determined using solutions prepared from pure samples of the amines and were found to be as follows: py, 0.83; bipy, 0.91; phen, 0.80. Presence of added complex did not affect the values of the distribution ratio. The visual end point gave the same result in the titration as did a photometric titration at 431 nm using a Beckman DU spectrophotometer. Titration of ammonia and ethylenediamine was done potentiometrically in aqueous solution.

The concentration of halide released during photolysis was measured with an Orion chloride, bromide, or iodide selective ion electrode and an Orion double-junction reference electrode with the Orion 404 meter. The limits of detection of halide were 5×10^{-5} *M* for Cl$^-$, 5×10^{-6} *M* for Br$^-$, and 5×10^{-8} *M* for I$^-$. Calibration curves were prepared after measurements on standard solutions of the same ionic strength and range of concentration as the sample solutions.

The vis-uv spectrum was obtained immediately after photolysis in order to provide evidence of any other reactions besides photoaquation of halide or amine, such as photoisomerization or photoredox reactions.

A series of measurements of the photolysis of 1×10^{-3} *M* trans-[Rh(py)$_4$Cl$_2$]Cl and cis-[Rh(bipy)$_2$Cl$_2$]Cl in the presence of varying amounts of NaNO$_3$ was carried out to test the effect of nitrate on the photoaquation reaction. No effect could be detected. Since determinations of halide released were more reliable when no anionic halide was present in the solution before photolysis, the complexes were converted from halide salts into the nitrate form by ion exchange on a Dowex 1-X8 column in the nitrate form. The concentration of the eluate was determined spectrophotometrically and adjusted to 1.00×10^{-3} *M* before photolysis.

The temperature of the samples during photolysis was 30°. The reference solutions kept in the dark were maintained at the same temperature. The duration of photolysis varied from about 10 sec to about 10 min for most cases. Measurements at 313, 334, 366, and 436 nm required several hours of photolysis. These latter cases were the only experiments in which a correction for thermal reaction, the aquation of halide, measured for the dark solution, had to be made.

Results

All the complexes studied underwent photosolvation of halide. The quantum yields at 254 nm and at 350 nm for this process, based on the measured concentration of free halide, are listed in Tables I and II. Photoaquation of amine could be detected by measurement of the concentration of free amine only for the complexes with pyridine. The quantum yields for this reaction are given in Tables I and II for 254 and 350 nm, respectively. Quantum yields for both processes at other wavelengths are listed in Table III.

The fraction of light absorbed by each sample was deter-

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Table I. Quantum Yields for Photoaquation of Halide and of Amine at 254 nm

Complex	X = Cl	X = Br	X = 1
	Φ_{X^-}		
cis-Rh(phen)$_2$X$_2^+$	0.0096^a	0.016	0.052
cis-Rh(bipy)$_2$X$_2^+$	0.013	0.021	0.13
cis-Rh(en)$_2$X$_2^+$	0.056		
trans-Rh(en)$_2$X$_2^+$	0.030	0.054	0.23
trans-Rh(NH$_3$)$_4$X$_2^+$	0.031		
trans-Rh(py)$_4$X$_2^+$	0.0094	0.016	
	Φ_{py}		
trans-Rh(py)$_4$X$_2^+$	0.0092	0.0085	

^{a} The values reported are averages of two or more determinations with deviations of 10% or less.

Table II. Relative Quantum Yields for Photoaquation of Halide and of Amine at 350 nm

Complex	X = Cl	X = Br	X = I
	Φ_{X^-}		
cis-Rh(phen)$_2$X$_2^+$	1.0^a	1.2	3.6
cis-Rh(bipy)$_2$X$_2^+$	1.5	1.7	6.7
cis-Rh(en)$_2$X$_2^+$	5.3		
trans-Rh(en)$_2$X$_2^+$	4.3	5.0	14
trans-Rh(NH$_3$)$_4$X$_2^+$	2.1		
trans-Rh(py)$_4$X$_2^+$	1.2	1.4	
	Φ_{py}		
trans-Rh(py)$_4$X$_2^+$	1.9	0.63	

^{a} The values reported are averages of two or more determinations with deviations of 10% or less. Due to the uncertainty in the absolute quantum yields, they are here reported relative to cis-Rh(phen)$_2$Cl$_2^+$, whose absolute quantum yield is of the magnitude of 0.02 ± 0.01.

Table III. Dependence of Quantum Yields for Photoaquation of Halide and of Amine on Wavelength

| Complex | Wavelength, nm | | | |
	436	366	334	313
	Φ_{X^-}			
cis-Rh(bipy)$_2$Cl$_2^+$	0.032	0.035		
cis-Rh(bipy)$_2$Br$_2^+$	0.035	0.037		
cis-Rh(bipy)$_2$I$_2^+$	0.112	0.122		
trans-Rh(py)$_4$Cl$_2^+$	0.020	0.023	0.018	0.034
	Φ_{py}			
trans-Rh(py)$_4$Cl$_2^+$	0.023	0.031	0.028	0.043

mined from the absorption spectrum, the concentration, and the path length of the reaction cell. No correction was made for internal filter effects. The incident intensities found for each wavelength region were as follows (nm, quanta/sec): 254, 1.44×10^{17}; 313, 2.60×10^{13}; 334, 3.14×10^{14}; 3.66, 1.79×10^{15}; 436, 2.82×10^{15}; 350, $\sim 8.2 \times 10^{16}$. The last figure is approximate because the radiation used has a wide bandwidth and it was not possible to determine accurately the fraction of light absorbed either by an actinometer system or by the samples. Because the complexes were measured relative to a standard complex which generally had a similar spectrum in that region, the relative values of the quantum yields listed in Table II for 350 nm should be reasonably precise. The error in the absolute values may be rather large.

Most of the quantum yields reported in Tables I-III are averages of two and usually more different determinations at varying times of photolysis. In a few cases the quantum yield decreased slightly but steadily with increasing time of photolysis. In these cases the value reported was obtained by extrapolating to zero time.

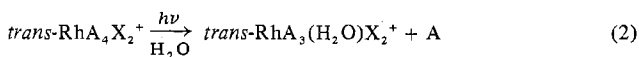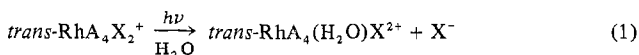Although the absorption spectra of the photolyzed samples were examined carefully for any changes which might indicate

photoisomerization or photoredox reactions, only one ex-
ample of photoisomerization could be observed. The spec-
trum of the cis complex with ethylenediamine changes upon
photolysis until it corresponds to the spectrum of the trans
isomer. It was not possible to determine the amounts of
cis-dichloro, *cis*-chloroaquo, *trans*-dichloro, and *trans*-chloro-
aquo isomers since the reaction was not allowed to go to
completion and the spectra of dichloro and chloroaquo com-
plexes are very similar for both the cis and trans complexes.
It was possible, however, to estimate the total amount of
cis to trans isomerization. From this a total quantum yield
for photoisomerization of *cis*-Rh(en)$_2$Cl$_2$$^+$ was calculated to
be 0.17 at 254 nm and 0.38 at 350 nm. These values in-
cluded any isomerization of *cis*-Rh(en)$_2$(H$_2$O)Cl^{2+} as well as
that of the dichloro complex.

Discussion

Since the effect of the geometry of the complex on the
nature of the photoproducts is of interest, the correct
assignment of geometrical isomers is important. In view of
the confusion which has existed in the literature with respect
to the geometrical isomers of some of these com-
plexes[4,14,16,18,25,26] the details of the X-ray powder patterns
and the vis–uv spectra have been included for all of the sam-
ples used in this work. These data confirm the observation
that only the complexes with en give both cis and trans iso-
mers. The complexes with bipy and phen apparently give
only cis isomers[26] while those with NH$_3$ and py give only
trans isomers.[27] Thus the complexes studied can be divided
into three groups: (A) trans complexes with monodentate
amines, (B) trans complexes with bidentate amines, and (C)
cis complexes with bidentate amines.

Since no evidence was found for photoredox reactions in
any of the photolyses, such reactions will be omitted from
this discussion. The possibility that some photoredox
processes occur cannot be completely eliminated, however.[28]

The quantum yields in Tables I–III were determined from
measurements of the yields of free halide[29] and of free
amine. For the complexes of group A, with monodentate
amines, these quantum yields could be taken as the yields for
reactions 1 and 2, respectively. Since the spectral changes

$$trans\text{-}RhA_4X_2^+ \xrightarrow[\text{H}_2\text{O}]{h\nu} trans\text{-}RhA_4(\text{H}_2\text{O})X^{2+} + X^- \qquad (1)$$

$$trans\text{-}RhA_4X_2^+ \xrightarrow[\text{H}_2\text{O}]{h\nu} trans\text{-}RhA_3(\text{H}_2\text{O})X_2^+ + A \qquad (2)$$

observed were consistent with these reactions, it was assumed
that there was no photoisomerization. Subsequent reactions
were shown to be slow relative to the time needed for the
analyses.

The interpretation of the measured yields for complexes in
group B is somewhat more difficult. The primary product
for photosolvation of amine is presumably unstable and could

(25) P. Andersen, J. Josephsen, G. Nord, C. E. Schaffer, and P. L.
Tranter, *Chem. Commun.*, 408 (1969).

(26) L. H. Berka, R. R. Gagne, G. E. Philippon, and C. E. Wheeler,
Inorg. Chem., 9, 2705 (1970).

(27) D. Dollimore, R. D. Gillard, and E. D. McKenzie, *J. Chem.
Soc.*, 4479 (1965).

(28) T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 94,
1797 (1972).

(29) The values in the tables are from experiments in which no
ionic halide was initially present. Measurements made on samples of
halide salts without conversion to the nitrate form showed some
differences in the free halide concentration. However, the precision
of these measurements was very poor and it was not possible to detect
any systematic variation which might be due to an effect of free
halide. Further experiments in which only small amounts of halide
are added to the samples are planned. Also planned are experiments
to test for photoredox reactions and possible Rh(I) catalysis.

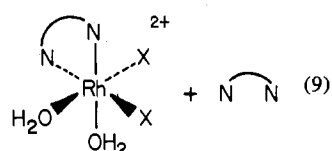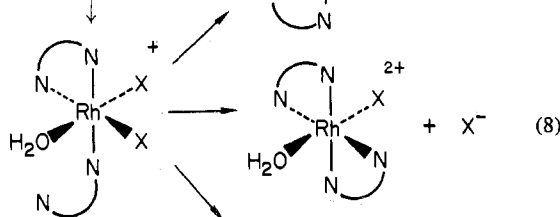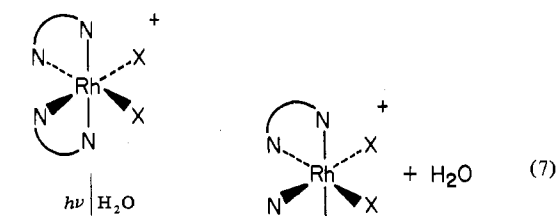react further to give several products, *i.e.*

The fact that no free diamine was detected means that re-
action 5 did not occur to any significant extent, but it does
not mean that reactions 3 and 4 did not occur. However, re-
action 4 was shown to be negligible by the spectral changes
during photolysis, since the spectra of the cis complexes are
known.[17] Thus the quantum yield for photoaquation of
amine should be the yield for reaction 3, but since the
product is the initial complex, this quantum yield could not
be determined with these data. Since (4) is negligible, the
yield based on free halide can be taken as the yield for photo-
aquation of halide for these complexes.

$$trans\text{-}Rh(AA)_2X_2^+ \xrightarrow[\text{H}_2\text{O}]{h\nu} trans\text{-}Rh(AA)_2(\text{H}_2\text{O})X^{2+} + X^- \qquad (6)$$

A similar ambiguity in the quantum yield for photoaqua-
tion of amine for complexes of group C was found. In addi-
tion there may be some error in the value for photoaquation
of halide, as shown below. The two possible primary prod-
ucts from photoaquation of amine can each undergo several
reactions. The negligible yields of free amine indicate only
that reactions 9 and 12 are negligible. Reactions 7 and 10
could be significant but are not detectable since they involve
return to starting material. For complexes with phen and
bipy, reaction 8 was not significant. For the complex with
en, however, reaction 8 may be an important mode of isomeri-
zation, as well as or instead of a direct process such as (13).
The products from (8) and (13) were both present, but the
trans-chloroaquo complex could have resulted from photo-
aquation of the *trans*-dichloro product of reaction 13.
Similarly the yield of (11) cannot be separated from the total
yield of free halide, which presumably includes the yield of
reaction 14.

In other words for complexes in group C the yield for
photoaquation of amine cannot be determined and the yield
for photoaquation of halide may be too large if reactions 11
and 8 occur to a significant extent. For complexes with
phen and bipy, reaction 8 can be neglected and reaction 11
probably causes little error in the yield for (14) since reaction
10 should be favored over reaction 11 on the basis of the
greater ease of replacement of H$_2$O relative to halide in such
complexes.[3,4] For complexes with en the error in the yield
for halide may be more significant. In order to resolve such
an ambiguity it would be necessary to do the photolyses with
much greater quantities of material and analyze the com-
plexes produced.

In spite of the uncertainties discussed above, several im-
portant conclusions can be drawn. First, the order of quan-

$$cis\text{-}Rh(en)_2X_2^+ \xrightarrow{h\nu} trans\text{-}Rh(en)_2X_2^+ \tag{13}$$

$$cis\text{-}Rh(AA)_2X_2^+ \xrightarrow[H_2O]{h\nu} cis\text{-}Rh(AA)_2(H_2O)X^{2+} + X^- \tag{14}$$
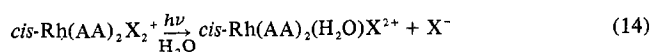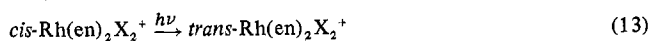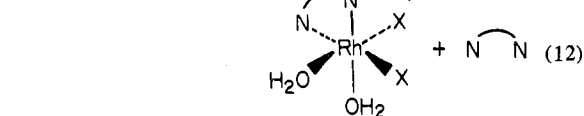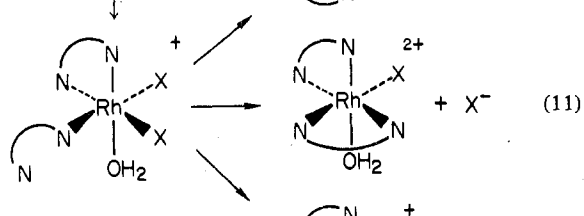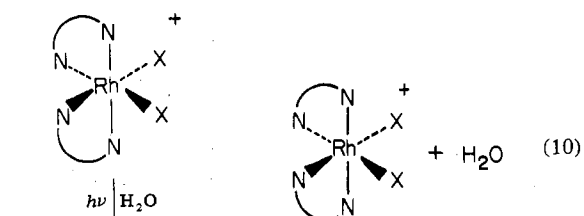
tum yields for photoaquation of halide was always I > Br > Cl, regardless of what amine was present, whether the complex was cis or trans, or the wavelength of radiation used.

This is of some interest since the wavelengths used correspond to several types of transitions. For *trans*-Rh(py)$_4$Cl$_2^+$ the bands at 411 and 310 nm have been assigned[20] as d–d transitions and the bands at shorter wavelengths to internal ligand transitions. The corresponding bromo complex has a charge-transfer transition at 312 nm as well as a d–d band at 443 nm and internal ligand bands in the uv region.[20] For the complexes of *cis*-Rh(AA)$_2$X$_2^+$ where AA is bipy or phen the absorption bands in the visible region have all been assigned[13] as d–d transitions with some possible charge-transfer character for the iodo complexes. The bipy complexes have a band at 312 nm assigned[13] to an internal ligand transition and have other internal ligand bands at shorter wavelengths. Similarly all the phen complexes have an internal ligand band at 273 nm. The bands at 337 and 224 nm for *cis*-Rh(phen)$_2$I$_2^+$ have been assigned to CT transitions.[13] Although detailed assignments have not been reported for the remaining complexes, the bands in the visible region are so weak they can probably be assumed to be d–d bands. These complexes,

with en or NH$_3$, lack the characteristic internal ligand bands in the uv which are shown by the aromatic amines. The bands observed in the uv for the en and NH$_3$ cannot easily be assigned, but the more intense ones are probably of CT character.

We can conclude that the order of the yields for halide photoaquation is not dependent on the type of transition. If the above assignments are accepted, it can be seen from Table III that the yields for photoaquation of both halide and amine are essentially independent of wavelength in the d–d region. This suggests that the reactions are occurring from the same low-lying excited state, perhaps the triplet state found to be responsible for the luminescence from some of these complexes.[12] Further work needs to be done to see if the excited state is indeed a triplet state. The quantum yields at 254 nm are always somewhat lower than the yields at other wavelengths, which is reasonable if internal ligand bands are involved. Similar behavior has been reported for Rh(NH$_3$)$_5$Cl^{2+} [10] and for Rh(NH$_3$)$_5$I^{2+} for which a plausible explanation[28] was offered.

Several other comparisons are of interest. The quantum yield of halide photoaquation varies as the amine is varied and the order is independent of both the wavelength and the nature of the halide. For the cis complexes the yield of halide decreased in the order en > bipy > phen and for the trans complexes in the order en ~ NH$_3$ > py.

The relative yields of halide and amine could only be determined for the complexes with monodentate amines. There is a large difference between the complexes of NH$_3$ and of py, since the former gave no significant photoaquation while the latter did. Perhaps this can be related to the greater steric problems for a tetrapyridine complex. The ratio of the yield of pyridine to the yield of halide, Φ_{py}/Φ_{X^-}, varied with wavelength and the nature of the halide. In the visible region, the ratio is about 1.3 for the chloro complex and 0.4 for the bromo complex. The ratios in the uv are 1 for the chloro complex and 0.5 for the bromo complex. Thus, the yield of pyridine is greater for the chloro complex. In all cases, however, the ratio of the quantum yields is less than 2.0, which would be the ratio on a purely statistical basis for a molecule with four pyridine and two halide ligands. In other words, the photoaquation of halide is apparently favored in these systems.

The only observed isomerization was for a cis complex. It was disappointing in view of the large quantum yields estimated for photoisomerization for *cis*-Rh(en)$_2$Cl$_2^+$, which were greater than the yields for photoaquation of halide both at 254 and at 350 nm, that the cis complexes with bipy and phen showed no evidence of photoisomerization. Such a reaction would have provided a synthetic route for the trans complexes, which have not been prepared by any other method.