$H_3)_6Cl_3$ contains three pairs of magnetically inequivalent $Ru(NH_3)_6{}^{3+}$ ions. The presence of these three different sites involves thus some uncertainty as to the g and a values. However the traces of g and a are very close for sites I and II ($|\bar{g}| = 1.93$, $|\bar{a}| = 48.3$ for site I and $|\bar{g}| = 1.92$, $|\bar{a}| = 48.7$ for site II) while they are smaller for site III ($|\bar{g}| = 1.88$, $|\bar{a}| = 46.7$). However, these experimental data indicate that the trigonal distortion is very small, at least for sites I and II. This result was already inferred from the MS–Xα calculation, which yields a δ_{max} of 400 cm^{-1} in D_{3d} symmetry.

In the isotropic case ($\delta = 0$), the expressions for g and a become, to first order

$$g = -(2 + 4k)/3 \tag{8}$$

$$a = -2P(4/7 - K/6) \tag{9}$$

The calculated g and a values are presented in Table V, together with values of the parameters used for their evaluation. Details concerning the evaluation of k, P, K and ζ_{4d} from Xα calculations may be obtained from ref 23 and 26. For both complexes, P has been evaluated for $4a_{1g}$ through a non-spin-polarized calculation.

Examination of Table V reveals a good agreement between the theoretical g and a values of $Ru(NH_3)_6{}^{3+}$ and those determined experimentally. The agreement is not so satisfactory for the $a_{\parallel}$ and $a_{\perp}$ values of $Ru(H_2O)_6{}^{3+}$. This discrepancy is probably generated by the use of parameters calculated in the D_{3d} case, with the exception of δ taken as 2500 cm^{-1}, which could differ in a lower symmetry, particularly P and thus K.

As expected from a comparison of the experimental a values of both ions, the orbital reduction factor k and the anisotropic hyperfine parameter P are significantly reduced for the hexaaqua complex, revealing a greater covalency between the metal and the oxygen ligands. Covalency is still more effective than it is apparent through the P values, since P_0 for $Ru(H_2O)_6{}^{3+}$ is stronger than for the hexaammine ion. This increase is due to the well-known trend of antibonding orbitals to place more charge near the metal nucleus, which leads to larger values of $\langle r^{-3}\rangle$ (let us recall that $4a_{1g}$ is antibonding in $Ru(H_2O)_6{}^{3+}$ and nonbonding in $Ru(NH_3)_6{}^{3+}$).

Core polarization contributes significantly to the hyperfine splitting for both complexes. However, its efficiency is reinforced in the case of $Ru(H_2O)_6{}^{3+}$ because of the strong values of its coefficients in the expressions in (5). Indeed, K is multiplied by $a_1{}^2 - a_2{}^2$ (0.81) for $a_{\parallel}$ and $a_1{}^2$ (0.91) for $a_{\perp}$ in the case of $Ru(H_2O)_6{}^{3+}$, while it contributes to the hyperfine tensor of $Ru(NH_3)_6{}^{3+}$ by a factor of $^1/_3$ (expression 9).

5. Conclusion

The aim of this work was to provide a consistent analysis of the electronic and magnetic properties of two d^5 Ru^{3+} complexes, namely $Ru(H_2O)_6{}^{3+}$ and $Ru(NH_3)_6{}^{3+}$. The conjoined use of different theoretical approaches (MS–Xα and ligand field methods and the angular overlap model) has allowed us to precisely determine the most important features of their optical and EPR spectra. The magnetic properties of $Ru(NH_3)_6{}^{3+}$ are described through a strong field octahedral model, with parameters derived from MS–Xα calculations. In contrast, the EPR single-crystal measurements of $Ru(H_2O)_6{}^{3+}$ are interpreted by considering a trigonal field splitting, which is evaluated at 2500 cm^{-1}. The relative orientation of the water molecules in the crystal is thus derived from a comparison of experimental and theoretical results.

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Registry No. $Ru(H_2O)_6{}^{3+}$, 30251-72-0; $Ru(NH_3)_6{}^{3+}$, 18943-33-4.

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(27) Performed with the same geometry as for the MS–Xα calculation. Single-ζ ligand—a double-ζ metal—STO's were used[23]. Standard VSIE's for neutral ligand atoms were taken, and for Ru, $H_{dd} = -12.7$ eV, $H_{ss} = -9.6$ eV, and $H_{p+} = -6.2$ eV.

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Photoracemization/Substitution of Optically Active Rhodium(III) Complexes, *cis*-L-$Rh(en)_2(OH)X^{n+}$

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The photochemistry of *cis*-L-$Rh(en)_2(H_2O)(OH)^{2+}$ and *cis*-L-$Rh(en)_2(OH)_2{}^+$ in aqueous solution is reported. Irradiation at 313 nm results in a photoracemization quantum yield of 0.05 ± 0.01 and 0.008 ± 0.002 mol/einstein, respectively. The results of this work and previous studies on the photochemistry of *cis*- and *trans*-$Rh(en)_2(OH)X^{n+}$ (X = OH, H_2O) and *cis*- and *trans*-$Rh(en)_2(H_2O)_2{}^{3+}$ are consistent with a photochemical mechanism involving excitation, ligand labilization, rearrangement of an excited-state, five-coordinate fragment, relaxation, and solvent addition. Ratios of the photochemical quantum yields for cis-L to cis-*rac* and cis to trans conversions agree with the conclusion that $Rh(en)_2(OH)^{2+*}$ is the species undergoing rearrangement in both the dihydroxo and aquo hydroxo systems.

Introduction

The ligand field photolysis of d^6 rhodium(III) amine complexes has been extensively studied over the past decade.[1] This activity is due, in part, to the substitutional inertness and stereoretention of the thermal reactions[2] and the lack of secondary photolysis processes. However, the photoaquation of *cis*-tetraaminerhodium(III) complexes does lead, in some cases, to trans-disubstituted products.[3-5] For example, the ligand field photolysis of *trans*- and *cis*-dihalobis(ethylenediamine)rhodium(III) complexes results in photoaquation of halo ligand in conjunction with stereoretention for the trans isomer and geometric isomerization for the cis isomer.[3]

Vanquickenborne and Ceulemans[6] have used an "additive point ligand model" to explain the stereochemical changes cited above.

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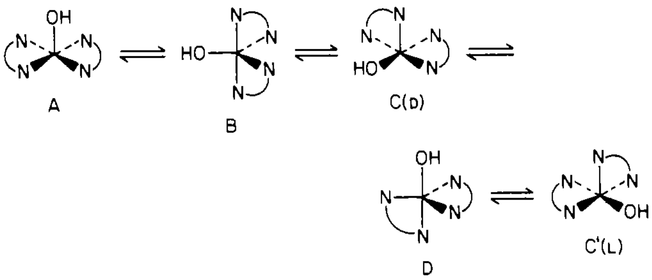
Table I. Electronic and CD Spectra of *cis*-L-$[Rh(en)_2XY]^{n+}$ and *trans*-$[Rh(en)_2XY]^{n+}$ ($X = H_2O, OH$; $Y = H_2O, OH^-$; $XY = C_2O_4^{2-}$)

	absorption			circular dichroism		
complex	λ_{max}[a]	ϵ, $M^{-1}\ cm^{-1}$	ϵ_{irr},[b] $M^{-1}\ cm^{-1}$	λ_{max}[a]	$\Delta\epsilon$, $M^{-1}\ cm^{-1}$	acid dissocn const
cis-L-$Rh(en)_2(C_2O_4)^+$	325	270[c]		348	−2.88[c]	
cis-$Rh(en)_2(H_2O)_2^{3+}$	318	180 175[d]	181 166[d]			$pK_1 = 6.34$,[d] 6.72[e]
cis-L-$Rh(en)_2(H_2O)(OH)^{2+}$	323	196 203[d]	184 196[d]	350	−2.37[f]	$pK_2 = 8.24$,[d] 7.64[e]
cis-L-$Rh(en)_2(OH)_2^+$	329	195 179[d]	173 150[d]	320 350	−0.89[g] −0.32[g]	
trans-$Rh(en)_2(H_2O)_2^{3+}$	352	58.4[d]				$pK_1 = 4.47$,[d] 4.43[e]
trans-$Rh(en)_2(H_2O)(OH)^{2+}$	344	87[d]				$pK_2 = 7.91$,[d] 7.81[e]
trans-$Rh(en)_2(OH)_2^+$	344	97[d]				

[a] Wavelength maximum of ligand fields bands in nm. [b] Molar extinction coefficient at 313-nm irradiation wavelength. [c] Reference 16. [d] Reference 12. [e] Reference 19. [f] $\mu = 1$ M ($NaClO_4$), pH 8. [g] $\mu = 1$ M ($NaClO_4$), pH 11.

Their conclusion is that the stereochemical changes that sometimes occur during the photosubstitution reaction are a result of rearrangement of a five-coordinate, triplet fragment that results directly from ligand loss out of the lowest triplet, ligand field excited state of the six-coordinate reactant. The five-coordinate fragment $[ML_4X]^{q*}$, which was considered initially by Vanquickenborne and Ceulemans,[6] involved an X ligand that was a poorer σ-donor than the L ligand (i.e., $e_\sigma(X) < e_\sigma(L)$) and led to a thermodynamic preference for X to appear apical in a square-pyramidal intermediate. This intermediate is the precursor for trans products. In an extention of this theory,[7] we studied the theoretical case where $e_\sigma(X) > e_\sigma(L)$, which predicts a thermodynamic preference for X to appear basal in the square-pyramidal intermediate and the resultant product to have a cis geometry. This was confirmed experimentally by us in the photochemistry of *trans*-$Co(en)_2(CN)X^{n+}$ ($X = Cl, H_2O$)[7] and by Skibsted and Ford[8] for the *trans*-$Rh(NH_3)_4(OH)X^+$ (X = Cl, Br) complexes. Recent studies in our laboratories have dealt with the thermodynamic vs. kinetic control of the rearrangement process,[9] the applicability to nonaqueous d^6 systems,[10] and the application of the general theory to d^5 systems.[11]

In our extension[7] of the Vanquickenborne and Ceulemans[6] theoretical treatment, an additional theoretical consideration was observed. For systems where trans (A) to cis (C) isomerization is preferred (i.e., ML_4X is more stable with X basal in the square pyramid), there should be a low barrier processes for isomerization between the two cis isomers. When $L_4 = (en)_2$, this conversion between C and C′ corresponds to a conversion between D and L isomers.



The study reported herein involves the photochemistry of optically active *cis*-$Rh(en)_2(OH)X^{n+}$ ($X = OH, H_2O$) complexes. The photochemistry of the trans isomers (A) are known to lead to cis products (C/C′);[12] thus, these systems will supply a critical experimental test to the theoretical studies[6,7] in the literature.

Experimental Section

Materials. All reagent used in compound preparation were analytical reagent grade and were used without further purification. $RhCl_3·3H_2O$ was obtained from Johnson-Matthey, Inc., and the ethylenediamine was supplied by Fisher Scientific. Water used as a solvent for synthesis and in the photochemical and spectroscopic measurements was redistilled from alkaline permanganate in an all-glass apparatus.

Syntheses. The resolving agent $[L-H_2His][D-Co(edta)]_2$ was prepared as described previously.[13] The complex to be resolved, $[Rh(en)_2(C_2O_4)]ClO_4·0.5H_2O$, was prepared as described in the literature[14,15] and resolved by the procedure of Gillard et al.[16] The complex ion L-(+)-$Rh(en)_2(C_2O_4)^+$ can be converted into the diaquo complex L-(+)-$Rh(en)_2(H_2O)_2^{3+}$ and isolated as the perchlorate salt. The optically active *cis*-aquohydroxo and *cis*-dihydroxo complexes (both L-(+)) are prepared in situ by dissolving the diaquo complex in solution and adjusting the pH with NaOH pellets.

Instrumentation. All absorption spectra and optical density measurements were recorded on a Bausch & Lomb Spectronic-2000 spectrophotometer. The optical activity measurements and circular dichroism spectra were recorded on a JASCO ORD/UV-5 recording spectropolarimeter. The pH measurements were recorded on an Orion 701 A pH-meter with a combination electrode using commercially available buffer solutions for calibration.

Photolysis Procedures. Quantum yields were measured with use of a Hanovia 200-W high-pressure mercury-arc lamp and optics described elsewhere.[17] Incident intensity at the irradiation wavelength of 313 nm was determined by ferrioxalate actinometry[18] and approximated 1.0 × 10^{18} quanta/min.

All photolyses were carried out at 25 °C in a 5-cm quartz cylindrical cell. The measurements were corrected for thermal reactions by running a parallel dark reaction. The pH of the solution was maintained at 8 (or 11) throughout the course of photolysis. The ionic strength was maintained at 1 M with $NaClO_4$.

Optical Density Measurement. A portion of racemic $[Rh(en)_2(C_2O_4)]ClO_4·0.5H_2O$ was treated with 2 M $HClO_4$ as described above. The final solution was carefully diluted to twice its original volume. The NaOH pellets were added to the resulting solution. The absorption spectra were recorded at various pH values. The pK_{a1} and pK_{a2} of *cis*-$Rh(en)_2(H_2O)_2^{3+}$ reported by Skibsted[12] were used to solve three linearly independent equations at three different pH values for the extinction coefficients of the three equilibrated species, *cis*-$Rh(en)_2(H_2O)_2^{3+}$, *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$, and *cis*-$Rh(en)_2(OH)_2^+$.

Results

The absorption spectra and circular dichroism spectra for the related $Rh(en)_2XY^{n+}$ complexes are listed in Table I.

***cis*-L-$Rh(en)_2(OH)_2^+$ Photoreactions.** At pH 11, *cis*-L-$Rh(en)_2(OH)_2^+$ is the dominant species in the solution (>99.8%). The 313-nm photolysis was monitored at 330 and 344 nm with a UV-vis spectrophotometer and at 320 nm with CD/ORD spectrophotometer. The quantum yield for cis to trans isomer-

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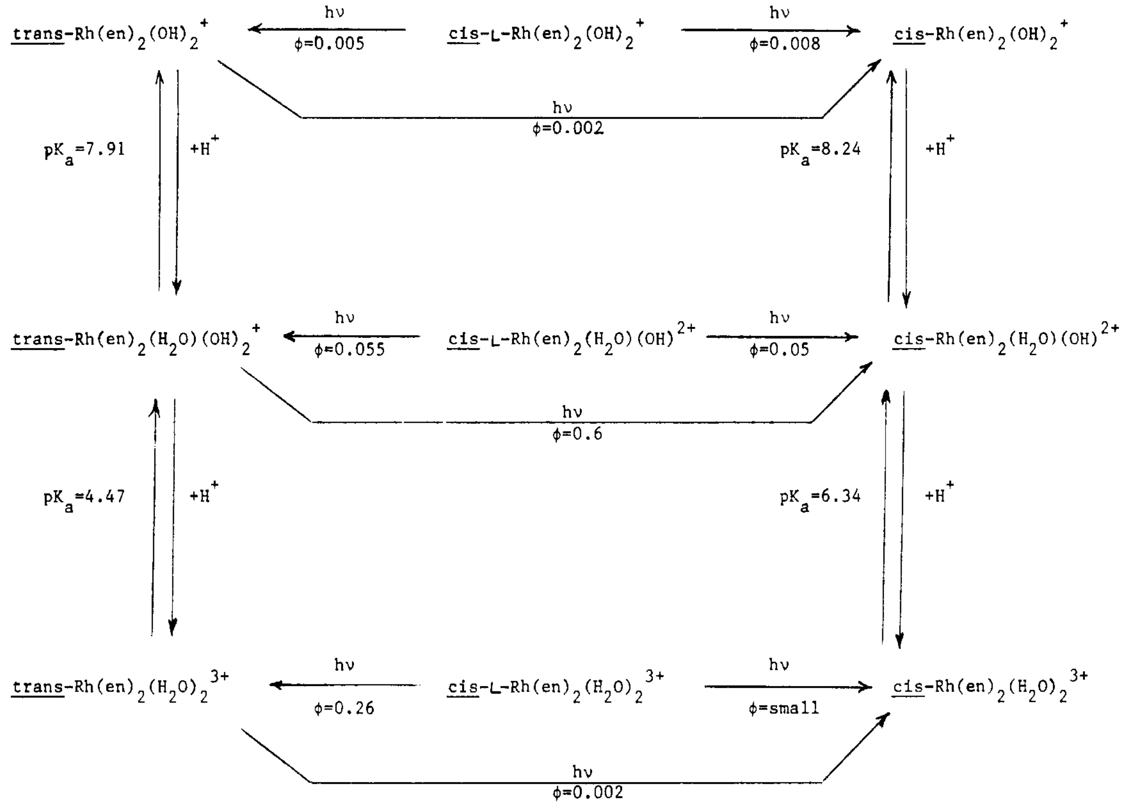
Scheme I



ization was calculated from the change of the electronic spectrum. The depletion of CD spectrum due to this isomerization was then calculated and subtracted from the total CD change. The remaining depletion of the CD spectrum was attributed to the racemization process of the complex. A dark sample was run in parallel to correct for any changes due to thermal processes. The quantum yields for both isomerization and racemization are reported in Table II.

***cis*-L-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$.** at pH 8, *cis*-L-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$ exists in equilibrium with its diaquo and dihydroxo counterparts, the percentages of these species are 62.6%, 1.4%, and 36%, respectively. The percentage of the diaquo complex was low enough so that the contribution of diaquo complex to photoracemization of aquo hydroxo compound could be ignored even though its quantum yield for cis to trans isomerization was not small.[20] Although the amount of dihydroxo compound was substantial, its quantum yields for both isomerization and racemization were relatively low and could be corrected (vide infra).

The photolysis reaction was monitored at 324, 330, and 344 nm in the electronic spectrum and at 350 nm in the CD spectrum. The fraction of light absorbed by the dihydroxo compound was estimated from

$$\delta_{(\mathrm{OH})_2} = \frac{\epsilon^{313}_{(\mathrm{OH})_2} K_{\mathrm{a}1} K_{\mathrm{a}2}}{\epsilon^{313}_{(\mathrm{H_2O})_2}[\mathrm{H}^+]^2 + \epsilon^{313}_{(\mathrm{H_2O})(\mathrm{OH})}[\mathrm{H}^+] K_{\mathrm{a}1} + \epsilon^{313}_{(\mathrm{OH})_2} K_{\mathrm{a}1} K_{\mathrm{a}2}} \qquad (1)$$

(ϵ^{313} values are listed in Table I.) The change of the electronic spectrum due to the photoreaction of the dihydroxo complex was calculated through the known quantum yield. Hence, the quantum yield for cis to trans isomerization of aquo hydroxo complex was obtained. These quantum yields were used further to determine the quantum yield for the photoracemization. The results are shown in Table II.

Discussion

The determination of the photosubstitution and photoracemization quantum yields for the *cis*-L- and *trans*-Rh(en)$_2$XY^{n+} systems is complicated by the similarity in band maxima and molar extinction coefficients in the electronic spectra. This is especially true in the case of the cis complexes (Table I) where the low-energy LF transition appears at the same maximum with virtually the same intensity for the diaquo, dihydroxo, and aquo hydroxo complexes. These spectral similarities, combined with the acid-base equilibrium, which leads to multiple species in solution, are the major factors contributing to the large error limits for the quantum yields reported in Table II.

Table II. Quantum Yields for Photoreactions of [*cis*-L-Rh(en)$_2$XY]$^{n+}$ (X = H$_2$O, OH$^-$; Y = H$_2$O, OH$^-$)

complex	photoproduct	ϕ,[a] mol/einstein
cis-Rh(en)$_2$(H$_2$O)$_2$$^{3+}$	*trans*-Rh(en)$_2$(H$_2$O)$_2$$^{3+}$	0.26[b]
trans-Rh(en)$_2$(H$_2$O)$_2$$^{3+}$	*cis*-Rh(en)$_2$(H$_2$O)$_2$$^{3+}$	0.002[b,c]
cis-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	*trans*-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	0.055 0.052[b,c]
cis-L-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	*cis*-*rac*-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	0.05 (1)[d]
trans-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	*cis*-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$	0.6[b]
cis-Rh(en)$_2$(OH)$_2$$^+$	*trans*-Rh(en)$_2$(OH)$_2$$^+$	0.005 0.002[b,c]
cis-L-Rh(en)$_2$(OH)$_2$$^+$	*cis*-*rac*-Rh(en)$_2$(OH)$_2$$^+$	0.008 (2)[d]
trans-Rh(en)$_2$(OH)$_2$$^+$	*cis*-Rh(en)$_2$(OH)$_2$$^+$	0.002[b,c]

[a] Quantum yield for rearrangement or racemization. λ_{irr} = 313 nm unless specified. [b] Reference 12. [c] λ_{irr} = 334 nm. [d] Uncertainty in value listed in parentheses.

The photochemical conversions and acid-base equilibria are summarized in Scheme I. The complexes fall into three categories: (1) high quantum yields for cis to trans conversion, (2) high quantum yields for trans to cis geometric and cis to cis optical interconversion, and (3) low quantum yields for loss of ligand/rearrangement from either isomer. These three classes arise from the nature of the leaving group and the geometric stability of the five-coordinate, excited-state fragment left behind after ligand labilization.

Examples of the first category of reactivity are very common in the literature for Rh(III) systems. Photoinitiated loss of a ligand such as Cl$^-$, Br$^-$, I$^-$, NH$_3$, or H$_2$O[3,4,9] from complexes of the type Rh(en)$_2$XY^{n+} is very common and usually occurs with a high

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[20] Ford, P. C.; Petersen, J. D. *Inorg. Chem.* **1975**, *14*, 1404.

quantum yield. In addition, the $Rh(en)_2X^{n+}$ excited-state fragment that is formed will prefer to have the X ligand apical or basal in a square-pyramidal intermediate depending on whether X is a poorer or better σ-donor ligand than en, respectively. For category 1, which includes *cis*- and *trans*-$Rh(en)_2(H_2O)_2^{3+}$, the five-coordinate fragment (i.e., $Rh(en)_2(H_2O)^{3+}$) prefers to have the poorer σ-donor (i.e., aquo ligand) apical and the cis to trans geometric isomerization dominates. This process has been extensively treated theoretically by Vanquickenborne and Ceulemans[6] and is expected whenever geometric isomerization can compete effectively with relaxation of the five-coordinate, excited-state fragment.[8,9] Experimentally, we are unable to measure the photoracemization of *cis*-L-$Rh(en)_2(H_2O)_2^{3+}$. The highly efficient loss of optical activity through cis to trans photoisomerization for this species prevents even an approximation for the optical interconversion process.

In the second category, corresponding to *cis*- and *trans*-$Rh(en)_2(H_2O)(OH)^{2+}$, ligand loss[21] still occurs with a relatively large quantum yield, but the resulting fragment, $Rh(en)_2(OH)^{2+}$, prefers OH in the basal plane[7,22] and cis product. Skibsted[12] has reported a quantum yield of 0.6 mol/einstein for the conversion of *trans*-$Rh(en)_2(H_2O)(OH)^{2+}$ to the cis isomer while the reverse photoisomerization has the quantum yield of 0.005 mol/einsteins.

In an earlier theoretical paper,[7] we discussed the trans to cis isomerization in MA_4X systems where X is a better σ-donor than A. An additional result of this theoretical study[7] was the prediction that those intermediate fragments that underwent trans to cis photoisomerization should also undergo cis to cis′ (C to C′) optical interconversion when irradiated. Our results show this to be the case. Irradiation of *cis*-L-$Rh(en)_2(H_2O)(OH)^{2+}$ leads to photoracemization to the racemic mixture of cis complexes with a quantum yield of 0.05 mol/einstein. This process requires the conversion between C and C′ (through D) in competition with relaxation of the five-coordinate, excited-state fragment and solvent addition.

The third category of reactivity (low quantum yield) exists for both *cis*-and *trans*-$Rh(en)_2(OH)_2^{+}$. Previous studies have indicated that neither hydroxo ligand[20] nor ethylenediamine[8,20,23] is a very good excited-state leaving group for Rh(III). Thus, the quantum yields for cis to trans and trans to cis isomerization are both small. However, when photodissociation of hydroxo ligand does occur, the intermediate should be $Rh(en)_2(OH)^{2+}$, just as in the photochemistry of the analogous $Rh(en)_2(H_2O)(OH)^{2+}$ species. Skibsted[12] shows similar quantum yields (both 0.002 mol/einstein) for both trans to cis and cis to trans interconversions although this similarity in quantum yields is probably more a measure of the inability of hydroxo ligand to photodissociate from the two complexes rather than any geometric predisposition of the complexes. Irradiation of the optically active *cis*-L-$Rh(en)_2(OH)_2^{2+}$ ion does result in photoracemization with a quantum yield of 0.008 mol/einstein. This quantum yield is higher than the cis to trans quantum yield of 0.005 mol/einstein that report in Table II.

The proposed mechanism[6,7] for the photosubstitution/rearrangement process has the presence of an excited-state, five-coordinate fragment as its crucial step. While no direct measurement of this state has been made to date, many experimental studies[3-5,7-10] suggest that this mechanism is likely. In this study, we have generated the OH basal intermediate $Rh(en)_2(OH)^{2+*}$ by irradiation of both *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ and *cis*-$Rh(en)_2(OH)_2^{+}$. When optically active cis starting material is used, the two possible photolysis products are the racemic cis isomer and the trans isomer. With the common intermediate (i.e., $Rh(en)_2(OH)^{2+*}$) proposed, the ratios of the quantum yields for formation of these products should be the same. While the dihydroxo complex shows quantum yields an order of magnitude lower than the aquo hydroxo complex for both pathways, the ratio of the quantum yield for racemization of cis to the quantum yield for cis to trans is 0.9 ± 0.3 for *cis*-L-$Rh(en)_2(H_2O)(OH)^{2+}$ and 1.6 ± 0.5 for the *cis*-L-$Rh(en)_2(OH)_2^{+}$ complex. Within the large experimental uncertainty associated with the quantum yield measurements, the ratios are consistent with the common intermediate proposed for the excited-state, five-coordinate fragment mechanism.

The rearrangement possibilities for the $Rh(en)_2(OH)^{2+*}$ fragments have been illustrated in Figure 1b of ref 7. As is pointed out in ref 7, photoracemization is a distinct possibility whenever trans (A) to cis (C or C′) isomerization is spontaneous. In fact, estimates using zero-order AOM orbital energies show that the trans (A) to cis (C) barrier should be nearly the same as the D to L racemization barrier.[7] However, the quantum yields for trans to cis isomerization far exceed the cis to cis′ racemization quantum yields in Table I. Experimentally, we might expect this discrepancy to be in conflict with the model.[6,7] However, the model only reflects electronic factors affecting the rearrangement process while the experimental results include steric constraints as well. Intermediate D (unlike B) requires an ethylenediamine ligand to span two equatorial sites of a trigonal-bipyramidal structure. The ability of this five-membered ring to accommodate this geometry may lead to a geometric contribution to the activation barrier. Further studies are currently under way to look at the cis to trans and optically active cis to racemic cis photochemical processes for the $Rh(tn)_2XY^{n+}$ (tn = 1,3-diaminopropane) series of complexes.[24]

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Registry No. *cis*-L-$Rh(en)_2(OH)_2^{+}$, 64599-01-5; *cis*-$Rh(en)_2(OH)_2^{+}$, 72748-20-0; *trans*-$Rh(en)_2(OH)_2^{+}$, 55683-53-9; *cis*-L-$Rh(en)_2(H_2O)(OH)^{2+}$, 64599-00-4; *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$, 53368-50-6; *trans*-$Rh(en)_2(H_2O)(OH)^{2+}$, 27842-81-5; *cis*-$Rh(en)_2(H_2O)_2^{3+}$, 41188-56-1; *trans*-$Rh(en)_2(H_2O)_2^{3+}$, 21863-10-5.

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(21) Although no direct measurement of aquo ligand exchange by labeling experiments are reported here, the overwhelming evidence in ref 3, 7, 8, 12, and 19 is that photodissociation of aquo ligand occurs, often with large quantum yields.[19]

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