Aqueous Solution Photochemistry of *cis*- and *trans*-Diaquabis(1,3-propanediamine)rhodium(III) Ions and Their Conjugated Bases. The Influence of Chelation on Photoisomerization and Photostationary States

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The syntheses of the isomeric 1,3-propanediamine complexes *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ were accomplished by thermal hydrolysis of the parent *cis*- and *trans*-dichloro compounds. The pK_a-values measured in 1.00 M NaClO$_4$ at 25 °C are p$K_{a,1}$=6.15 and p$K_{a,2}$=8.20 for the *cis*-isomer, and p$K_{a,1}$=4.39 and p$K_{a,2}$=8.20 for the *trans*-isomer, respectively. Upon ligand field excitation in acidic aqueous solution the diaqua species form a photostationary state with a *cis* to *trans* photoisomerization quantum yield of 0.29±0.05 and a *trans* to *cis* photoisomerization quantum yield of 0.10±0.05 mol/einstein, respectively. The *trans*-aquahydroxo species photoisomerizes very efficiently with a quantum yield close to unity, whereas its *cis*-counterpart shows only little photoisomerization with a quantum yield of 0.033±0.005 mol/einstein. The dihydroxo-species are photoinert. For all the species which undergo photoisomerization, secondary or competitive photochemical amineaquation constitutes minor but significant reaction paths.

INTRODUCTION

Ligand field excitation of *cis*- or *trans*-[Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ in aqueous solution leads to *cis/trans* photostationary states [1]

cis-[Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ $\underset{h\nu}{\overset{h\nu}{\rightleftarrows}}$
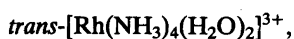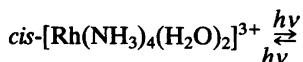
trans-[Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$,

whereas *trans*-[Rh(NH$_3$)$_4$(H$_2$O)(OH)]$^{2+}$ photoisomerizes completely [1]

trans-[Rh(NH$_3$)$_4$(H$_2$O)(OH)]$^{2+}$ $\overset{h\nu}{\rightarrow}$

cis-[Rh(NH$_3$)$_4$(H$_2$O)(OH)]$^{2+}$.
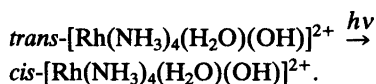
The corresponding ethylenediamine complexes respond differently to light. *cis*-[Rh(en)$_2$(H$_2$O)$_2$]$^{3+}$ photoisomerizes completely to its *trans* counterpart and the aquahydroxo species form *cis/trans* photostationary states [2]

cis-[Rh(en)$_2$(H$_2$O)(OH)]$^{2+}$ $\underset{h\nu}{\overset{h\nu}{\rightleftarrows}}$

trans-[Rh(en)$_2$(H$_2$O)(OH)]$^{2+}$
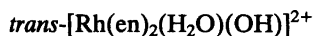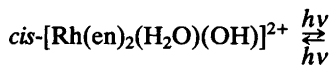
cis/trans-photoisomerization of aquarhodium(III) complexes is initiated by the dissociation of a water ligand as shown by isotopic labelling,[3] and the extent of isomerization is, according to recent theories [4–7] on ligand field excited states of rhodium(III) complexes, determined by the relative energies of the generated *basal/apical* pentacoordinated excited state isomers. The energy difference between these triplet intermediates appears essentially to be a function of the σ-donor strengths of the five ligator atoms, and the composition of the photostationary states should therefore be predictable from the ligand field spectra.

This purely spectroscopic model has proven successful in explaining the different photochemical behaviour of the tetraammine- and the *bis*(ethylenediamine)rhodium(III) complexes.[2] However, the model does not provide any simple means of correcting for the excited state energetics due to chelate effects present in the ethylenediamine but not in the ammonia complexes. In the search for a series of tetraaminerhodium(III) complexes with a bidentate chelating amine similar to ethylenediamine but with σ-donor properties corresponding to the σ-donor properties of ammonia we have synthesized the hitherto unknown 1,3-propanediaminerhodium(III) complexes *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ and report here the result of a photochemical investigation of these complexes in aqueous solution over a wide pH range.

EXPERIMENTAL

Materials. The complexes *cis*-[Rh(tn)$_2$Cl$_2$]ClO$_4$·2H$_2$O and *trans*-[Rh(tn)$_2$Cl$_2$]ClO$_4$ were prepared and purified by the method of Hancock.[8] Other chemicals were of analytical grade.

Absorption spectra were recorded on a Cary 219 spectrophotometer.

pH measurements. A Radiometer PHM 52 pH-meter with a combination glass electrode with 1.0 M NaCl in the reference part was used for the pH measurements. Since all measurements were made in 1.00 M (H,Na)(ClO$_4$,OH) media the definition pH=−log[H$^+$] was used throughout, using standardized perchloric acid in 1.00 M NaClO$_4$ as pH standards.

Photolysis experiments. Photolyses with 312, 334, or 366 nm monochromatic light (λ$_{irr}$) were carried out in an optical train consisting of a light source, an Osram HBO 100/2 high pressure Hg lamp, a light condenser, a heat filter, an interference filter, a precision shutter connected to an electronic timer and lenses focusing the light into the thermostatted (25.0±0.5 °C) photolysis cell. The photolysis solution was stirred by means of a teflon-coated magnetic bar. All optical parts and cells were of quartz (Spindler und Hoyer, Göttingen, GFR). An Oriel 6035 low-pressure Hg–Ar penlight equipped with an Oriel 6041 short-wave filter mounted in a thermostatted (25.0±0.5 °C) light- and cell-holder unit was used as a diffuse light source for 254 nm photolyses. Light intensities were determined by standard ferrioxalate actinometry[9] and monitored by an

Oriel Photodiode Detection System 7072.

Dark reactions. For all the complex ions under investigation, experiments were made to ensure that no thermal reactions occurred during photolysis.

Calculation of quantum yields. Quantum yields were calculated from spectral changes in combination with changes in solution pH by methods previously outlined.[1,2]

Synthesis of new complexes. 1. cis-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$. A mixture of *cis*-[Rh(tn)$_2$Cl$_2$]ClO$_4$.2H$_2$O (615 mg, 1.34 mmol) and AgNO$_3$ (570 mg, 3.35 mmol) in water (10 ml) was heated under reflux for 3 h, protected against light. The volume was reduced to 5 ml by evaporation and 1.0 M HCl (0.90 ml) was added to the cooled solution, which was subsequently filtered through a fine-porosity sintered glass funnel. The AgCl was washed with 5 ml of warm water, and the washings were added to the filtrate. pH was then adjusted to approximately 7 by dropwise addition of 1.0 M NaOH (≈2.2 ml) under magnetic stirring. Saturated, aqueous NaClO$_4$ (12.5 ml) was added slowly under continuous stirring, and the reaction mixture was left in the refrigerator (≈5 °C) overnight, and subsequently cooled in ice for 8 h with stirring. The crude product was isolated by filtration, washed with ice-cold water (0.3 ml), absolute ethanol (1 ml) and finally ether, and air-dried. Yield 450 mg (70 %).

The crude product was purified by dissolution in 3 ml of warm H$_2$O and reprecipitated by dropwise addition of saturated, aqueous NaClO$_4$ (3 ml) to the filtered solution. The product was filtered off after cooling for 2 h in ice with stirring, and washed and dried as before. The product was reprecipitated 4 times by this procedure with an overall yield of 200 mg (30 %). The absorption spectrum did not change between the third and fourth reprecipitation (see Table 1 and Fig. 1). Anal. C, H, N, Cl were performed by the Microanalytical Laboratory of the H. C. Ørsted Institute, University of Copenhagen.

2. trans-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$. A mixture of *trans*-[Rh(tn)$_2$Cl$_2$]ClO$_4$ (1.70 g, 4.03 mmol) and HgO (4.0 g, 18 mmol) was dissolved in 0.33 M HClO$_4$ (240 ml) and heated under reflux for 2 h, protected against light. The volume was then reduced to 60 ml by evaporation and the resulting solution cooled in ice. pH of the cold solution was subsequently adjusted to≈10 by dropwise addition of 10 M NaOH, and the HgO formed was removed by filtration through a fine-porosity sintered glass funnel. Crude *trans*-[Rh(tn)$_2$(H$_2$O)$_2$]Br$_3$ was precipitated by addition of ice-cold 65 % HBr (60 ml) and collected on a sintered glass filter. This product was dissolved in

water (20 ml) on the filter, and after addition of saturated, aqueous $NaClO_4$ (20 ml), pH was immediately adjusted to approximately 6.5 by dropwise addition of 1.0 M NaOH ($\approx$3.8 ml). The product formed after cooling of the reaction mixture in ice, crude *trans*-[Rh(tn)_2(H_2O)(OH)](ClO_4)_2, was filtered off, washed with ice-cold water (2 ml), absolute ethanol (2 ml) and finally ether, and air-dried. Yield 1.3 g (67 %).

The crude product was purified by the following procedure. After dissolution in 1.0 M HBr (5.5 ml), ice-cold saturated, aqueous LiBr (5.5 ml) was added and the reaction mixture was cooled in ice for 1 h. The product was collected on a sintered glass filter and redissolved on the filter in H_2O (6.0 ml). 3.5 g of $LiClO_4.3H_2O$ dissolved in 6.0 ml of water was added and pH again adjusted to 6.5 with 1.0 M NaOH. *trans*-[Rh(tn)_2(H_2O)(OH)](ClO_4)_2 was collected and washed as before. Reprecipitation of the product was performed after dissolving it in 0.5 M $HClO_4$ (6.0 ml) and then adjusting the pH of the filtered solution as before. The washed product (also same procedure as before) was reprecipitated once more, giving a final yield of 0.85 g (43 %). The absorption spectrum did not change between the two reprecipitations. Anal. C, H, N, Cl.

RESULTS

Syntheses. The two new diaquatetraaminerhodium(III) ions *cis*- and *trans*-[Rh(tn)_2(H_2O)_2]^{3+} have been synthesized from *cis*-[Rh(tn)_2Cl_2]-ClO_4 · 2H_2O and *trans*-[Rh(tn)_2Cl_2]ClO_4, respectively. pK_{a1} and pK_{a2} were determined by published methods [10,11] and are compared in Table 1 with literature values for the analogous ammonia and ethylenediamine complexes. Fig. 1 shows the UV-absorption spectra of purified *cis*- and *trans*-[Rh(tn)_2(H_2O)(OH)](ClO_4)_2 dissolved in acidic, neutral and alkaline aqueous 1.00 M perchlorate,
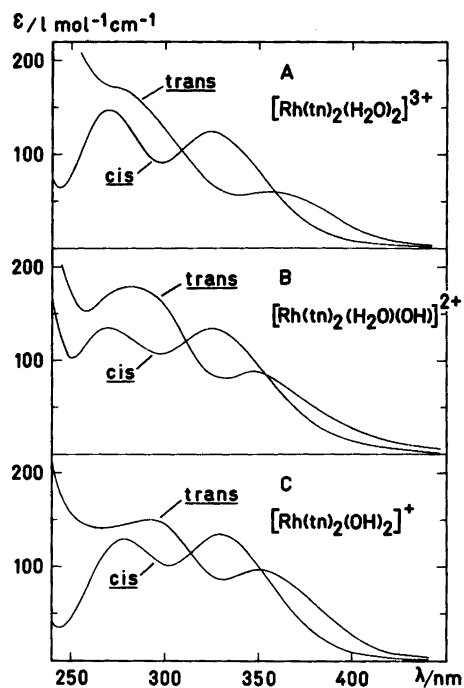
Fig. 1. UV-absorption spectra of *cis*- and *trans*-[Rh(tn)_2(H_2O)(OH)](ClO_4)_2 dissolved in (A) aqueous 0.10 M $HClO_4$, 0.90 M $NaClO_4$, (B) aqueous 1.00 M $NaClO_4$ with pH=$\frac{1}{2}$ ($pK_{a,1}+pK_{a,2}$), and (C) aqueous 0.040 M NaOH, 0.96 M $NaClO_4$.

and the spectral characteristics necessary for the discussion of the photochemical results are listed in Table 2.

Halide aquation in neutral or acidic solution is known to proceed with stereoretention for Rh(III) low-spin complexes.[7] This was confirmed for the present complexes by the following experiments. *cis*-[Rh(tn)_2(H_2O)](ClO_4)_2 was dis-

Table 1. pK_a values for diaquatetraaminerhodium(III) complexes in 1.0 M $NaClO_4$ at 25.0 °C.[a]

	cis			trans			Ref.
	$pK_{a,1}$	$pK_{a,2}$	Δ_{cis}	$pK_{a,1}$	$pK_{a,2}$	Δ_{trans}	
[Rh(NH_3)_4(H_2O)_2]^{3+}	6.40	8.32	1.92	4.92	8.26	3.34	11
[Rh(en)_2(H_2O)_2]^{3+}	6.34	8.24	1.90	4.47	7.91	3.44	2,12
[Rh(tn)_2(H_2O)_2]^{3+}	6.15	8.20	2.05	4.39	8.20	3.81	This work[b]

[a] $\Delta = pK_{a,2} - pK_{a,1}$. en=ethylenediamine. tn=1,3-propanediamine. [b] Estimated standard deviation on the pK_a values ranged from 0.005 to 0.02.

Table 2. Spectral characteristics of cis- and trans-diaquabis(1,3-propanediamine)rhodium(III) ions and their conjugated bases in aqueous 1.0 M (Na,H)(ClO$_4$,OH).

Complex Ion [a]	λ/nm (ε/l mol^{-1}cm^{-1})		
	$\lambda_{max}(\varepsilon_{max})$	$\lambda_{min}(\varepsilon_{min})$	$\lambda_{irr}(\varepsilon_{irr})$ [b]
cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	325(123), 270(147)	298(91), 244(64)	366(43), 334(115), 312(109), 254(94)
cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ [c]	325(134), 270(135)	298(108), 250(103)	366(58), 334(128), 312(123), 254(114)
cis-[Rh(tn)$_2$(OH)$_2$]$^{+}$	330(135), 279(130)	303(101), 244(35)	366(57), 334(113), 312(109), 254(58)
trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	357(60), 274(171) [d]	338(57)	366(57), 334(58), 312(98), 254(246)
trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ [c]	348(88), 283(179)	330(82), 258(154)	366(69), 334(82), 312(119), 254(156)
trans-[Rh(tn)$_2$(OH)$_2$]$^{+}$	351(97), 294(150)	332(87), 263(142)	366(83), 334(88), 312(117), 254(147)

[a] Medium for the diaqua complexes: 0.10 M HClO$_4$, 0.90 M NaClO$_4$; for the aquahydroxo complexes: 1.00 M NaClO$_4$ adjusted to pH=$\frac{1}{2}$(p$K_{a,1}$+p$K_{a,2}$); and for the dihydroxo complexes: 0.04 M NaOH, 0.96 M NaClO$_4$. [b] λ_{irr} are the wavelengths of irradiation and ε_{irr} the molar absorption coefficients at these wavelengths. [c] $\lambda_{max}(\varepsilon_{max})$ reported is that measured for a mixture at pH=$\frac{1}{2}$(p$K_{a,1}$+p$K_{a,2}$), whereas $\lambda_{irr}(\varepsilon_{irr})$ has been corrected for the presence of the diaqua and the dihydroxo species. [d] Shoulder.

solved in aqueous 0.050 M HCl and heated to ~100 °C for 1 h rigorously protected against light. The UV-absorption spectrum of this solution at room temperature [$(\lambda,\varepsilon)_{max}$=(351 nm, 122 $l \cdot$mol$^{-1} \cdot$cm^{-1}); (289,126); $(\lambda,\varepsilon)_{min}$=(318,77.6); (276,115.1)] showed only minor deviation from that of authentic cis-[Rh(tn)$_2$Cl$_2$]ClO$_4 \cdot$2H$_2$O[8] heated in HCl by the same procedure $(\lambda,\varepsilon)_{max}$= (351,125); (289,128); $(\lambda,\varepsilon)_{min}$=(319,78.3); (276,115.7). trans-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ anated under similar conditions had an UV-absorption spectrum $(\lambda,\varepsilon)_{max}$=(417, 81.3); $(\lambda,\varepsilon)_{sh}$=(286, 146); $(\lambda,\varepsilon)_{min}$=(362,13.3), virtually identical to that of authentic trans-[Rh(tn)$_2$Cl$_2$]-ClO$_4$[8] heated in HCl by the same procedure [$(\lambda,\varepsilon)_{max}$=(417, 79.6); $(\lambda,\varepsilon)_{sh}$=(285, 138); $(\lambda,\varepsilon)_{min}$=(364, 15.1)]. From the small spectral deviations it was estimated that less than 0.3 % of the cis-isomer and less than 0.8 % of the trans-isomer, respectively, had undergone isomerization during the thermal aquation. Thirst and Vaughan,[13] report that base hydrolysis of trans-[Rh(tn)$_2$Cl$_2$]$^+$ gives a product with the following spectral characteristics $(\lambda,\varepsilon)_{max}$=(328 nm, 135 l$\cdot$mol$^{-1} \cdot$cm^{-1}); (279, 149), and that this is independent of hydroxide ion concentration (0.1−1.0 M) and temperature (70−90 °C). The spectral data now available for both of the diaqua species and their conjugated bases (cf. Table 2) allow an identification of the principal hydrolysis product, and it can be concluded that thermal base hydrolysis leads to essentially complete trans to cis photoisomerization. This high stereomobility is in contrast to the the stereoretention observed for hydrolysis- and anation reactions in neutral or acidic solution and, more significantly, rather different from what is observed for the ethylenediamine analogue.[14]

cis- and trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ photoreactions. Ligand field photolysis of cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ in aqueous acidic 1.00 M perchlorate solution ([H$^+$]≥0.010 M) led to a product mixture with a composition depending on the wavelength of irradiation. A ca. 10^{-3} M solution of cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ in 0.10 M HClO$_4$, 0.90 M NaClO$_4$ exhaustively photolyzed (λ_{irr}=334 nm) had a UV-absorption spectrum which is compared in Fig. 2 with those of cis- and trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ in the same medium. Also shown in this figure is the product spectrum from a 254 nm photolysis of cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ under identical conditions.
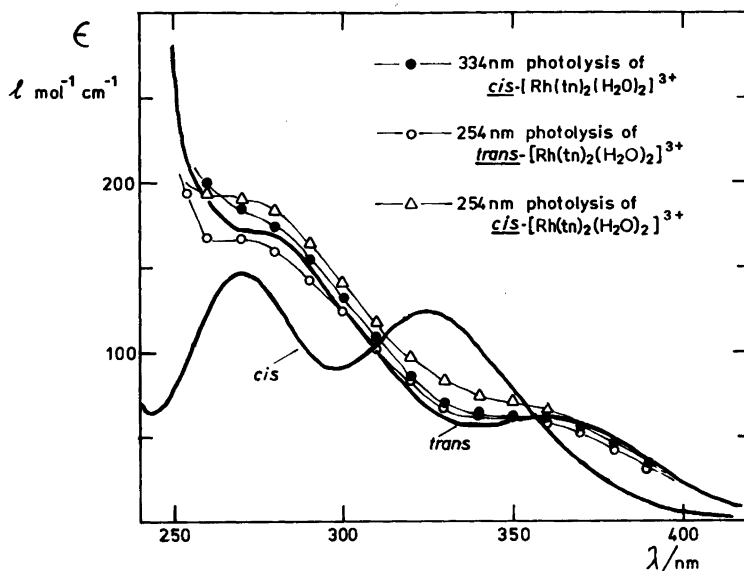
Fig. 2. UV-absorption spectra of product solutions from long term photolysis of *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ in aqueous 0.10 M HClO$_4$, 0.90 M NaClO$_4$ in comparison with spectra of *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ (full lines).
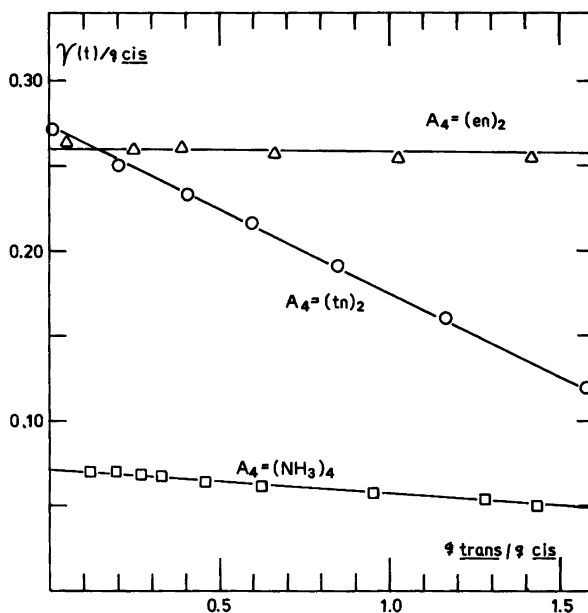
Fig. 3. Quantum yields for *cis*-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ $\underset{h\nu}{\overset{h\nu}{\rightleftarrows}}$ *trans*-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ in 0.10 M HClO$_4$, 0.90 M NaClO$_4$ at 25 °C determined from *cis*-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ photolysis experiments. The observed net *cis* to *trans* isomerization quantum yield, $\gamma(t)/q_{cis}$, is plotted *vs.* q_{trans}/q_{cis}, the ratio of light quanta absorbed by product and reactant:

$$\gamma(t)/q_{cis} = \Phi_{cis}^{(H_2O)_2} - \Phi_{trans}^{(H_2O)_2}(q_{trans}/q_{cis}).$$

A=NH$_3$: λ_{irr}=350 nm.[1] A=$\frac{1}{2}$en: λ_{irr}=312 nm.[2] A=$\frac{1}{2}$tn: λ_{irr}=312 nm. The *cis* to *trans* isomerization quantum yield is determined by the intercept and the *trans* to *cis* isomerization quantum yield by minus the slope.

The isosbestic points which can be identified from the figure persisted in both photolyses during *ca.* 90 % of reaction. The two product spectra show similarities with the spectrum of *trans*-[Rh(tn)₂(H₂O₂)]³⁺ and a comparison shows that the photoreaction caused by 334 nm irradiation proceeds to a greater extent than that resulting from 254 nm excitation. This observation suggests that the product solution is in a photostationary state, and direct evidence for a photostationary state between *cis*- and *trans*-[Rh(tn)₂(H₂O)₂]³⁺ was obtained by irradiation of solutions of *trans*-[Rh(tn)₂(H₂O)₂]³⁺ under identical conditions. The UV-absorption spectrum of the product solution resulting from exhaustive 254 nm photolysis of *trans*-[Rh(tn)₂(H₂O)₂]³⁺ is included in Fig. 2. The changes in the absorption spectrum (increasing absorbance in the near-UV region and decreasing absorbance at higher energy) indicate *trans* to *cis* isomerization. However, a spectral analysis revealed that the product mixtures, in addition to the isomeric [Rh(tn)₂(H₂O)₂]³⁺ ions contained significant amounts of at least one other component, and amine photoaquation was suspected.

The solution pH (initially 2.7) of a solution of either *cis*- or *trans*-[Rh(tn)₂(H₂O)₂]³⁺ increased slightly over long periods of photolysis (254 nm) and a quantum yield for proton consumption of *ca.*. 0.01 mol/einstein and *ca.* 0.005 mol/einstein was estimated for the *cis*- and *trans*-isomers, respectively. Titration of photolyzed solutions indicated formation of a Rh(III)-species with a monodentate 1,3-propanediamine ligand, [Rh(tn)(tnH)(H₂O)₃]⁴⁺, with pK_a<7 for the "extra" coordinated water and pK_a>7 for the 3-aminopropylammonium ligand. The proton consumption quantum yield can thus be identified with the quantum yield for formation of monodentate amine.

Evaluation of the quantum yields for the major photoreactions, *i.e.* the *cis/trans*-photoisomerizations, was based on spectral changes. In Fig. 3 the isomerization quantum yields for *cis*-[Rh(tn)₂(H₂O)₂]³⁺ determined graphically by Method B of Ref. 1 for a 312 nm photolysis are compared with data for the corresponding ethylenediamine and ammonia complexes taken from Refs. 1 and 2. The calculations were based on changes in absorbance at the wavelength of irradiation, 320, 330 and 340 nm (see Fig. 1), ignoring any interference in the absorption spec-

Table 3. Cis/trans- and trans/cis photoisomerization quantum yields and cis/trans photostationary states calculated from photolyses of cis-[Rh(tn)₂(H₂O)₂]³⁺ in aqueous 1.00 M (H,Na)ClO₄ at 25 °C.ᵃ

λ_{irr} nm	pH	$\Phi^{(H_2O)_2}_{cis}$ mol·einstein⁻¹ ᵇ	$\Phi^{(H_2O)_2}_{trans}$ mol·einstein⁻¹ ᵇ	$C^\infty_{cis}/C^\infty_{trans}$ ᶜ	$(\Phi^{(H_2O)_2}_{trans}/\Phi^{(H_2O)_2}_{cis})\cdot(\varepsilon^{irr}_{trans}/\varepsilon^{irr}_{cis})$
334	0.0	0.26±0.02	0.10±0.01	0.19±0.01	0.21±0.01
254	1.0	0.21±0.02	0.3±0.1ᵈ	0.8±0.2	4±1ᵈ
312	1.0	0.27±0.01	0.10±0.01	0.34±0.03	0.28±0.03
334	1.0	0.28±0.01	0.09±0.02	0.17±0.04	0.16±0.06
366	1.0	0.29±0.01	0.07±0.01	0.31±0.01	0.32±0.08
334	2.0	0.27±0.01	0.11±0.01	0.21±0.03	0.22±0.04

ᵃ All experiments in duplicate. ᵇ Quantum yield calculated by Method B of Ref. 1 (see Fig. 3). ᶜ *cis/trans* concentration coefficient in solution photolyzed to completion. ᵈ Numerically unstable due to undefined value of $\varepsilon^{254}_{trans}$ (see Fig. 1).

tra caused by the amine aquation products. Although this introduces a certain arbitrariness in the calculations, consistent results were obtained (see Fig. 3 and Table 3), and no significant pH- or wavelength dependence on isomerization quantum yields was observed. Consistency was also obtained between the *cis/trans* ratio in the product solution, $C_{cis}^{\infty}/C_{trans}^{\infty}$, calculated from the product solution spectrum and the same ratio calculated from[1]

$$\frac{C_{cis}^{\infty}}{C_{trans}^{\infty}} = \left(\frac{\Phi_{trans}^{(H_2O)_2}}{\Phi_{cis}^{(H_2O)_2}} \right) \cdot \left(\frac{\varepsilon_{trans}^{irr}}{\varepsilon_{cis}^{irr}} \right)$$

at each of the irradiation wavelengths, as seen in Table 3.

Photolysis of *trans*-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ under the same conditions as employed for the *cis*-isomer resulted in significant formation of *cis*-isomer (see Fig. 2). However, for the *trans*-isomer, photochemical amine aquation interferes significantly in the evaluation of quantum yields, although comparable results were obtained for the two isomers.

The photoreactions of the isomeric [Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ are summarized in Table 5 together with photoreaction quantum yields with realistic (*vide supra*) error limits.

cis- and *trans*-[Rh(tn)$_2$(OH)$_2$]$^+$ *photoreactions.* Long term ligand field photolysis (334 nm) of either isomer of the dihydroxobis(1,3-propane-diamine)rhodium(III) ion in aqueous 0.04 M NaOH, 0.96 M NaClO$_4$ led to minor spectral changes, and these changes did not indicate any photoisomerization. The photoisomerization quantum yields presented in Table 5 for the dihydroxo species are estimated upper limits.
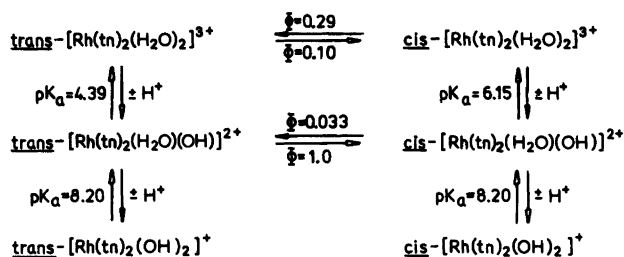
cis- and *trans*-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ *photo-*

reactions. trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ in 1.00 M aqueous NaClO$_4$ solution showed a very high photoreactivity, whereas *cis*-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ was only moderately photoreactive.

A *ca.* 10^{-3} M *trans*-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ solution with pH 6.30 was photolyzed with 334 nm monochromatic light until no further spectral changes were observed. During the first *ca.* 20 % of reaction isosbestic points at *ca.* 356 and *ca.* 309 nm were maintained. The long term photolysis product solution had a pH value of 6.72 and the following spectral characteristics: $\lambda_{max}(\varepsilon_{max})$=324 nm (140 l·mol^{-1}·cm^{-1}), $\lambda_{sh}(\varepsilon_{sh})$=260 (204), and $\lambda_{min}(\varepsilon_{min})$=304 (132). The pH- and spectral changes during the initial stages of photolysis clearly indicate a very efficient *trans* to *cis* photoisomerization. However, competitive and/or secondary photoreactions are significant. Photoproduct solution spectra showed deviations from the spectrum predicted for a mixture of *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ in thermal acid/base equilibria with the corresponding diaqua and dihydroxo complex ions, especially in the wavelength region λ<300 nm. This deviation was of the same nature as the deviation observed for the spectra of the product mixture from *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ photolysis in acid solution. Titration of photolyzed solutions confirmed that some amine aquation occurred during photolysis. $\phi_{trans}^{(H_2O)(OH)}$, the *trans* to *cis* photoisomerization quantum yields, were estimated from spectral changes at the wavelength of irradiation, as well as at 320 and 340 nm (*cf.* Fig. 1) by Method A of Ref. 1. This extrapolation method eliminates interference from secondary processes. Results for 254, 334 and 366 nm excitation are reported in Table 4.

Table 4. Photoisomerization quantum yields for *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ in aqueous 1.00 M NaClO$_4$ at 25 °C.

Complex ion	λ_{irr}/nm	pH[a]	$\Phi^{(H_2O)(OH)}$/mol·einstein^{-1}[b]	No. of exp.
trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	334	5.5−6.3	1.03±0.10	4
	366	5.8	1.01±0.08	1
	254	6.1	1.3±0.2	1
cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	334	8.36	0.029±0.005[c]	1
	366	8.35−8.52	0.036±0.005[c]	2

[a] Initial pH, see Results. [b] Calculated on the basis of the light absorbed by the aquahydroxo complex, *cf.* Ref. 2. [c] Corrected for photoreaction of *cis*-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$, *cf.* Ref. 2.

$$
\begin{array}{ccc}
\underline{trans}\text{-}[Rh(tn)_2(H_2O)_2]^{3+} & \xrightleftharpoons[\phi=0.10]{\phi=0.29} & \underline{cis}\text{-}[Rh(tn)_2(H_2O)_2]^{3+} \\[1ex]
pK_a=4.39\ \updownarrow\ \pm H^+ & & pK_a=6.15\ \updownarrow\ \pm H^+ \\[1ex]
\underline{trans}\text{-}[Rh(tn)_2(H_2O)(OH)]^{2+} & \xrightleftharpoons[\phi=1.0]{\phi=0.033} & \underline{cis}\text{-}[Rh(tn)_2(H_2O)(OH)]^{2+} \\[1ex]
pK_a=8.20\ \updownarrow\ \pm H^+ & & pK_a=8.20\ \updownarrow\ \pm H^+ \\[1ex]
\underline{trans}\text{-}[Rh(tn)_2(OH)_2]^{+} & & \underline{cis}\text{-}[Rh(tn)_2(OH)_2]^{+}
\end{array}
$$

Scheme 1.

Photolysis experiments to establish photoreactivity of cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ were carried out at pH≥8.35, where the fraction of both 334 and 366 nm monochromatic light absorbed by the highly photoreactive cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ is less than 0.002. Long term photolysis under these mildly alkaline conditions led to slight but significant photoisomerization of the cis-species present. As cis-[Rh(tn)$_2$(OH)$_2$]$^+$ is photoinert, the observed reaction could be attributed to cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$, and $\phi_{cis}^{(H_2O)(OH)}$ values calculated from three experiments by the same method as used for the reverse photoreaction (*vide supra*) are presented in Table 4.

cis/trans-*photostationary states*. cis- and trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$, and cis- and trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$ are all photoreactive with respect to isomerization. A combination of the quantum yields for these photoreactions (shown in Scheme 1) with the pK$_a$-values for the relevant complex ions (Table 1) and their molar absorptivities (Table 3) allow a calculation of the cis/trans-photostationary state resulting from long term irradiation as a function of pH. The observed cis-fraction in exhaustively photolyzed (334 nm) solutions with intermediate pH agreed qualitatively with that predicted. However, a more quantitative spectral analysis was hampered

by the above mentioned secondary and competitive amine photoaquation.

DISCUSSION

The aqueous solution photochemistry of the isomeric [Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ and their conjugated bases follows the same general pattern which is observed for the analogous ammonia and ethylenediamine complexes,[1,2] and which again is consistent with the generalized model for photoreactions of low spin d^6 complexes.[4-7,16] The dominant photoreactions for the present type of complexes are the photoisomerizations,[1,2,15] and in Scheme 1 a summary of photoisomerizations for the 1,3-propanediamine complexes is given together with the relevant reaction quantum yields. Despite the similarities between the three closely related series of tetraaminerhodium(III) complexes, significant differences are noted. The ensuing discussion will focus on these differences in relation to the excited state reaction dynamics.

Excitation of low spin rhodium(III) complexes with light of wavelength matching the energy of the multiplicity-allowed ligand field transitions $^1T_1 \leftarrow {}^1A_1$ and $^1T_2 \leftarrow {}^1A_1$ (assuming pseudo octahedral symmetry) results, *via* an efficient intersystem crossing, in population of the $^3T_1$

Table 5. Photoreaction quantum yields for cis- and trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$ and their conjugated bases in aqueous 1.0 M (Na,H)(ClO$_4$) at 25 °C.

Complex Ion	Photoproduct	pH	Φ/mol · einstein^{-1}
cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	0.0−2.0	0.29±0.05
	"[Rh(tn)(tnH)(H$_2$O)$_3$]$^{4+}$"	0.0−2.0	ca. 0.01
trans-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	cis-[Rh(tn)$_2$(H$_2$O)$_2$]$^{3+}$	0.0−2.0	0.10±0.05
	"[Rh(tn)(tnH)(H$_2$O)$_3$]$^{4+}$"	0.0−2.0	ca. 0.005
cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	8.4−8.5	0.033±0.005
trans-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	cis-[Rh(tn)$_2$(H$_2$O)(OH)]$^{2+}$	5.5−6.3	1.0±0.1
cis-[Rh(tn)$_2$(OH)$_2$]$^{+}$	trans-[Rh(tn)$_2$(OH)$_2$]$^{+}$	12.6	<0.003
trans-[Rh(tn)$_2$(OH)$_2$]$^{+}$	cis-[Rh(tn)$_2$(OH)$_2$]$^{+}$	12.6	<0.002

apical   basal

trans-product   cis-product
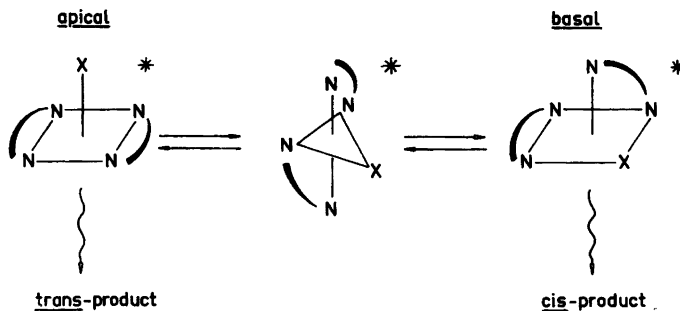
Scheme 2.

state. This lowest triplet state (from which weak luminescence is observed[17,18]) has been identified as the photochemically reactive state.[4-6,15] The presence of an electron in a σ-antibonding e_g orbital is *a priori* expected to facilitate ligand dissociation, and a wide variety of experimental results is in strong support of such a dissociative reaction mode.[3,18-21] In full agreement with the limiting dissociative model, ^{18}O-labelling studies show that photoisomerization of aquaaminerhodium(III) complexes such as the one investigated in the present study is initiated by the dissociation of a water ligand.[3,22]

The step following ligand dissociation in the excited state reaction sequence is the key step for *cis/trans* photoisomerizations. During this step the pentacoordinated intermediates, still in their triplet state, rearrange *via* a proposed trigonal bipyramidal intermediate in competition with deactivation[4-7,23] to the ground state (X=H$_2$O, or OH); see Scheme 2.

The relative energies of the *apical* and *basal* intermediates are controlled mainly by the σ-donor strengths of the five ligator atoms, and AOM calculations indicate[4-6] that the isomer with the weaker σ-donor in the *apical* position is the more stable. Petersen and Lee[24] recently reported preliminary results from a study of the photoracemization of optically active *cis*-[Rh(en)$_2$(H$_2$O)(OH)]$^{2+}$ and the analogous 1,3-propanediamine complex. Measurement of the photoisomerization/photoracemization ratio facilitated an estimation of the energy difference between the trigonal bipyramidal intermediate leading to isomerization (depicted in Scheme 2) and the trigonal bipyramidal intermediate in which one chelate spans two equatorial sites and which leads to optical interconversion. The σ-donor strength series $\sigma_{OH^-} > \sigma_{saturated\ amine} >$

$\sigma_{H_2O} \approx 3\sigma_{Cl^-}$ predicts *apical*-[RhA$_4$(H$_2$O)]$^{3+*}$ to be more stable than *basal*-[RhA$_4$(H$_2$O)]$^{3+*}$, but *basal*-[RhA$_4$(OH)]$^{2+*}$ to be more stable than *apical*-[RhA$_4$(OH)]$^{2+*}$. For all three series of amine complexes investigated *cis* to *trans* photoisomerization dominates the [RhA$_4$(H$_2$O)$_2$]$^{3+}$ photochemistry and *trans* to *cis* photoisomerization the [RhA$_4$(H$_2$O)(OH)]$^{2+}$ photochemistry, in qualitative agreement with these arguments. However, significant differences are noted when the three amine series are compared, as seen in Table 6.

The *apical/basal* excited state equilibrium is expected to be sensitive to even minor changes in the σ-strength of the five ligands and also to any strain introduced by the chelate rings. Of the three amine ligands in question, ammonia and 1,3-propanediamine have comparable σ-donor properties, whereas ethylenediamine is a significantly stronger σ-donor in this class of compound, as seen from data in Ref. 13 and from the energy of the $^1T_1 \leftarrow ^1A_1$ transition (Table 7). In accordance with the spectroscopic parameters, the photochemical behaviour of 1,3-propanediamine resembles that of the ammonia complexes rather than that of the ethylenediamine complexes. The *cis/trans* diaqua complexes of ammonia as well as 1,3-propanediamine photoisomerize to each other, forming a product photostationary state, whereas in the ethylenediamine series only *cis*-[Rh(en)$_2$(H$_2$O)$_2$]$^{3+}$ is photoactive with respect to isomerization. The predominant photoreaction of the aquahydroxo complexes in all three series is *trans* to *cis* photoisomerization, although *cis* to *trans* photoisomerization with small quantum yields has been detected for the two bidentate amine complexes. The quantum yields for the 1,3-propanediamine complexes are in general higher than those for

Table 6. Comparison between the photoisomerization quantum yields for bis(1,3-propanediamine)rhodium(III) and the corresponding bis(ethylenediamine)rhodium(III) and tetraamminerhodium(III) complexes in aqueous 1.00 M perchlorate solution at 25 °C.

Photoreaction	[a] Bis(1,3-propanediamine) Φ/mol·einstein^{-1}	[b] Bis(ethylenediamine) Φ/mol·einstein^{-1}	[c] Tetraammine Φ/mol·einstein^{-1}
cis-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ $\xrightarrow{h\nu}$ trans-[RhA$_4$(H$_2$O)$_2$]$^{3+}$	0.29	0.27	0.072
cis-[RhA$_4$(H$_2$O)(OH)]$^{2+}$ $\xrightarrow{h\nu}$ trans-[RhA$_4$(H$_2$O)(OH)]$^{2+}$	0.033	0.048	d
cis-[RhA$_4$(OH)$_2$]$^{+}$ $\xrightarrow{h\nu}$ trans-[RhA$_4$(OH)$_2$]$^{+}$	d	d	d
trans-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ $\xrightarrow{h\nu}$ cis-[RhA$_4$(H$_2$O)$_2$]$^{3+}$	0.10	d	0.012
trans-[RhA$_4$(H$_2$O)(OH)]$^{2+}$ $\xrightarrow{h\nu}$ cis-[RhA$_4$(H$_2$O)(OH)]$^{2+}$	1.0	0.61	0.59
trans-[RhA$_4$(OH)$_2$]$^{+}$ $\xrightarrow{h\nu}$ cis-[RhA$_4$(OH)$_2$]$^{+}$	c	d	d

[a] A$_4$=(tn)$_2$; present work. [b] A$_4$=(en)$_2$; from Ref. 2. [c] A$_4$=(NH$_3$)$_4$; from Ref. 1. [d] Photoisomerization not detected.

the ethylenediamine complexes, which are again higher than those measured for the ammonia complexes. Both thermodynamic and kinetic factors could in principle be responsible for this. The strain introduced by the chelate rings could provide additional affinity for the rearrangement reactions. Notably, the quantum yields for both cis/trans- and trans/cis-photoisomerization are increased upon chelation. This suggests an increase in rate of rearrangement *relative* to deactivation rather than a more negative $\Delta G'$ for rearrangement. The available excited-state lifetime data[25] support this (*cf*. Table 8). In a 77 K 4:1 CH$_3$OH/H$_2$O glass the excited-state lifetimes for the 1,3-propanediamine complexes are significantly longer than for the analogous ammonia complexes. The decrease in the number of hydrogen atoms on the N-ligators in combination with the increase in hydrophobicity for the chelate complexes results in a less efficient vibronic coupling to the solvent. The time available for rearrangement (of the order of nanoseconds at ambient temperature [17,18]) simply increases.

The observation of photochemical amine aquation in the 1,3-propanediamine- but not in the ethylenediamine complexes is in accordance with the general tendency of ethylenediamine to form thermodynamically more stable complexes with transition metal ions than 1,3-propanediamine.[26] The stabilities of the latter complexes are, when corrected for the chelate (entropy) effect, very similar to the stabilities of the ammonia complexes. Thus, the Rh—N bond energies in the ammonia and 1,3-propanediamine complexes are comparable, whereas they are smaller than in the ethylenediamine complexes. This is consistent with the σ-donor strength of the amine ligands. In agreement with this is the observation that a reexamination of the photoreactions of cis- and trans-[Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ has revealed a small degree of photochemical amine aquation, and a study of the stereochemistry of the resulting triammine complexes and their photochemical interconversion in connection with photochemical water exchange is now in progress.[22]

CONCLUSION

The bis(1,3-propanediamine)rhodium(III) complexes investigated resemble the analogous tertaamminerhodium(III) complexes as regards

Table 7. Energies (kK[a]) of the $^1T_1 \leftarrow {}^1A_1$ transition (pseudo octahedral summetry assumed) for cis-$[Rh(NH_3)_4(H_2O)_2]^{3+}$, cis-$[Rh(en)_2(H_2O)_2]^{3+}$, and cis-$[Rh(tn)_2(H_2O)_2]^{3+}$ and their conjugated bases.

	Tetraammine[b]	Bis(ethylenediamine)[c]	Bis(1,3-propanediamine)[d]
cis-$[RhA_4(H_2O)_2]^{3+}$	30.7	31.4	30.8
cis-$[RhA_4(H_2O)(OH)]^{2+}$	30.4	31.0	30.8
cis-$[RhA_4(OH)_2]^+$	29.9	30.4	30.3

[a] 1 kK=11.95 kJ·mol⁻¹. [b] A_4=(NH₃)₄, Ref. 1. [c] A_4=(en)₂, Ref. 2. [d] A_4=(tn)₂, present work.

Table 8. $^3T_1$ excited state lifetimes $(\tau/\mu s)$[a] of disubstituted tetraamminerhodium(III) and bis(1,3-propanediamine)rhodium(III) complexes in 4:1 CH_3OH/H_2O glass at 77 K.[26]

	Tetraammine[b]	Bis(1,3-propanediamine)[c]
cis-$[RhA_4(H_2O)_2]^{3+}$	0.2	0.8
trans-$[RhA_4(H_2O)_2]^{3+}$		0.4
cis-$[RhA_4Cl_2]^+$	0.7	2
trans-$[RhA_4Cl_2]^+$	7.6	15

[a] Calculated from exponential luminiscence decay curves.[25] [b] A_4=(NH₃)₄. [c] A_4=(tn)₂.

the photoreactions which are of significance (including amine photoaquation). This observation is in accordance with the Rh−N bond energies and the σ-donor strength differences. The photoreaction quantum yields are, however, comparable to those for the analogous bis(ethylenediamine)rhodium(III) complexes, which is proposed to be the result of less efficient deactivation of the excited state for the chelate complexes relative to the ammonia complexes.

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