Photochemistry of *cis-* and *trans*-Amminebis(1,2-ethanediamine)-rhodium(III) Complexes. Water Exchange, Stereochemical Rearrangements and Reaction Mechanism

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Excitation at 313 nm or 366 nm of the isomeric $[Rh(en)_2(NH_3)Cl]^{2+}$ ions (en = 1,2-ethanediamine) at 25 °C in 0.50 M $HClO_4$ + 0.50 M $NaClO_4$ results in competitive ammonia and chloride ligand photoaquation with reaction quantum yields of: φ_{cis} (NH_3): 0.0041(7), φ_{cis} (Cl^-): 0.075(2), φ_{trans} (NH_3): 0.0569(12), and φ_{trans} (Cl^-): 0.075(3) mol einstein^{-1}, respectively. The *cis/trans* photoproduct ratio for formation of $[Rh(en)_2(NH_3)(OH_2)]^{3+}$ is the same for the two reactants, as expected from the dissociative reaction mechanism proposed earlier.

The pentaamine photoproduct $[Rh(en)_2(NH_3)(OH_2)]^{3+}$ forms a photostationary state in which isomerization, racemization of the *cis* isomer and water exchange of both isomers occur. On the assumption that the stereochemical changes are accompanied by water exchange, the following quantum yields are calculated: φ_{cis} (OH_2): 0.33(2) and φ_{trans} (OH_2): 0.05(2) mol einstein^{-1} for *stereoretentive* water exchange and $\varphi(cis \rightarrow trans)$: 0.113(6), $\varphi(trans \rightarrow cis)$: 0.276(12) and $\varphi(cis \rightarrow cis)$: 0.152(7) mol einstein^{-1} for the *isomerization* and *racemization* reactions, respectively. The *cis/trans* photoproduct ratio for these tripositive species depends on the reactant stereochemistry, which suggests a change in mechanism towards associative activation for these species.

Rate constants for *thermal* water exchange and acid dissociation constants at 25 °C for the isomeric $[Rh(en)_2(NH_3)(OH_2)]^{3+}$ ions are: k_{cis}: 3.2(3) $\cdot$ 10^{-5}s^{-1}, $-\log(K_{a,cis}/M)$: 6.828(7), k_{trans}: 7.5(5) $\cdot$ 10^{-6}s^{-1} and $-\log(K_{a,trans}/M)$: 6.440(8) in a 1.0 M perchlorate medium.

Studies[1,2] of photoaquation of *cis-* and *trans*-tetraammine-dichlororhodium(III) ions and of photochemical water exchange in *cis-* and *trans*-tetraammineaquachlororhodium(III) ions have shown that the $[Rh(NH_3)_4(OH_2)Cl]^{2+}$ products are formed in a ratio which is independent of both the leaving ligand, i.e. chloride or water, respectively, and of the reactant stereochemistry. This points towards a dissociative reaction mechanism, although similar studies[3] of photochemical water exchange in *cis-* and *trans*-tetraamminediaquarhodium(III) ions have given some indication of a less simple behaviour for these tripositive complexes. Rhodium(III) ammines have served as the prototype[4-7] in the elucidation of the reaction dynamics for light-induced chemical processes in d^6 metal complexes, and these indications of a gradual change from a purely dissociative towards a greater degree of associative behaviour within such closely related complexes have provided a strong incentive to include another series of rhodium(III) amines in the studies. The amminebis(1,2-ethanediamine)-chloro- and amminebis(1,2-ethanediamine)aquarhodium(III) ions, which are the subject of the present photochemical study, constitute a suitable series of pentaamine complexes for

which a number of photochemical processes can readily be followed.[8-10]

Results

cis- and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$ are conveniently prepared as the nitrate salts.[11] Judged from HPLC experiments they are, however, more effectively purified as the chloride and trifluoromethanesulfonate salts, respectively (cf. Experimental). Spectral data for photoproduct identification and quantum yield calculations were obtained for compounds reprecipitated to have constant spectral characteristics (Table 1), except for *cis*-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$. This latter complex ion was isolated only as the bromide salt, which, however, invariably contained traces of $[Rh(en)_2(NH_3)Br]Br_2$. The required spectral data for this ion were therefore obtained using *cis*-$[Rh(en)_2(NH_3)(NO_3)](ClO_4)_2$ hydrolyzed in the reaction medium, and were corrected for nitrate absorption. The UV-absorption spectra for the four pentaamine complexes are presented in Fig. 1.

Thermal ligand substitution processes and rearrangements were found to be negligible under the conditions

Table 1. Ligand field spectra of amminebis(1,2-ethanediamine)rhodium(III) complexes in aqueous 0.50 M $HClO_4$ + 0.50 M $NaClO_4$.

Compound	λ_{max}/nm (ε/M^{-1}cm^{-1})	λ_{min}/nm (ε/M^{-1}cm^{-1})
cis-[Rh(en)$_2$(NH$_3$)Cl]Cl$_2$[a]	343(150), 274(178)	315(122), 246(62)
trans-[Rh(en)$_2$(NH$_3$)Cl](CF$_3$SO$_3$)$_2$[b]	344(98), 274(133)	320(77), 250(67)
cis-[Rh(en)$_2$(NH$_3$)(NO$_3$)](ClO$_4$)$_2$	312(225)	286(178)
cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+c}$	309(171), 263(140)	280(124), 235(47)
trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)](ClO$_4$)$_3$[a]	304(118), 261(122)	281(102), 235(54)

[a]Spectral data in agreement with Refs. 20 and 26, respectively. [b]Spectral data in disagreement with Ref. 27. [c]Spectrum of hydrolyzed solution of *cis*-[Rh(en)$_2$(NH$_3$)(NO$_3$)](ClO$_4$)$_2$, see text.

employed for the photochemical experiments, except for exchange of coordinated water in the isomeric [Rh(en)$_2$ (NH$_3$)(OH$_2$)]$^{3+}$ ions. Thermal rate constants, necessary for obtaining accurate quantum yields, were determined from oxygen-18 labelling experiments, as shown in Fig. 2, and are reported in Table 3 together with the pK_a values determined by titrations of *cis*- and *trans*-[Rh(en)$_2$(NH$_3$) (OH$_2$)]$^{3+}$ and [Rh(NH$_3$)$_5$(OH$_2$)]$^{3+}$.

Photolysis of cis- *and* trans-*[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$.* The absorption spectra of photolyzed acidic aqueous solutions of each of the isomers of [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ could, at any stage of the photolysis, be accounted for on the basis of linear combinations of the spectra of the pure isomers, and neither photoaquation of coordinated ammonia nor photo-aquation of coordinated 1,2-ethanediamine could be detected. The exhaustively photolyzed solutions had a common absorption spectrum, independent of initial reactant stereochemistry, corresponding to a *cis-trans*-photo-stationary state, as shown in Figs. 3 and 4.

$(-)_{436}$-*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ loses optical activity by a photochemical process, as shown in Fig. 5. Spectral changes and changes in optical rotation were therefore interpreted on the basis of the reactions shown in Scheme 1. Fig. 6 shows photoinduced release of coordinated oxygen-18 labelled water. This type of photochemical reactivity is greater for both isomers than the photoracemization and photoisomerization which are both thought to occur via exchange of a water ligand. This indicates a significant stereoretentive contribution to the water exchange quantum yields Φ_{cis} and Φ_{trans}, i.e.:

$$\Phi_{cis} = \Phi_{ct} + \Phi_{cc}^{rac} + \Phi_{cc}^{ret}$$

$$\Phi_{trans} = \Phi_{tc} + \Phi_{tt}$$

cf. Scheme 1. Numerical values are given in Table 2.

Photolysis of cis- *and* trans-*[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$.* Ligand field excitation of *cis*- and *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ in acidic aqueous solution leads to photoaquation of coordinated ammonia and chloride. Photoaquation of the coordinated 1,2-ethanediamine could not be detected, in agreement with previous reports.[8,10]
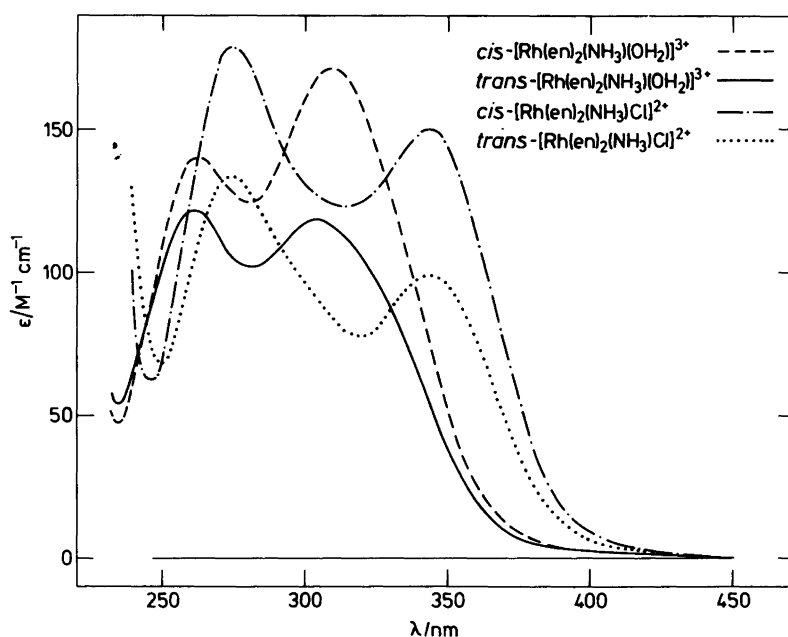

Fig. 1. Absorption spectra of *cis*- and *trans*-ammineaquabis(1,2-ethanediamine)-rhodium(III) and *cis*- and *trans*-amminechlorobis(1,2-ethanedi-amine)rhodium(III) in 0.50 M $HClO_4$ + 0.50 M $NaClO_4$.
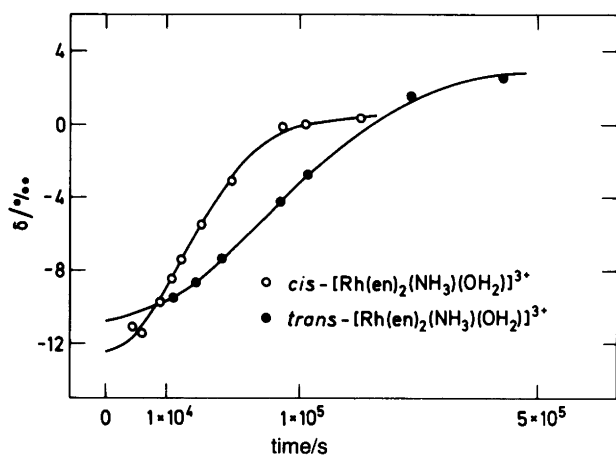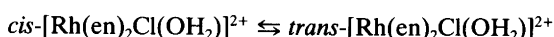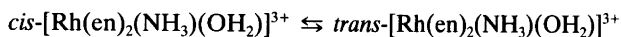
Fig. 2. Oxygen-18 content of solvent as the result of thermal water exchange of *cis*- and *trans*-[Rh(en)$_2$(NH$_3$) (^{18}OH$_2$)]$^{3+}$, respectively, in 0.50 M NaClO$_4$ + 0.50 M HClO$_4$ at 25 °C. The experimental points are expressed relative to V-SMOW (Vienna Standard Mean Ocean Water),[19,33] and the solid curves were calculated from the parameters of Table 3.

Photoaquation of coordinated chloride is the dominant reaction for both isomers, but ammonia ligand photo-aquation is more significant for the *trans*- than for the *cis*-isomer. This was confirmed in independent experiments both by measuring [H$^+$] changes for solutions in 1.0 M NaClO$_4$ with an initial hydrogen ion concentration of 0.0100 M and by measuring the released ammonia after sublimation from basic solution. Exhaustively photolyzed solutions therefore have different absorption spectra corresponding to different contents of the two photostationary systems:

cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ $\leftrightarrows$ *trans*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$

cis-[Rh(en)$_2$Cl(OH$_2$)]$^{2+}$ $\leftrightarrows$ *trans*-[Rh(en)$_2$Cl(OH$_2$)]$^{2+}$

This is demonstrated in Fig. 3.

Fig. 4. Photoisomerization of [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ isomers during 313 nm photolysis at 25 °C of ~ 2 mM aqueous solutions of *cis*- and *trans*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$, respectively, in 0.50 M HClO$_4$ + 0.50 M NaClO$_4$. The points are experimental values derived from a multi-wavelength spectral analysis of the reaction mixtures,[23] and the solid curves are calculated from the quantum yields in Table 2, the molar absorption coefficients at 313 nm and the light intensitites.

Fig. 5. Photoracemization of (−)$_{436}$-*cis*[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ during 366 nm photolysis at 25 °C of a ~ 8 mM solution in 0.50 M HClO$_4$ + 0.50 M NaClO$_4$. The points are molar rotations at 436 nm, and the solid curve is calculated according to Scheme 1 from the quantum yields in Table 2, the molar absorption coefficients at 366 nm and the light intensities.
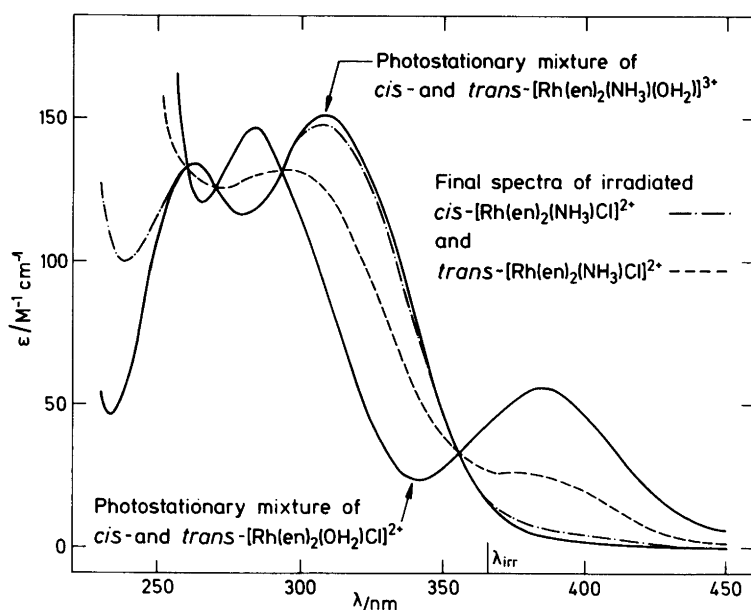

Fig. 3. Absorption spectra of exhaustively photolyzed solutions of *cis*- and *trans*-[Rh (en)$_2$(NH$_3$)Cl]$^{2+}$ and of the photostationary states of the [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ and [Rh(en)$_2$(OH$_2$)Cl]$^{2+}$ isomers. The results shown are for 366 nm excitation of solutions in 0.50 M NaClO$_4$ + 0.50 M HClO$_4$ at 25 °C. The existence of four common isosbestic points shows that only ammonia and chloride ligand photoaquations are significant reactions, and that these processes can be studied without disturbance from subsequent photochemical and thermal reactions (cf. Scheme 2). Photosubstitution of coordinated ammonia is seen to be more significant in *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ than in the corresponding *cis* isomer.
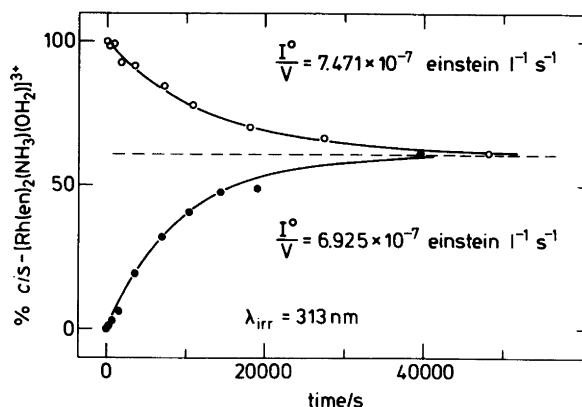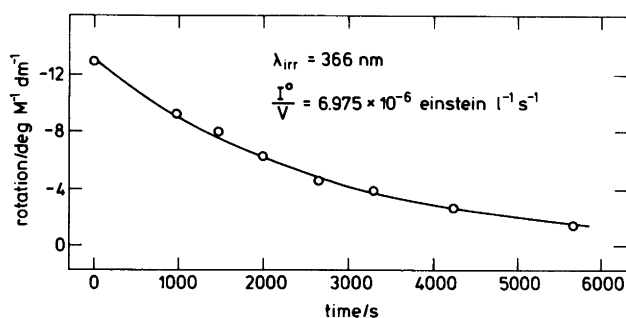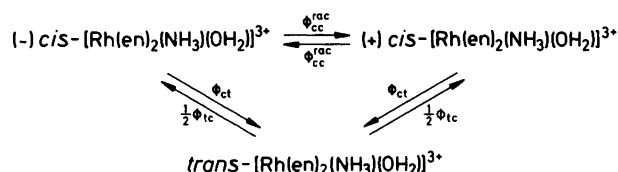
Table 2. Ligand photosubstitution quantum yields for amminebis(1,2-ethanediamine)rhodium(III) complexes resulting from 313 or 366 nm excitation in aqueous 0.50 M HClO$_4$ + 0.50 M NaClO$_4$ at 25 °C.

Reactant	Product	Φ/mol · einstein^{-1}		R_{tc}^a
		(313 nm^b)	(366 nm^b)	
cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$	*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.075(6)	0.070(2)	} 0.060(16)
	trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.000(7)	0.0043(10)	
	[Rh(en)$_2$(OH$_2$)Cl]$^{2+}$	0.0044(8)	0.0031(14)	
trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$	*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.073(12)	0.075(3)	} 0.00(5)
	trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.000(14)	0.000(4)	
	[Rh(en)$_2$(OH$_2$)Cl]$^{2+}$	0.0539(19)	0.0589(15)	
cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.33(29)^d		} 0.35(3)
	trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.114(6)	0.106(14)	
$(-)_{436}$-*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	$(+)_{436}$-*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$		0.152(7)^c	
trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.269(13)	0.310(28)	} 0.18(8)
	trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$	0.05(2)^e		

$^a R_{tc}$ is the ratio between the quantum yield for the formation of *trans*-product and that for the formation of *cis*-product, i.e. Φ_{tt}/Φ_{tc} for *trans*-complexes and Φ_{ct}/Φ_{cc} for *cis*-complexes. ^{b}Wavelength of irradiation. ^{c}Photoracemization yield, Φ_{cc}^{rac} (cf. Scheme 1). ^{d}Quantum yield for water exchange, Φ_{cc}^{rac} + Φ_{cc}^{ret} (cf. Scheme 1). ^{e}Quantum yield for stereoretentive water exchange.

$(-)$*cis*- [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ $\xrightleftharpoons[\Phi_{cc}^{rac}]{\Phi_{cc}^{rac}}$ $(+)$*cis*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$

trans- [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$

Scheme 1.

Fig. 7 shows the concentration vs. time dependence in a photolysis experiments starting from *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$. In addition to the [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ isomers, only *trans*-[Rh(en)$_2$Cl(OH$_2$)]$^{2+}$ is seen as a product, in agreement with previous data for the photo-stationary state for the latter system.[12]

Quantum yields for the two wavelengths of irradiation, calculated in accordance with Scheme 2, incorporating data for experiments with *cis*- and *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$, and including the isomerization yields for [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ are given in Table 2. In agreement with previous results for other rhodium(III) amine complexes,[1,2] no wavelength dependence could be detected.

Discussion

The two isomers of both [Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ and [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ have very similar absorption spectra in the ligand field region (Table 1), except for the expected somewhat higher absorption of the *cis* isomers as compared to the *trans* isomers (Fig. 1). This similarity makes the absorption spectra less suitable as criteria of isomeric purity, which is far better determined by the chromatographic method described earlier.[13] A lower limit of detection of isomeric impurities of about 1 % has been established by the addition of known amounts of impurities. The spectral data in Table 1 and Fig. 1 are based on compounds in which impurities were not detected.

The chemical properties of *cis*- and *trans*-amminebis-(1,2-ethanediamine)rhodium(III) complexes are different, despite the close similarity of the first coordination sphere of the isomers (Table 3). Thus, *trans*-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ is a stronger acid and exchanges the coordinated water ligand more slowly than the corresponding *cis* isomer. Both these results are in agreement with general trends within rhodium(III) chemistry, as evidenced by the data shown in Table 3.
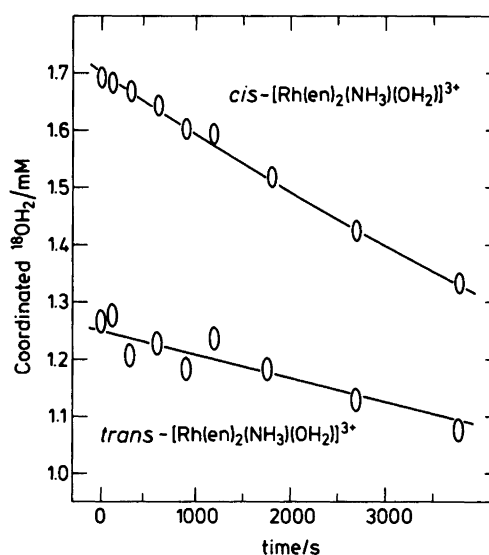

Fig. 6. Concentrations of coordinated ^{18}OH$_2$ in the isomeric [Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ ions during 313 nm photolysis at 25 °C in 0.50 M HClO$_4$ + 0.50 M NaClO$_4$ as a function of irradiation time. The points are obtained from mass spectrometric measurements, and the solid curves are calculated from the quantum yields in Table 2, the molar absorption coefficients at 313 nm, the rhodium(III) concentrations and the degree of oxygen-18 enrichment, respectively. *cis*: 3.46 mM; 0.269 μ einstein l^{-1}s^{-1} and 0.49 mol ^{18}OH$_2$/mol Rh(III). *trans*: 2.90 mM; 0.250 μ einstein l^{-1}s^{-1} and 0.43 mol ^{18}OH$_2$/mol Rh(III).

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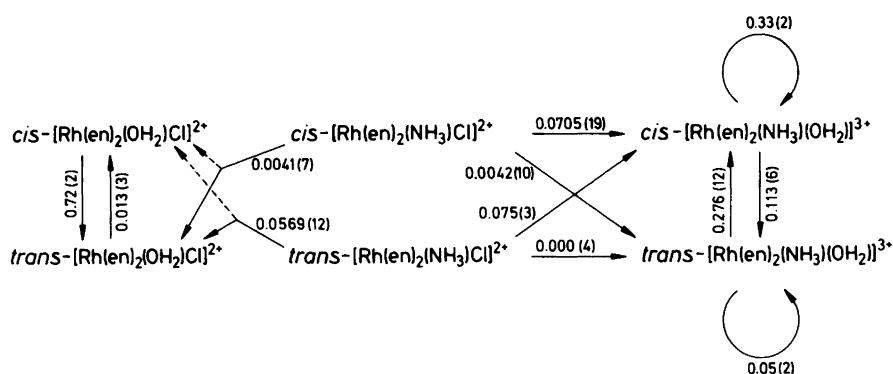
Scheme 2.

As for the thermal properties, a dependence on the stereochemistry is also found for the photochemical reactions of these pentaamines. Ammonia ligand aquation is thus significant for *trans*-[Rh(en)₂(NH₃)Cl]²⁺ but is only a minor reaction for the *cis* isomer (Table 2). In this respect [Rh(NH₃)₅Cl]²⁺ is intermediate, as 20 % of the photoreaction of this latter complex is ammonia-ligand aquation.[14] For all these pentaaminechloro complexes, however, the chloride-ligand aquation is the most significant photoreaction.

Moreover, for these three pentaaminechloro complexes, chloride-ligand photoaquation entails equilibration between the five nitrogen-donors, as evidenced by ammonia ligand scrambling in [Rh(NH₃)₅Cl]²⁺, [15] and by the common *trans*/*cis* distribution in the [Rh(en)₂(NH₃)(OH₂)]³⁺ photoproducts resulting from chloride-ligand photoaquation in either isomer of [Rh(en)₂(NH₃)Cl]²⁺. The [Rh(en)₂(NH₃)(OH₂)]³⁺ photoproduct has a very strong *cis* preference, as may be seen from the quantum yields of Table 2, and chloride-ligand photoaquation of *trans*-[Rh(en)₂(NH₃)Cl]²⁺ results in nearly complete *trans*-to-*cis* photoisomerization. This is in clear contrast to a previous report on the photochemical behaviour of these complexes, as is also the detection of the significant ammonia-ligand photoaquation

in the latter complex.[8] The common quantum yield ratio for the production of *cis*- and *trans*-[Rh(en)₂(NH₃)(OH₂)]³⁺ from either isomer of [Rh(en)₂(NH₃)Cl]²⁺ is, however, in agreement with what has previously been found for the photoaquation of *cis*- and *trans*-[Rh(NH₃)₄Cl₂]⁺ and [Rh(NH₃)₄Cl(OH₂)]²⁺.[1,2] All these data are therefore consistent with the reaction mechanism entailing ligand dissociation prior to thermal equilibration in an excited state of reduced coordination number, which has previously been proposed.

Irradiation of solutions of [Rh(en)₂(NH₃)(OH₂)]³⁺ led to efficient water exchange for which the quantum yields of Table 3 were determined from 18-oxygen labelling studies. *cis*- and *trans*-[Rh(en)₂(NH₃)(OH₂)]³⁺ photoisomerize to each other in aqueous solution at 25 °C with moderately large quantum yields (Table 2) which, however, are smaller in each case than the quantum yields for water exchange. The previously reported[10] photoinertness at 25 °C but not at 50 °C could *not* be confirmed, and *cis*- and *trans*-[Rh(en)₂ (NH₃)(OH₂)]³⁺ behave normally in the sense that they photoisomerize like the isomers of [Rh(en)₂(OH₂)₂]³⁺, [Rh(en)₂(OH₂)(OH)]²⁺ and other similar complexes.[5,16,17] On the assumption that photoisomerization for these complexes is accompanied by water exchange, it is possible to
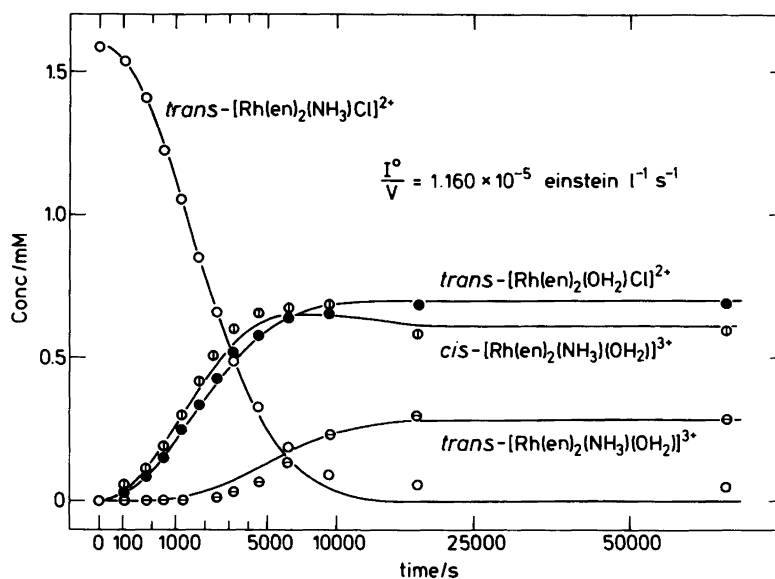

Fig. 7. 366 nm photolysis of *trans*-[Rh(en)₂ (NH₃)Cl]²⁺ at 25 °C in 0.50 M HClO₄ + 0.50 M NaClO₄. The points are experimental values, as derived from multi-wavelength spectral analysis, and the solid curves are calculated from the quantum yields in Table 2, the molar absorption coefficients at 366 nm and the light intensity.

Table 3. Thermal and photochemical water exchange in amineaquarhodium(III) complexes in acidic aqueous solution at 25.0 °C,[a] and acid dissociation constants.

Complex	k/s^{-1}	$\Phi/\text{mol einstein}^{-1}$	$-\log (K_a/M)$	References
$[Rh(NH_3)_5(OH_2)]^{3+}$	$8.41(18)\times10^{-6}$	0.43(3)	6.870(8)[d]	28, 29; this work
cis-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$	$3.2(3)\times10^{-5}$	0.44(2)	6.828(7)[d]	This work
$trans$-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$	$7.5(5)\times10^{-6}$	0.33(2)	6.440(8)[d]	This work
cis-$[Rh(NH_3)_4(OH_2)_2]^{3+}$	$1.50(6)\times10^{-5b}$	0.143(3)[c]	6.391(9)[e]	32, 3, 30
$trans$-$[Rh(NH_3)_4(OH_2)_2]^{3+}$	$1.42(6)\times10^{-8b}$	0.0251(6)[c]	4.860(11)[e]	32, 3, 30
cis-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$	$2.38(3)\times10^{-5}$	0.66(2)	7.84(1)	32, 1, 31
$trans$-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$	$3.38(9)\times10^{-5}$	0.39(4)	6.75(1)	32, 1, 31

[a] 1.0 M (H,Na)ClO₄ except $[Rh(NH_3)_5(OH_2)]^{3+}$, for which media with ionic strength of 0.24 were employed for the water exchange studies. [b] First-order rate constants based on complex concentration, i.e. $2 \times k_{obs}$ (cf. Ref. 32). [c] Quantum yields based on complex concentration, $2 \times \Phi_{obs}$ (cf. Ref. 3). [d] Obtained by titration of $[Rh(NH_3)_5(OH_2)](ClO_4)_3$, cis-$[Rh(en)_2(NH_3)(OH_2)]Br_3$ and $trans$-$[Rh(en)_2(NH_3)(OH_2)](ClO_4)_3$, respectively. [e] First acid dissociation constant.

determine the quantum yield for stereoretentive water exchange (cf. Table 2 and Results). The observation that $\Phi_{cc}^{ret} \approx \Phi_{cc}^{rac}$ shows that the energy barrier between the enantiomers is low enough to be insignificant, since the two enantiomers are formed in equal yields when one is exchanging water photochemically (Fig. 8). Contrary to what was earlier referred to for a number of lower-charged complexes, the relative photoproduction of the *cis*- and *trans*-isomers depends upon the $[Rh(en)_2(NH_3)(OH_2)]^{3+}$ reactant stereochemistry and is notably different from the common ratio found for the $[Rh(en)_2(NH_3)Cl]^{2+}$ isomers (Table 2). This is in agreement with results for *cis*- and *trans*-$[Rh(NH_3)_4(OH_2)_2]^{3+}$, and clearly points towards some associative character for these trivalent cations, as opposed to the dissociative behaviour of the tetraamminedichloro- and tetraammineaquachlororhodium(III) complexes of lower charge.

In conclusion, contrary to previous reports, the photochemistry of *cis*- and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$ and *cis*- and *trans*-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$ provides no exception to the general behaviour of other series of rhodium(III) amine complexes. The light-induced reactions of all the complexes of lower charge are well understood on the basis of a dissociative mechanism and thermal equilibration in an intermediate of reduced coordination number. For tri-

0.13 (2)   0.113 (6)   0.199 (12)

Fig. 8. Quantum yields (mol einstein⁻¹) for water exchange in *cis*-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$.

positive species the behaviour is more complicated, and further work on such systems is definitely needed.

Experimental

Caution! Although we have not experienced difficulties with the present perchlorate and nitrate salts, they should all be regarded as potentially explosive and be handled accordingly.

Chemicals. RhCl₃ · xH₂O was obtained from Johnson Matthey Chemicals, ¹⁸O-enriched water from Alfa Products and trifluoromethanesulfonic acid ('triflic acid') from the 3 M Company. Other commercial chemicals were of analytical grade. $[Rh(NH_3)_5Cl]Cl_2$,[18] cis-$[Rh(en)_2Cl_2]_2Cl(ClO_4)$,[18] $trans$-$[Rh(en)_2Cl_2]NO_3$,[11,12] *cis*- and *trans*-$[Rh(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$,[12] *cis*- and *trans*-$[Rh(en)_2(NH_3)Cl](NO_3)_2$[11] and Ag(tos)[19] were prepared by published methods (en $\equiv$ 1,2-ethanediamine, tos $\equiv$ p-toluene-sulfonate anion). *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$ was resolved as the $(+)_D$bromocamphorsulfonate by a modified literature method.[20]

1. *cis*-$[Rh(en)_2(NH_3)Cl]Cl_2$ was prepared by dissolving 1.0 g of the nitrate salt in 2.5 ml of water at room temperature and precipitating with 5 ml of 12 M hydrochloric acid and cooling in ice. The crude compound was reprecipitated once more and its isomeric purity tested by HPLC.[13] Anal. Rh C₄H₁₉N₅Cl₃: C, H, N, Cl.

2. *trans*-$[Rh(en)_2(NH_3)Cl](CF_3SO_3)_2$ was prepared from a concentrated aqueous solution of the nitrate salt by precipitation with trifluoromethanesulfonic acid at room temperature and cooling in ice. The crude compound was recrystallized from water at 90 °C (5 ml per g of compound.) The isomeric purity was tested by HPLC. Anal. Rh C₆H₁₉N₅S₂O₆ClF₆: C, H, N, Cl, S.

3. Crude *cis*-$[Rh(en)_2(NH_3)(CF_3SO_3)](CF_3SO_3)_2$. 800 mg of *cis*-$[Rh(en)_2(NH_3)Cl]Cl_2$ (preparation No. 1) was treated with 10 ml of CF₃SO₃H at 100 °C for 1 h under gentle

bubbling with nitrogen. The dark-yellow solution was allowed to cool to room temperature and was cooled further in ice. 25 ml of diethyl ether was added and the resulting precipitate of crude cis-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$ was isolated by filtration, washed with ether and stored in a dessicator. Yield 1.5 g.

4. cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]Br$_3$. 600 mg of crude cis-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$ was dissolved in 1 ml of water and heated to 100°C for 1 min. The solution was filtered through a fine-porosity sintered-glass funnel and mixed with 12 ml of ethanol. The solution was immediately cooled in ice and subsequently mixed with 6 ml of 63 % hydrobromic acid, and the resulting precipitate of crude cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]Br$_3$ was isolated by filtration and washed with a little ice-cold ethanol (100%), then ether, and reprecipitated from 1 ml of water by the addition of 2 ml of a saturated aqueous solution of LiBr. The product was isolated and washed as before. Yield 90 mg. This compound contained some cis-[Rh(en)$_2$(NH$_3$)Br]Br$_2$.

5. cis-[Rh(en)$_2$(NH$_3$)(NO$_3$)](ClO$_4$)$_2$. 1.0 g of cis[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$ and 2.0 of HgO were disolved in 100 ml of 0.5 M HNO$_3$ and boiled under reflux for 2 h. The solution was allowed to cool to room temperature and was filtered through a fine-porosity sintered-glass funnel. The filtrate was mixed with HClO$_4$ (70 %, 30 ml), and kept at 5°C for 17 d. During this period of time a crystalline precipitate was slowly formed. The product was isolated by filtration and washed with 1 ml of 2 M HClO$_4$. The crude product was extracted with 25 ml of boiling 4 M HNO$_3$, and the volume of the filtered extract was reduced to 10 ml by gentle boiling. 10 ml of 70 % HClO$_4$ was added, and the solution was kept at 5°C overnight. The desired product, cis-[Rh(en)$_2$(NH$_3$)(NO$_3$)](ClO$_4$)$_2$, was isolated and washed as before. Yield 0.42 g (33 %). Anal. Rh C$_4$H$_{19}$N$_6$O$_{11}$Cl$_2$: C, H, N, Cl.

6. Crude trans-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$. 1.4 g of trans-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$ and 25 ml of Amberlite IRA-400 resin in the chloride form were stirred in 100 ml of water for 2 h. The mixture was filtered and the filtrate was evaporated to dryness at 55°C, followed by drying in an oven at 105°C. The oily product was dissolved in 20 ml of CF$_3$SO$_3$H and treated as described in preparation No. 3 for the cis-isomer. This gave 1.5 g of crude trans-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$, which contained some trans-[Rh(en)$_2$(NH$_3$)Cl](CF$_3$SO$_3$)$_2$.

7. trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)](ClO$_4$)$_3$. 1.5 g of crude trans-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)](CF$_3$SO$_3$)$_2$ was dissolved in 8 ml of water by heating, and 8 ml of 70 % HClO$_4$ was added to the filtered solution. A crystalline product of trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)](ClO$_4$)$_3$ was slowly formed, and was isolated by filtration after 2 h of cooling in ice. The product was washed with ice-cold 2 M HClO$_4$, then with ethanol and ether, and subsequently reprecipitated from 1 ml of 2 M

HClO$_4$ by addition of 1 ml of 70 % HClO$_4$. The reprecipitated trans-[Rh(en)$_2$(NH$_3$)(OH$_2$)](ClO$_4$)$_3$ was isolated and washed as before. Yield 0.30 g. Anal. Rh C$_4$H$_{21}$N$_5$O$_{13}$Cl$_3$: C, H, N, Cl.

Analyses for C, H, N, S and Cl were carried out by the Microanalytical Laboratory at the H. C. Ørsted Institute, University of Copenhagen.

UV-visible absorption spectra were recorded on a Cary Varian 219 spectrophotometer and *optical rotation* on a Perkin-Elmer 141 polarimeter. The experimental techniques employed in the present study have all been described in detail elsewhere: *high-performance ion-exchange chromatography,*[13] *^{18}OH$_2$/OH$_2$-exchange kinetic experiments,*[19] *photolysis experiments,*[1-3] *mass spectrometric measurements,*[19] and *potentiometric* determination of pK_a values.[21] An aqueous 1.0 M perchlorate medium was used for all of the investigations described.

Determination of photoreleased ammonia. Photolyzed solutions were made basic by adding an excess of 1 M NaOH. The resulting solution was rapidly frozen, and ammonia and water were sublimed *in vacuo* into an excess of aqueous hydrochloric acid. The resulting solution was analyzed for ammonia using Nessler's reagent.[22]

Preparation of solutions for photolysis. Solutions of cis-[Rh(en)$_2$(NH$_3$)(OH$_2$)]$^{3+}$ for photolysis were prepared from cis-[Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ or, for the enantiomer, from the (+)-bromocamphorsulfonate, by mercury(II)-assisted hydrolysis in acidic perchlorate solution at 60°C for ½h and purified by cation-exchange chromatography on Sephadex SP-C25 (cf. Ref. 1). For the other complex ions, solutions were made by simple dissolution of purified salts. Enrichment of the complexes with ^{18}O was performed by silver ion assisted chloride ligand aquation of cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ in ^{18}OH$_2$ at 70°C, as described previously,[1,32] or by aquation of trans-[Rh(en)$_2$(NH$_3$)(CF$_3$SO$_3$)]$^{2+}$ in ^{18}OH$_2$ for 16 h at room temperature.

Methods of calculation. The calculations were made within the framework of non-linear regression analysis and have been described in detail in Refs. 3, 21 and 23–25.

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