to be $x(1-x)$. This is consistent with the linear concentration dependence since the Mn(II)–Ni(II) dipolar term is too small to produce the observed increase in line width.

The only free parameter is H_e^1, all others having been previously fixed or calculated. A value of $H_e^1 = 3500$ G produces the best fit to the observed data (Figure 1).

This value of an exchange field is consistent with the assumption that the system is in the intermediate exchange range. Since the anisotropic and antisymmetric exchange line-broadening terms[24,25] are expected to vary as $(\Delta g/g)^4 H_{ex}$[12] and $(\Delta g/g)^2 H_{ex}$,[12] respectively, and $\Delta g/g \simeq 0.1$, these terms are clearly smaller than H_e^2 itself. This provides the justification for considering only the isotropic exchange terms in the line-broadening expression.

Finally it should be emphasized that the treatment of these data is based on several simplifying assumptions. Most notably these are (1) a simple form for the line-width dependence for the Mn(II)–Mn(II) interaction and (2) the use of the $^{10}/_3$ factor over the full concentration range, which may not be applicable. Thus the value of H_e^1 should be regarded as an order of magnitude estimate of the Mn(II)–Ni(II) isotropic exchange interaction at room temperature.

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Ligand Field Photochemistry of *cis*-α- and *cis*-β-Triethylenetetramine Complexes of Rhodium(III)

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The photosensitivity of *cis*-α- and *cis*-β-[Rh(trien)ClX]$^{n+}$ (X = Cl, H$_2$O) toward chloride loss and isomerization is dependent upon the geometric configuration of the trien ligand. *cis*-α- and *cis*-β-[Rh(trien)Cl(H$_2$O)]$^{2+}$ and *cis*-α-[Rh(trien)Cl$_2$]$^+$ give *trans*-[Rh(trien)Cl(H$_2$O)]$^{2+}$ as the sole photoproduct, while *cis*-β-[Rh(trien)Cl$_2$]$^+$ yields a mixture of 65% *cis*-β- and 35% *trans*-[Rh(trien)Cl(H$_2$O)]$^{2+}$ as primary photoproducts. The cis-β ions undergo aquation/isomerization at quantum efficiencies ($\phi \approx 0.4$) typical of chloride labilization from less chelated haloamine complexes of Rh(III), and the cis-α ions are at least 2 orders of magnitude less photoreactive than the isomeric cis-β ions. A model, involving excited-state distortion toward a trigonal-bipyramid (TBP) geometry, is proposed to account for the photoinduced isomerizations at efficiencies dependent upon the ground-state geometry.

Introduction

Ligand field irradiation of Rh(III) complexes in aqueous solution typically leads to efficient ligand substitution (aquation) with no measurable interference from redox processes.[1] The semiempirical and theoretical models used to describe the ligand field photochemistry of Cr(III)[2] and Co(III)[3] have been extended to Rh(III)[4] complexes, but with limited success.[5] Theoretical analysis of Rh(III) photochemistry is complicated by an inner-system crossing, as low-lying triplet states have been identified as the photoreactive states in the halopentaammine rhodium(III) cations.[6] The interpretation is further hampered by the stereochemical consequences of ligand field irradiation.

The available studies reveal a tantalizing mixture of stereoretention and stereomobility upon ligand field irradiation of Rh(III) complexes; models have not yet been presented which account for this seemingly inconsistent behavior. Stereoretentive aquation of the low-field ligand appears to be the norm for trans-disubstituted tetramine complexes of Rh(III),[7a] in contrast to the stereomobility observed for several cis-disubstituted tetramines. Photolysis of *cis*-[Rh(NH$_3$)$_4$Cl$_2$]$^+$ [8] and *cis*-[Rh(en)$_2$Cl$_2$]$^+$ [7b] leads to the corresponding *cis*-chloroaquo ions, while photolysis of *cis*-[Rh(cyclam)Cl$_2$]$^+$ [9,10] at "natural pH" in H$_2$O/CH$_3$CN solution leads to chloride labilization with retention of the cis configuration. Chloride labilization occurs upon ligand field photolysis, as well as thermal aquation, for $[Rh(tren)Cl_2]^+$. Different chlorides are released during the thermal and photochemical processes,[11] however, implying a stereospecific excited-state reactivity unrelated to the ground-state reaction path.

The lack of any apparent pattern in the stereochemistry of the ligand field photolysis of Rh(III) complexes, the evidence of stereospecific excited-state reactions, and the observation of photoinduced isomerizations of thermally stereorigid ions have led us to a study of the stereochemistry of the photoinduced reactions of Rh(III) complexes. We report here on the photochemical behavior of *cis-α-* and *cis-β*-$[Rh(trien)ClX]^{n+}$ (X = Cl, H_2O). Photolysis of the analogous Co(III) complexes[12] showed that the ground-state configuration of the multidentate amine has a profound effect upon the photochemical behavior of the ion, even though no amine labilization could be detected. The fundamental questions we address here are whether the ground-state stereochemistry of the amine chelate has any effect on the normally efficient photoinduced Rh–Cl bond cleavage and, if so, whether that information could lead to insight into the nature of the photoproduced, and chemically reactive, excited state.

Experimental Section

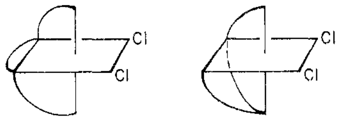
Preparation of Compounds. ***cis-α*-Dichloro(triethylenetetramine)rhodium(III) Chloride.** The method of Basolo and Johnson,[13] as amended by Gillard et al.,[14] was used to prepare *cis-α*-$[Rh(trien)Cl_2]Cl$. Each sample was recrystallized from HCl before photolysis. The electronic spectra agreed with the previously reported spectrum: given,[14] λ_{max} 352 nm (ε 240), λ_{max} 292 (210); found, λ_{max} 352 (235), λ_{max} 292 (195). The infrared spectrum was virtually identical with that reported[14] for the cis-*α* complex.

***cis-β*-Dichloro(triethylenetetramine)rhodium(III) Chloride.** Repeated crystallization of the mother liquor separated from *cis-α*-$[Rh(trien)Cl_2]Cl$ eventually led to the isolation of *cis-β*-$[Rh(trien)Cl_2]Cl$.[14] The electronic spectrum is similar to that previously observed: given, λ_{max} 350 (270), λ_{max} 300 (290); found, λ_{max} 350 (273), λ_{max} 300 (290). The infrared spectrum was virtually identical with that reported for the *cis-β* ion. On the basis of the infrared and electronic spectra, we estimate any contamination of the *cis-α* ion to be less than 5%.

***cis-α*- and *cis-β*-Chloroaquo(triethylenetetramine)rhodium(III) Cations.** The chloroaquo ions were prepared by thermal aquation of the corresponding dichloro ions. At 60 °C, aquation of each isomer was complete within 5 h, as indicated by the generation of a stable electronic spectrum. During the aquation, 1.0 mol (±0.05) of chloride/mol of initial complex is released to the solution, and negligible pH changes occur. The chloroaquo samples were stored in the dark at room temperatue, and no change in the electronic spectrum was noticed in such samples for several months. The electronic spectra of the *cis-α*- and *cis-β*-chloroaquo ions are distinct (cis-*α*, λ_{max} 347 nm (ε 212), λ_{max} 295 (157); cis-*β*, λ_{max} 292 (280), shoulder at 340 nm).

Photolyses. Photolyses were perfomed with a 200-W high-pressure Hg short-arc lamp (Illumination Industries Inc.). Quantum yields for the two cis-*β* ions were determined using an interference filter (Baird Atomic) with a transmittance maximum centered at 343 nm and a fwhh of 20 nm. This closely corresponds to the maximum of the lowest energy ligand field bands. Incident light intensities were measured by ferrioxalate actinometry and averaged 3.0×10^{-10} einstein/s over a rectangular (0.8 cm × 2.0 cm) cell face. A hot mirror (Baird Atomic) was used to reduce thermal interference.

The radiation transmitted by the interference filter was not sufficiently intense to allow complete photolysis within a reasonable period so a higher photon flux was allowed by replacing the interference filter with a Corning color glass filter (CS5-57) which transmitted light of wavelengths greater than 360 nm. This corresponded to the low-energy third of the lowest energy ligand field bands, and the spectral changes induced by broad band-pass irradiation were indistinguishable from those induced by monochromatic light at 343 nm. By using the solution's optical density at 360 nm to calculate the percent absorption, quantum yields could be estimated for photolyses perfomed with the broad band-pass filter. Photolyses were performed in room-temperature 0.1 N H_2SO_4 solutions; a dark reaction was monitored, but only during the prolonged photolysis of *cis-α*-$[Rh(trien)Cl_2]^+$ (ca. 80 h) was significant thermal reaction detected during the photolysis period.



cis−α cis−β

Figure 1. Representative structures of *cis-α*- and *cis-β*-$[Rh(trien)Cl_2]^+$.

Instrumentation. Electronic spectra were recorded on a Beckman Acta M IV spectrophotometer in the absorbance mode. A Radiometer (Copenhagen) PHM 64 pH meter and a GK2320C combined electrode (Radiometer) were used for pH measurements, and a F1012Cl Selectrode and K701 calomel reference were used for chloride determinations.

Product Analysis. Two previously described[15] graphical techniques were used to analyze solution composition. The photoinduced changes in the spectra of *cis-α*-$[Rh(trien)Cl_2]^+$ and both chloroaquo ions could be successfully analyzed by a two-component scheme which showed that all of the intermediate spectra could be regenerated as linear combinations of the initial and final product spectra. For the photolysis of *cis-β*-$[Rh(trien)Cl_2]^+$, a triangular graph method[15] was needed to account for the presence of three absorbing species in solution.

Quantum Yields. Maximum values for amine release yields were detected by pH changes, and chloride release was monitored with a chloride electrode and by electronic spectral changes. Each reported quantum yield is the average of at least three separate experiments, and typical precision was ±5%. Photolysis of *cis-β*-$[Rh(trien)Cl_2]^+$ involved formation of two photoproducts, and the quantum yields were determined during the early stages of photolysis (less than 15% total reaction). For the systems where only one photoproduct formed, a more complete analysis, as described earlier,[11,15] was employed as it used data throughout the photolyses.

Results

The structures of *cis-α*- and *cis-β*-$[Rh(trien)Cl_2]^+$ are represented in Figure 1. The electronic absorption spectra of the ions consist of two ligand field transitions labeled as ${}^1T_1 \leftarrow {}^1A_1$ and ${}^1T_2 \leftarrow {}^1A_1$ (using O_h terminology) at lower energies than the intense LMCT transitions in the ultraviolet. The asymmetry of the ${}^1T_1 \leftarrow {}^1A_1$ transition, characteristic of *cis-α*-$[M(trien)Cl_2]^+$ ions (M = Co,[16] Cr,[17] Rh[14]), is evident as a weak shoulder on the low-energy side of the absorption band. The dichloro ions are relatively stable in room-temperature aqueous solution, slowly releasing chloride ion and forming the chloroaquo ions. The spectra of the two chloroaquo thermal products are distinct (see Experimental Section) and the aquation is thus assumed to proceed with retention of geometric configuration. The *cis-α*- and *cis-β*-$[Rh(trien)Cl(H_2O)]^{2+}$ ions are stable indefinitely in room-temperature acidic aqueous solution.

Photolyses. ***cis-α*-$[Rh(trien)Cl_2]^+$.** Acidic solutions of *cis-α*-$[Rh(trien)Cl_2]^+$ lose chloride ion upon irradiation of the low-energy, ${}^1T_1 \leftarrow {}^1A_1$ absorption band and undergo the spectral changes represented in Figure 2. The spectrum of the final photoproduct has λ_{max} at 298 nm with a shoulder near 400 nm. Prolonged photolysis leads to only minimal pH changes ($\phi_{H^+} < 10^{-4}$), while 0.9 mol (±0.1) of chloride/mol of initial complex is released into solution. The analytical and spectral data imply that photolysis leads to the formation of *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$ (eq 1). The photoproduct

$$\textit{cis-}\alpha\text{-}[Rh(trien)Cl_2]^+ + H_2O \xrightarrow[H^+]{h\nu} \textit{trans-}[Rh(trien)Cl(H_2O)]^{2+} + Cl^- \quad (1)$$

trans-$[Rh(trien)Cl(H_2O)]^{2+}$ has not been previously reported, but the spectrum is similar to that of *trans*-$[Rh(en)_2Cl_2]^+$,[13]

Table I

compd	ϕ_{Cl^-}	ϕ_{H^+}	photoproducts
cis-α-$[Rh(trien)Cl_2]^+$	5×10^{-4} [a]	$<10^{-4}$	*trans*-$[Rh(trien)Cl(H_2O)]^{2+}$
cis-α-$[Rh(trien)Cl(H_2O)]^{2+}$	3×10^{-3} [a]	$<10^{-4}$	*trans*-$[Rh(trien)Cl(H_2O)]^{2+}$
cis-β-$[Rh(trien)Cl_2]^+$	0.21	$<10^{-4}$	65% *cis*-β- and 35% *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$
cis-β-$[Rh(trien)Cl(H_2O)]^{2+}$	0.23	10^{-4}	*trans*-$[Rh(trien)Cl(H_2O)]^{2+}$

[a] Extended (24-h) photolyses using an interference filter caused no detectable spectral changes, so ϕ_{Cl^-} for the two cis-α ions must be less than 5×10^{-3}. The ϕ_{Cl^-} values reported here for the cis-α ions were estimated upon photolysis with a CS5-57 Corning glass filter (see Experimental Section).

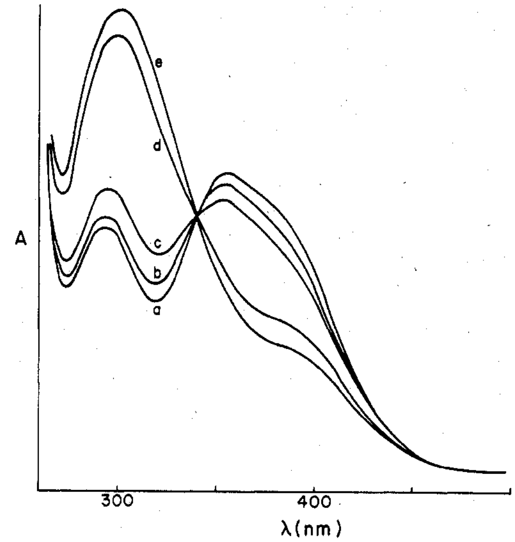


Figure 2. Spectral changes induced by ligand field photolysis of *cis*-α-$[Rh(trien)Cl_2]^+$. Photolysis times for curves a–e respectively are 0, 1.75, 4.25, 28.5, and 77.5 h.

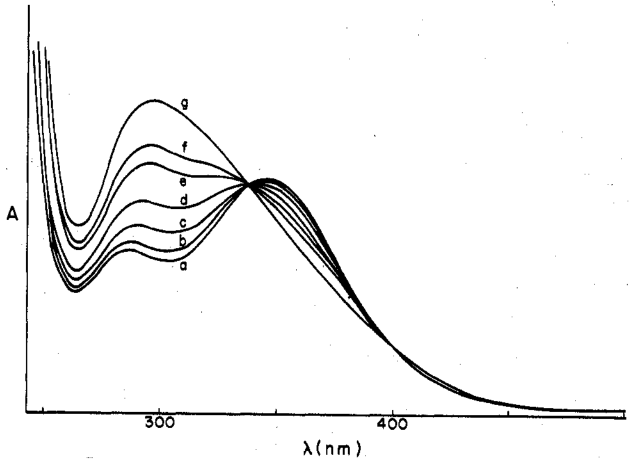


Figure 3. Spectral changes induced by ligand field photolysis of *cis*-α-$[Rh(trien)Cl(H_2O)]^{2+}$. Photolysis times for curves a–g respectively are 0, 2.3, 5.45, 12.1, 24.0, 36.0, and 42.0 h.

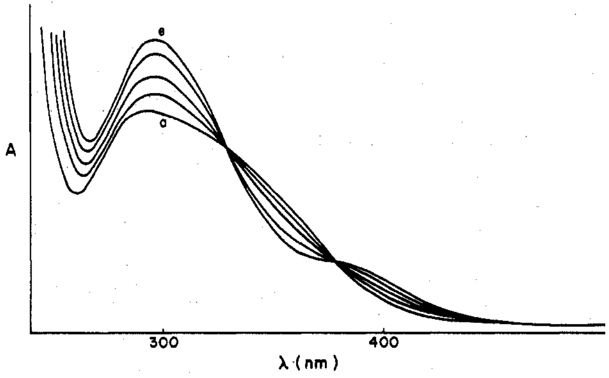


Figure 4. Spectral changes induced by ligand field photolysis of *cis*-β-$[Rh(trien)Cl(H_2O)]^{2+}$. Photolysis times for curves a–e respectively are 1, 50, 100, 180, and 400 s.

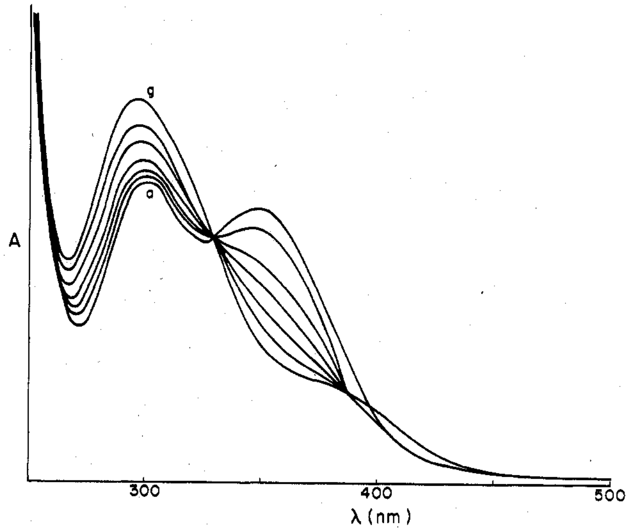


Figure 5. Spectral changes induced by ligand field photolysis of *cis*-β-$[Rh(trien)Cl_2]^+$. Photolysis times for curves a–g respectively are 0, 200, 400, 700, 1300, 1900, 3100, and 9000 s.

trans-$[Rh(trien)Cl_2]^+$,[14] and *trans*-$[Rh(2,3,2\text{-tet})Cl_2]^+$,[18] with the anticipated blue shift due to substitution of a water molecule for the lower ligand field strength chloride ion.

The protoinduced aquation/isomerization of *cis*-α-$[Rh(trien)Cl_2]^+$ is atypically inefficient for haloamine cations of Rh(III) (Table I), yet the spectral changes are clean, with isosbestics at 396 and 338 nm. All intermediate spectra can be regenerated as linear combinations of the spectra of the starting material and photoproduct, and careful spectral analysis revealed no evidence of any other absorbing species in the photolyzed solution.

cis-α- **and** *cis*-β-$\mathbf{[Rh(trien)Cl(H_2O)]^{2+}}$**.** Photolysis of acidic aqueous solutions of either *cis*-α- or *cis*-β-$[Rh(trien)Cl(H_2O)]^{2+}$ causes only minor pH or Cl^- concentration increases ($\phi_{H^+} < 1 \times 10^{-4}$), but the spectral changes shown in Figures 3 and 4 occur. The final spectra are identical with that observed upon prolonged photolysis of *cis*-α-$[Rh(trien)Cl_2]^+$ so the photoproduct is again assigned as *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$. All intermediate spectra are linear combinations of the initial and final spectra, and no evidence of any other absorbing species could be observed. As with analogous dichloro ion, the quantum yield for isomerization of *cis*-α-$[Rh(trien)Cl(H_2O)]^{2+}$ is atypically low for rhodium(III) chloroamine complexes, while the isomerization of the *cis*-β-aquochloro ion is several orders of magnitude more efficient (Table I).

cis-β-$\mathbf{[Rh(trien)Cl_2]^+}$**.** The gross spectral changes (Figure 5) which occur upon ligand field irradiation of acidic solutions of *cis*-β-$[Rh(trien)Cl_2]^+$ are similar to those observed for the cis-α ion, as the final photoproduct is again *trans*-$[Rh(trien)Cl(H_2O)]^{2+}$. The pH changes are minor ($\phi_{H^+} < 1 \times$

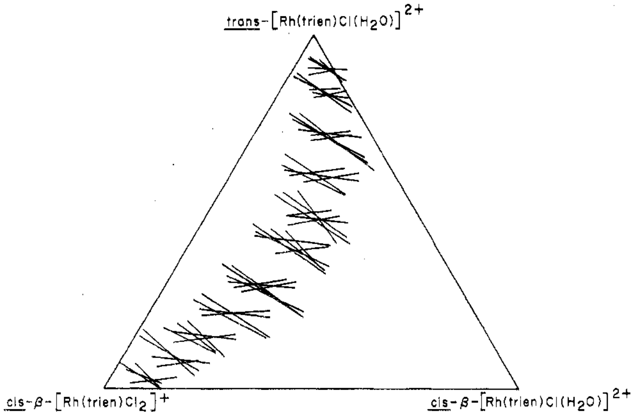


Figure 6. Composition analysis for the solution obtained upon photolysis of *cis*-β-[Rh(trien)Cl_2]$^+$. The intersection of lines represents the fractional composition after a given period of photolysis. The initial solution would be represented by the point at the lower left vertex, and the final spectrum (due to *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$) is represented by the apex of the triangle.

10^{-4}), and 0.9 mol (±0.1) of chloride ion is released/mol of complex. Closer analysis of the spectral changes, however, reveals fundamental differences in the photochemical behavior of *cis*-α- and *cis*-β-[Rh(trien)Cl_2]$^+$.

Irradiation of the low-energy d–d bands causes a monotonic increase in absorption at 410 nm and a monotonic decrease at 350 nm, but at 300 nm ($^1T_2 \leftarrow {}^1A_1$) the absorption decreases slightly in the early stages of the photolysis and then increases sharply. The intermediate spectra cannot be generated as linear combinations of the starting material and final photoproduct, and an isosbestic point does not occur where the spectra cross near 390 nm; it is clear that a third absorbing species must be present in the solutions. The analytical results clearly imply photoinduced chloride release, and while the eventual photoproduct is *trans*-[Rh(trien)Cl(H_2O)$^{2+}$, the intermediate formation of *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$ must also be considered.

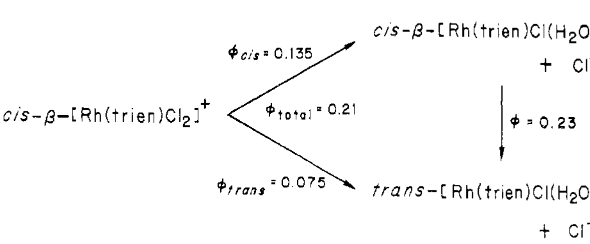
The absorption spectra of *cis*-β-[Rh(trien)Cl_2]$^+$ and *cis*-β- and *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$ can be determined to a high degree of accuracy (±1%), so a triangular graph technique, described previously[15] for the analogous Co(III) ions, could be used to analyze the composition of the photolyzed solutions. As shown in Figure 6, such an analysis confirms that both *cis*-β- and *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$ are primary photoproducts, as the intermediate spectra can be shown to result from unique combinations of *cis*-β-[Rh(trien)Cl_2]$^+$ and the two chloroaquo ions. The formation of *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$ as the eventual photoproduct must then result from primary aquation/isomerization of the dichloro ion and secondary photolysis of *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$

One possible problem inherent in this analysis is that two geometric isomers of *cis*-β-[Rh(trien)Cl(H_2O)$^{2+}$ may exist, with the chloride trans to a primary amine in the cis-β′ ion but trans to a secondary amine in the cis-β″ ion.[12] Separation of the cis-β′ and cis-β″ isomers has not been reported, nor is the isomeric composition of *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$ formed upon thermal aquation of the dichloro ion known. The success of the triangular graph (Figure 6) in regenerating the intermediate photolysis spectra suggests that either (a) the photoproduced aquochloro ion has the same isomeric composition as thermally produced species or (b) the electronic spectra of the cis-β′ and cis-β″ ions are so similar that this technique cannot distinguish between them. The latter explanation would seem applicable, as similar spectra would be expected for these two ions, but a surprising difference was observed in the electronic spectra of α- and β-[Rh(trien)Cl(H_2O)]$^{2+}$.[11]

Absolute quantum yields for the formation of the two chloroaquo ions can be obtained by monitoring spectral changes at appropriate wavelengths. *cis*-β- and *trans*-[Rh(trien)Cl(H_2O)$^{2+}$ have an isosbestic point at 380 nm (Figure 4), so photoinduced absorbance changes in the spectrum of the dichloro ion at 380 nm are not dependent on the isomeric composition of the photoproducts. As a result, the changes at 380 nm can be used to calculate the efficiency of photoinduced Rh–Cl bond cleavage ($\phi_{\text{total}} = 0.21$).

Thermal aquation of *cis*-β-[Rh(trien)Cl_2]$^+$ leads to *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$ with an isosbestic point at 294 nm. Therefore, photoinduced changes in the absorption spectrum of the dichloro ion at 294 nm must be due to the formation of the *trans*-chloroaquo ion, as formation of the *cis*-β-chloroaquo ion would induce no change in the absorption at 294 nm. The quantum yield for formation of the trans ion can then be calculated from the rate of photoinduced absorbance changes at 294 nm ($\phi_{\text{trans}} = 0.075$). The efficiency of formation of *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$ can then be calculated as $\phi_{\text{cis}} = \phi_{\text{total}} - \phi_{\text{trans}} = 0.135$.

The photochemical behavior of *cis*-β-[Rh(trien)Cl_2]$^+$ can be summarized as in eq 2. Chloride aquation occurs with a quantum yield of 0.21, with 65% (0.135/0.21 × 100%) of the primary photoproduct being *cis*-β-[Rh(trien)Cl(H_2O]$^{2+}$ and the other 35% being the isomeric trans ion. This conclusion is supported by the triangular graph (Figure 6), for in the early stages of the photolysis the photoproduct composition is about two-thirds cis-β- and one-third *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$.



(2)

Discussion

The photoinduced reactions of *cis*-α- and *cis*-β-[Rh(trien)ClX]$^{n+}$ (X = Cl, H_2O) are clearly nonthermal processes. In the absence of irradiation the *cis*-dichloro ions aquate to distinct *cis*-chloroaquo ions, presumably with retention of geometric configuration. Such behavior is consistent with the stereorigidity generally observed for substitutions at Rh(III) centers.[1] Trans trien complexes of Rh(III) are not well-known, and a general synthetic pathway to such complexes is not available, as the only previously reported complex *trans*-[Rh(trien)Cl_2]$^+$ was isolated, with some difficulty, as a minor component during the synthesis of the cis isomers.[14] The formation of *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$ as a common photoproduct indicates specific excited-state reactions which differ substantially from the stereoretentive reactions of the ground-state complexes.

The photochemical behavior of these Rh(III) ions is reminiscent of the pattern observed for the analogous Co(III) complexes.[12] Irradiation of *cis*-β-[M(trien)Cl_2]$^+$ (M = Co, Rh) leads to mixtures of *cis*-β- and *trans*-[M(trien)Cl(H_2O)$^{2+}$ as the primary photoproducts, with secondary photolysis of the *cis*-β-chloroaquo ion driving the reaction to the thermally inaccessible *trans*-[M(trien)Cl(H_2O)]$^{2+}$. The quantum yield for the aquation and isomerization of the cis-β complexes is similar to that observed for the analogous ethylenediamine complexes.[7b]

The similarities extend to the cis-α configuration, for cis-α trien complexes of both Rh(III) and Co(III) are orders of magnitude less photosensitive than the isometric cis-β complexes. The quantum yield of the aquation/isomerization of *cis*-α-[Rh(trien)Cl_2]$^+$ is almost 3 orders of magnitude less than the quantum yield for the analogous reaction of the cis-β ion, and the photoinduced isomerization of *cis-α*-[Rh(trien)Cl(H_2O)]$^{2+}$ is at least 2 orders of magnitude less efficient than the same reaction of the *cis-β*-chloroaquo ion.

These results indicate that the bonding geometry of the trien ligand affects the efficiency of photoinduced Rh–Cl bond cleavage. Changes in quantum yield can result from differences in nonreactive decay rates, and two modes of deactivation have been proposed to dominate for Rh(III) complexes. A weak coupling mechanism,[20] involving deactivation through vibrational activation of N–H bonds,[21] has been proposed as the major deactivation pathway in methanol/water glasses at 110 K.[22] A strong coupling mechanism, thought to be more important in room-temperature aqueous solutions,[6] results from a crossing of the excited-state and ground-state potential surfaces due to a severe distortion of the excited state. This distortion has generally been interpreted to be the lengthening of the Rh–Cl bond which is eventually cleaved.

The cis-α and cis-β trien complexes of Rh(III) are isomeric ions, with identical molecular weights and an identical number of N–H bonds with similar stretching frequencies. Both ions have *cis*-dichloro structures, with similar rates of chloride aquation, and there is no reason to expect significant differences in the nature or strength of the Rh–Cl bonds in either ion. We are forced to conclude that there would not be substantial differences in either the weak or strong coupling mechanisms, so that the marked differences in the photosensitivities of the cis-α and cis-β ions must result from differences in the rate of reactive decay of the photoproduced excited states.

An edge-displacement model was used to account for the stereochemical rearrangements observed in the analogous Co(III) complexes.[15] The model was derived from the semiempirical photolysis rules of Adamson,[2] with the additional corollary that if the labilized ligand is a chelated amine, edge-displacement of the amine to a cis coordination site can occur. The edge-displacement model would successfully account for the observed photosensitivity of the cis-α and cis-β trien complexes of Rh(III), but rules-based models for ligand field photochemistry have been less successful for Rh(III) than for Co(III) and Cr(III).[5] For example, irradiation of [Rh(NH_3)$_5$Cl]$^{2+}$ [6] and *cis*-[Rh(NH_3)$_4$$Cl_2$]$^{+}$ [8] leads to chloride labilization, rather than the amine loss predicted by the photolysis rules. Evidence for amine loss as the primary photochemical process in analogous unchelated amine complexes would be necessary to invoke the edge-displacement model for the chelated ions. While the edge-displacement model is a useful mnemonic, we conclude that it does not convincingly account for the mechanics of the ligand field photochemistry of these Rh(III) complexes.

The purely dissociative model,[1] with Rh–Cl bond cleavage leaving a rectangular-pyramid intermediate which is rapidly aquated, cannot be occurring, as such a model does not account for the photoinduced isomerizations or for the differences between cis-α and cis-β complexes. The importance of amine configuration to the efficiency of Rh–Cl bond cleavage efficiency suggests that vibrational relaxation of the Franck–Condon excited state toward the chemically reactive thexi state must involve a distortion which involves the nonlabilized amines. Whatever the nature of that distortion, a trien ligand in the cis-β configuration must not offer significant interference, as indicated by the typical quantum efficiencies for cis-β complexes of Rh(III). When the tetradentate is in the cis-α configuration, however, this distortion must occur with reduced efficiency, or the complex may be forced into a different reaction path by the inability of the cis-α trien complex to distort as did the cis-β ion. The inability of the cis-α complexes to reach the distorted thexi state results in nonreactive deactivation, and a complex which is orders of magnitude less photoreactive than would have been anticipated.

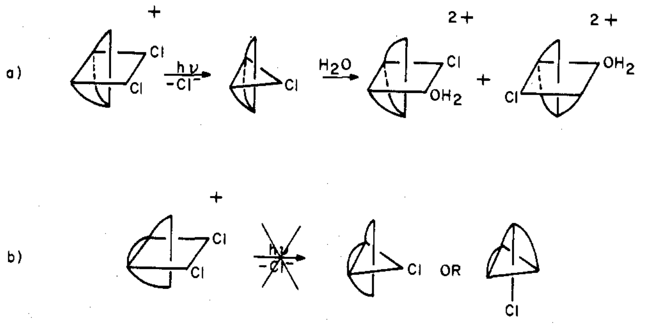


Figure 7. (a) Model of the photoinduced distortions of *cis-β*-[Rh(trien)Cl_2]$^+$ which accounts for the observed photoproduct mixture of *cis-β*- and *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$. (b) Representation of the distortions which would be required for a cis-α trien complex to reach a TBP geometry. Collapse to such a geometry is hindered as a five-membered chelate ring would be forced to span two equatorial coordination sites.

A non-rules-based mechanism, involving distortion of the pseudooctahedral excited state toward a trigonal-bipyramid (TBP) geometry can account for the available results. According to this TBP model, vibrational relaxation of the Franck–Condon excited state toward a TBP structure requires two simultaneous processes: (a) lengthening of the metal–ligand bond which is eventually cleaved and (b) collapse of the remaining ligands toward a TBP geometry. Formation of a TBP geometry may result from electronic effects which follow from population of the $\sigma^*(e_g)$ orbitals upon excited-state formation—such an analysis has recently been presented[23] for Cr(III) complexes. At a more rudimentary level, however, formation of a TBP geometry upon removal of a ligand from the primary coordination sphere can also be attributed to intraligand repulsions among the five remaining ligands.

A key point in the TBP model is that the radial movement of one ligand (bond lengthening) and the angular motions of the remaining ligands are concerted processes, and interruption of either process leads to nonreactive deactivation of the excited state.

The suitability of the TBP model to the photochemical behavior of [Rh(tren)Cl_2]$^+$ has been discussed previously.[11] The generation of *cis-β*- and *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$ upon photolysis of *cis-β*-[Rh(trien)Cl_2)$^+$ can be represented as in Figure 7. The structure of the photoproduct is thus dependent upon the direction of water attack of the TBP species. Water attack adjacent to the chloride would lead to the cis-β ion, and backside attack would lead to *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$.

The relative photoinertness of *cis-α*-[Rh(trien)Cl_2]$^+$ is due, according to the TBP model, to the inability of the trien ligand in the cis-α configuration to form a TBP structure. Collapse of the nonlabilized ligands toward a TBP structure is impossible, as any TBP species would be forced to have adjacent amines in the trien chain spanning equatorial sites in the TBP species (Figure 7). This situation does not occur with the cis-β configuration, where axial–equatorial bonding of the chelated groups is possible. The bite of the five-membered chelate ring is simply not large enough to span the 120° between equatorial sites in the pure TBP geometry, so vibrational relaxation of the excited state would be interrupted by radiationless and nonreactive deactivation.

The TBP model cleanly accounts for the photoinduced behavior reported here and can readily be extended to most *cis*-dihalomine complexes of Rh(III) and Co(III).[26] An appealing feature of the TBP mechanism is that ligand labilization and stereochemical rearrangements are treated as interrelated components of a single reaction pathway. With the exception of the edge-displacement model, other models of ligand field photolysis treat photoinduced isomerization as a secondary, and unexplained, phenomenon which occurs after the primary step of ligand aquation. Stereochemical rearrangements are common to the ligand field photochemistry of Co(III), Rh(III), and even Cr(III),[24] and several studies[15,25] have now shown that the bonding configuration of innocent, nonlabilized ligands can affect the course of a photoinduced reaction. The clear implication is that photochemical models must be developed which deal with the distortion of the entire complex in the excited state rather than merely the radial distortion of a single ligand. Work is currently in progress to test the validity of the TBP model in the photochemical behavior of other d^6 complexes.

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Registry No. *cis*-α-[Rh(trien)Cl_2]$^+$, 67951-70-6; *cis*-α-[Rh(trien)Cl(H_2O)]$^{2+}$, 67951-71-7; *cis*-β-[Rh(trien)Cl_2]$^+$, 67951-72-8; *cis*-β-[Rh(trien)Cl(H_2O)]$^{2+}$, 68035-69-8; *trans*-[Rh(trien)Cl(H_2O)]$^{2+}$, 67999-49-9.

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(10) Abbreviations used throughout: cyclam = 1,4,8,11-tetraazacyclotetradecane, trien = 1,4,7,10-tetraazadecane, tren = β,β′,β″-triaminotriethylamine.

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(25) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).

(26) An apparent anomaly has been reported,[9] as ligand field excitation of complexes of the form *cis*-[Rh(cyclam)X_2]$^+$ (X = Cl, Br, I) "proceed by halide aquation with complete isomeric retention in the hydrolyzed product". These photolyses were done at "natural pH" in 90%/10% H_2O–CH_3CN solutions, no limits were set on the amount of *trans* product which would have gone undetected, and the extent of photolysis was not reported, so it is not clear whether comparison to the *cis*-[Rh(trien)Cl_2]$^+$ studies is appropriate. Assuming such comparisons are valid, the lack of photoinduced aquation/isomerization of *cis*-[Rh(cyclam)X_2]$^+$ is not inconsistent with the reaction model invoked for the less chelated amines. Work with molecular models shows that for *cis*-[Rh(cyclam)X_2]$^+$, and even for [Rh(cyclam)X]$^{2+}$ in a trigonal-bipyramid geometry, the region trans to the coordinated halide(s) is quite hydrophobic due to the methylene groups of the aliphatic cyclam chelate. Nucleophilic water attack in this region, necessary for formation of trans product, could not readily occur, so less hindered cis attack may lead to the observed *cis*-aquochloro ion.

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Photochemistry of Dithiocarbamato Complexes. 2.[1] Photolysis of Iron(III) and Iron(IV) Complexes

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The photochemistry of $Fe(S_2CNR_2)_3$, $[Fe(S_2CNR_2)_3]BF_4$, and $Fe(S_2CNR_2)_2[S_2C_2(CF_3)_2]$ (R = alkyl) in chlorocarbon solvents has been studied. Quantum yield determinations, quantitative organic product analyses, and spectroscopic analyses have led to mechanistic conclusions. $Fe(S_2CNR_2)_3$ is activated by a combination of charge-transfer-to-metal (CTTM) and charge-transfer-to-solvent (CTTS) absorptions, and reaction with RCl to give $Fe(S_2CNR_2)_2Cl$ is thought to occur via electron transfer to RCl from CT-activated $Fe(S_2CNR_2)_3$. CTTS excitation gives this electron transfer directly. The resulting species $Fe(S_2CNR_2)_3^+$ and Cl^- react giving the observed products. Chemical evidence for this reaction sequence will be presented. The CT photoreactivity of $Fe(S_2CNR_2)_3^+$ is thought to occur by dissociation of $S_2CNR_2^+$ from the excited state with subsequent reaction of $Fe(S_2CNR_2)_2$ with RCl giving $Fe(S_2CNR_2)_2Cl$. The CT excited state of $Fe(S_2CNR_2)_2[S_2C_2(CF_3)_2]$ dissociates the neutral dithietene molecule. Photochemical studies of NaS_2CNR_2, the disulfide $(S_2CNR_2)_2$, and the phenyl ester $PhSC(S)NR_2$ have also been carried out in order to verify the reaction sequences of the metal complexes.

Introduction

The charge-transfer photochemistry of transition-metal complexes with sulfur-containing ligands has proved to be an area of increasing interest.[1,3-8] The first reaction studied using metal complexes of the dithiocarbamate ligand (*N,N*-dialkyldithiocarbamate = $S_2CNR_2^-$ = R_2dtc^-) was the reversible photobleaching of tris(*N,N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, $[Ni(Bu_2dtc)_3]Br$, in acetonitrile solution given by eq 1.[3,6] $(Bu_2dtc)_2$ is tetra-*n*-butylthiuram disulfide.

$$\mathrm{Ni(Bu_2dtc)_3^+ + Br^- \underset{dark}{\overset{h\nu}{\rightleftharpoons}} {}^1/_2Ni(Bu_2dtc)_2 + {}^1/_2NiBr_2 + (Bu_2dtc)_2} \quad (1)$$

A previous communication from our laboratory showed that tris(*N,N*-dialkyldithiocarbamato)iron(III) complexes, $Fe(R_2dtc)_3$, react photochemically with chlorocarbon organic