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Dihalo- and Aquahalobis(1,3-propanediamine)rhodium(III): Aqueous Solution Photochemistry and Photophysics. Steric Effects on Ligand Field Excited-State Reactivities

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Ligand field excitation of each of the 1,3-propanediamine complexes *cis*- and *trans*-$[Rh(tn)_2X_2]^+$ (X = Cl, Br) leads in acidic aqueous solution at 25 °C to halide photoaquation with the following quantum yields: 0.080 (*trans*-dichloro), 0.055 (*trans*-dibromo), 0.56 (*cis*-dichloro), 0.64 (*cis*-dibromo) mol einstein^{-1}. Exhaustive photolysis produces $[Rh(tn)_2(H_2O)X]^{2+}$ in a cis/trans photostationary state with a trans preference that is especially pronounced for the bromo complexes. The room-temperature phosphorescence lifetimes of the four dihalo complexes in aqueous solution have been measured by pulse laser techniques and range from 0.3 to 1.4 ns. Excited-state halide dissociation rate constants were evaluated from the lifetime and photoaquation quantum yield values. Comparison with previously determined rate constants of tetraammine analogues shows a significant reaction rate acceleration in *cis*-$[Rh(tn)_2Br_2]^+$ ascribed to steric effects. Also described are the syntheses of the dithionate salts of *trans*- and *cis*-$[Rh(tn)_2(H_2O)X]^{2+}$.

Introduction

Ligand field (LF) excitation of rhodium(III) amines in aqueous solution results in ligand photoaquation with relatively large, wavelength-independent quantum yield.[4,5] A wide variety of photochemical and photophysical experiments imply excited-state ligand substitution via limiting dissociative reaction pathways.[6-10] In accordance with experiments, theoretical models for excited-state substitution and rearrangement processes of d^6 low-spin complexes explicitly assume a dissociative reaction mode.[6,11,12]

The combination of photoreaction quantum yields and excited-state lifetimes measured under identical conditions in ambient-temperature aqueous solution for $[Rh(NH_3)_5X]^{2+}$ (X = Cl, Br, I)[8,13,14] and *cis*- and *trans*-$[Rh(NH_3)_4XY]^{2+}$ (X = Cl, Br; Y = X, H$_2$O, OH)[15,16] has allowed the evaluation of rate constants for reactions from the lowest energy LF excited states of these complexes. Such rate constants have proven superior to reaction quantum yields in characterizing the excited-state reactivities and facilitated valuable correlations between reactivity and systematic parameters such as the ligand field strength of the reacting and nonreacting ligands and the stereochemistry of the coordination sphere. However, the effect of chelation upon the excited-state reactivities has been explored only with regard to the stereochemical course and the magnitude of reaction quantum yields. Since significant differences were noted between the aqueous solution photochemistry of chelated and unchelated aminerhodium(III) complexes,[7,17-19] a direct comparison between excited-state intrinsic reactivities and solvent interactions was considered valuable.

Reported herein are the results of an investigation of the photochemical and photophysical properties of the well-characterized[20] 1,3-propanediamine (tn) complexes *cis*- and *trans*-$[Rh(tn)_2X_2]^+$ (X = Cl, Br) under the same conditions as those previously employed for the corresponding ammonia complexes.[16]

Experimental Section

Materials. ***trans*-$[Rh(tn)_2X_2]ClO_4$ (X = Cl, Br)** were prepared as described previously.[20] *trans*-$[Rh(tn)_2Cl_2]Cl$ and *trans*-$[Rh(tn)_2Br_2]Br$ were prepared from the perchlorate salts by stirring them in water for 3 h with Amberlite IRA-400 anion-exchange resin in the appropriate halide form (10 mL of ion-exchange resin and 100 mL of water/g of perchlorate salt). The filtered solution was then evaporated to dryness on a vacuum rotary evaporator at ca. 50 °C, and the product dried for ca. 2 h at 100 °C in an oven.

***cis*-$[Rh(tn)_2X_2]ClO_4$ (X = Cl, Br).** The anhydrous perchlorate salts were obtained by slight modification of the methods described previously[20] for the preparation of *cis*-$[Rh(tn)_2Cl_2]ClO_4{\cdot}2H_2O$ and *cis*-$[Rh(tn)_2Br_2]ClO_4{\cdot}1^1/_2H_2O$:

a. *cis*-$[Rh(tn)_2Cl_2]ClO_4$. $[Rh(tn)_2(C_2O_4)]ClO_4{\cdot}2^1/_2H_2O$ (4.60 g, 9.5 mmol) is boiled for 1 min in 4 M HCl (50 mL). Perchloric acid (70% (w/w); 25 mL) is added to the bright yellow solution, which is then stirred vigorously until crystallization begins. The mixture is kept in a refrigerator (ca. 5 °C) for 3 days, and the fine lemon yellow crystals are isolated by filtration, washed thoroughly with 96% ethanol and ether, and dried in air; yield 3.59 g (90%).

b. *cis*-$[Rh(tn)_2Br_2]ClO_4$. This complex is obtained in exactly the same way as the dichloro analogue, starting from $[Rh(tn)_2(C_2O_4)]ClO_4{\cdot}2^1/_2H_2O$ (4.95 g, 10.2 mmol) and 5 M HBr (50 mL); yield 4.35 g (84%).

Comparison of the electronic absorption spectra of the products with those of the pure hydrated perchlorates[20] showed the former to be anhydrous and of adequate purity for synthetic purposes. The crystalline form of the anhydrous products is also quite clearly different from that of the hydrated salts, the latter being obtained as long needles on slow cooling of the undisturbed solutions.

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All other chemicals employed were of analytical or reagent grade and were used without further purification.

Spectra. Electronic absorption spectra were recorded on a Cary Varian 219 spectrophotometer. Unless otherwise indicated all complexes were recrystallized until no change in the spectrum was observed following one further recrystallization.

Analyses. Microanalyses for C, H, N, S, Cl, and Br were carried out by the Microanalytical Laboratory at the H. C. Ørsted Institute, University of Copenhagen. Satisfactory analyses were obtained for all of the complexes described here.

Syntheses of New Complexes. *trans*-Aquachlorobis(1,3-propanediamine)rhodium(III) Dithionate, *trans*-[Rh(tn)$_2$(H$_2$O)Cl]S$_2$O$_6$. *trans*-[Rh(tn)$_2$Cl$_2$]Cl (2.10 g, 5.9 mmol) is dissolved in anhydrous trifluoromethanesulfonic acid ("triflic acid") (10 mL) in a 100-mL conical flask with magnetic stirring and with gentle bubbling with nitrogen gas (hood!). The solution is heated rapidly to 100 °C and kept at that temperature for $1^1/_2$ h. After being allowed to cool spontaneously to room temperature, the solution is cooled further in an ice bath and ether (50 mL) is added cautiously in ca. 2-mL aliquots (stirring and N_2 bubbling are maintained throughout). A finely crystalline yellow precipitate of crude *trans*-[Rh(tn)$_2$Cl(OSO$_2$CF$_3$)]OSO$_2$CF$_3$ is formed, and after brief stirring, the product is isolated by suction filtration on a sintered-glass funnel and washed quickly with ether (2 × 3 mL). The crude product is transferred to a desiccator containing silica gel; yield 2.80 g.

The aqua chloro complex is then obtained as follows: The crude chlorotriflato complex (2.80 g) is stirred at room temperature in 0.1 M HClO$_4$ (50 mL) for 1 h. The complex dissolves rapidly, giving a orange solution that is then filtered through a fine-porosity sintered-glass funnel. A saturated solution of sodium dithionate (25 mL) is added, whenupon rapid precipitation of the desired aqua chloro complex begins. After the mixture is allowed to stand for 2 h at room temperature, followed by $1^1/_2$ h in an ice bath, the orange crystals are isolated by filtration and washed with ice-cold water, then 96% ethanol, and finally ether. Drying in the air gives 1.98 g.

The crude product is reprecipitated by dissolving it on the filter in hot (90–95 °C) water in portions (total dissolution volume ca. 250 mL) and filtering the solution into a 500-mL suction flask. Saturated sodium dithionate (50 mL) and 0.1 M HClO$_4$ (10 mL) are added to the filtrate, and the mixture is then kept in an ice bath with occasional agitation for $3^1/_2$ h. The resulting pure product is isolated and washed as before and dried overnight in a desiccator; yield 1.60 g (58%).

***trans*-Aquabromobis(1,3-propanediamine)rhodium(III) Dithionate, *trans*-[Rh(tn)$_2$(H$_2$O)Br]S$_2$O$_6$.** The procedure employed here is analogous to that for the aqua chloro complex, with *trans*-[Rh(tn)$_2$Br$_2$]Br (2.50 g, 5.1 mmol) and anhydrous triflic acid (10 mL) maintained at 100 °C for $^3/_4$ h. The red-brown precipitate (2.3 g) of crude *trans*-[Rh(tn)$_2$Br(OSO$_2$CF$_3$)]OSO$_2$CF$_3$ obtained by precipitation and washing with ether and drying in a desiccator is stirred at room temperature in 0.1 M HClO$_4$ (40 mL) for 20 min. The mixture is filtered through a fine-porosity sintered-glass funnel to remove a little insoluble brownish impurity, and to the clear wine red filtrate is added saturated sodium dithionate solution (20 mL). After the solution is agitated briefly to promote precipitation, the mixture is kept in a refrigerator (ca. 5 °C) for 24 h. The product is then isolated and reprecipitated in the same way as the analogous aqua chloro complex, using hot (~95 °C) water (ca. 140 mL) and adding saturated sodium dithionate (70 mL) to the filtered solution. After the mixture is kept in a refrigerator for 6 h, the product is isolated as before and dried overnight in a desiccator; yield 1.03 g (40%).

***cis*-Aquachloro- and *cis*-Aquabromobis(1,3-propanediamine)rhodium(III) Dithionate, *cis*-[Rh(tn)$_2$(H$_2$O)X]S$_2$O$_6$·*n*H$_2$O (X = Cl, *n* = 1; X = Br, *n* = 0).** *cis*-[Rh(tn)$_2$X$_2$]ClO$_4$ (X = Cl, Br) (2.0 mmol) is stirred in the dark in a solution containing silver(I) perchlorate (2.0 mmol) and 0.1 M perchloric acid (5 mL) in water (20 mL) at room temperature for 6 days. The mixture is filtered through a fine-porosity sintered-glass funnel, and the silver halide precipitate is washed with water (2 mL). To the combined filtrate and washings is added saturated sodium dithionate (10 mL), followed by 96% ethanol (35 mL) with stirring. The solution is then kept in a refrigerator (ca. 5 °C) for 24 h, and the resulting crystalline precipitate of sodium dithionate is removed by filtration and discarded. To the filtrate is added more 96% ethanol (25 mL), and the solution is again placed in a refrigerator. Any further crystals of sodium dithionate that may have formed after ca. 8 h are removed by filtration. The solution is allowed to stand for a further 24 h in the refrigerator, and the pale yellow (X = Cl) or golden yellow (X = Br) crystals of the desired complex are isolated by filtration on a fine-porosity sintered-glass funnel, washed with 1:1 aqueous ethanol (5 × 2 mL) then 96% ethanol and ether, and dried in the air. Yields are as follows: X = Cl, ca. 0.5 g (50%); X = Br, ca. 0.35 g (35%). The crude product is recrystallized by dissolving it in the minimum volume of water at room temperature with vigorous stirring (X = Cl, ca. 20 mL/g of complex; X = Br, ca. 25 mL/g of complex) and adding the double volume of 96% ethanol to the filtered solution under stirring. The solution is kept in a refrigerator for 24 h, and the product is isolated and washed as before and dried in a desiccator overnight. Yields are as follows: X = Cl, ca. 0.35 g (35%); X = Br, ca. 0.21 g (20%).

Table I. Ligand Field Spectra of Bis(1,3-propanediamine)rhodium(III) Complexes in Dilute Aqueous Solution[a]

complex ion[b]	λ_{max} (ϵ)[c]	λ_{min} (ϵ)[c]
trans-[Rh(tn)$_2$Cl$_2$]$^+$	418 (80), 289 (136)	363 (10.7), 281 (132)
cis-[Rh(tn)$_2$Cl$_2$]$^+$	353 (123), 293 (125)	321 (71), 278 (105)
trans-[Rh(tn)$_2$(H$_2$O)Cl]$^{2+}$	395 (55), 282 (164)	350 (24), 272 (157)
cis-[Rh(tn)$_2$(H$_2$O)Cl]$^{2+}$	342 (116), 281 (131)	310 (78), 255 (55)
trans-[Rh(tn)$_2$(OH)Cl]$^+$	374 (96), 288 (151)	336 (43), 234 (64)
cis-[Rh(tn)$_2$(OH)Cl]$^+$	343 (121), 279 (106)	304 (87), 259 (80)
trans-[Rh(tn)$_2$Br$_2$]$^+$	441 (119), 342 (58)[d]	379 (11.8)
cis-[Rh(tn)$_2$Br$_2$]$^+$	405 (125),[d] 368 (158)	339 (114)
trans-[Rh(tn)$_2$(H$_2$O)Br]$^{2+}$	410 (59), 475 (36)	361 (23), 465 (35)
cis-[Rh(tn)$_2$(H$_2$O)Br]$^{2+}$	358 (128)	318 (88)
trans-[Rh(tn)$_2$(OH)Br]$^+$	385 (112), 284 (170)[d]	340 (38)
cis-[Rh(tn)$_2$(OH)Br]$^+$	354 (130)	309 (94)

[a] 0.10 M NaOH + 0.90 M NaClO$_4$ for the hydroxo complexes; 10^{-3} M HClO$_4$ for the aqua complexes. [b] Perchlorate salts for dihalo complexes from ref 20; dithionate salts for aqua and hydroxo complexes. [c] λ in nm; ϵ in L mol^{-1} cm^{-1}. [d] Shoulder.

p*K*$_a$ Values. pK_a values were determined by experimental procedures previously described for the analogous ammonia complexes.[21]

Photolysis Experiments. Continuous-wave photolyses were carried out in dilute aqueous solutions by the same methods previously described.[10,19] Temperature control was better than ±1 °C. Light intensities were measured by standard ferrioxalate actinometry.[22] The quantum yields were evaluated from spectral and pH changes (glass electrode measurements) by numerical procedures also previously described.[23]

Emission Lifetime Measurements. The emission lifetimes were measured in room-temperature dilute aqueous solutions by using single-photon correlation techniques in the same manner as previously described.[16] A Spectra Physics Model 171 mode-locked argon ion laser provided 458-nm, 200-ps excitation pulses at a repetition rate of 82 MHz. The observed emission profiles were fitted to a sum of exponentials by using an iterative convolution technique based on Marquardt's algorithm as previously described.[24]

Results

The aqueous solution photochemistry of *cis*- and *trans*-[Rh(tn)$_2$X$_2$]$^+$ (X = Cl, Br) has been thoroughly investigated at 25 °C, and the emission lifetimes of the four complexes have been measured under similar conditions. As the four complex ions *cis*- and *trans*-[Rh(tn)$_2$(H$_2$O)X]$^{2+}$ (X = Cl, Br) were required for photoproduct analyses, synthetic schemes were developed. The trans complexes were obtained by the "triflic

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Table II. pK_a Values for Aquahalobis(1,3-propanediamine)rhodium(III) Complexes in Aqueous 1.0 M $NaClO_4$ at 25 °C[a]

	trans	cis
$[Rh(tn)_2(H_2O)Cl]^{2+}$	6.39	7.53
$[Rh(tn)_2(H_2O)Br]^{2+}$	6.46	7.51

[a] $pK_a = -\log K_a$. K_a in mol L^{-1}.

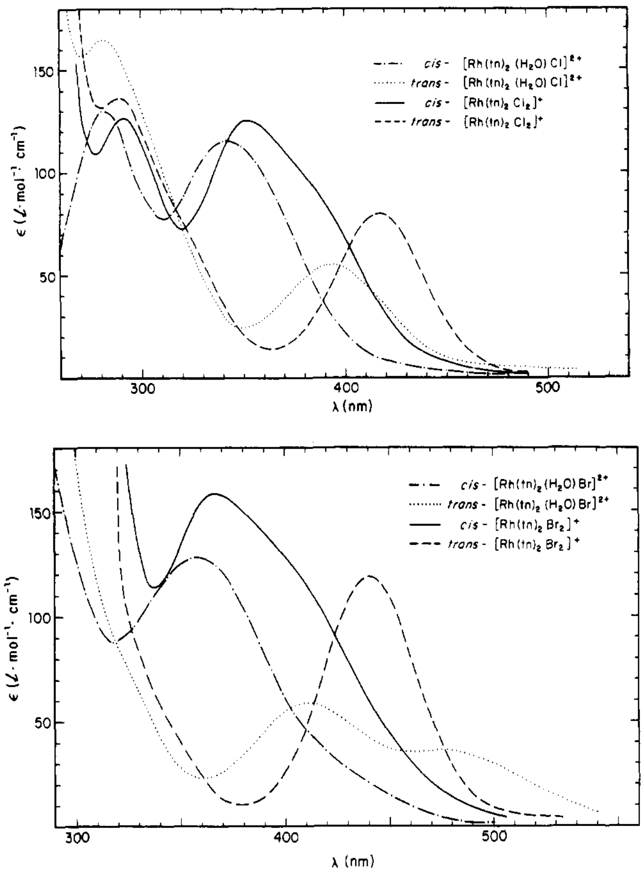

Figure 1. Electronic spectra of bis(1,3-propanediamine)rhodium(III) complexes in dilute aqueous solution.

acid method" as described by Lay[25] for the analogous ethylenediamine complexes, whereas silver(I)-assisted hydrolysis was employed for the cis isomers as done previously for the corresponding ammonia complexes.[6] The four new compounds have been characterized by their absorption spectra (Table I; Figure 1) and by their pK_a values (Table II).

The photochemistry of the four 1,3-propanediamine complexes proved to follow the general patterns previously observed for the analogous ammonia complexes[6,10] with the important exception that no amine photoaquation could be detected for any of the tn complexes. Thermal reactions were likewise found to be of no significance for any of the complexes investigated under the present conditions. Our observations on the photochemistry following ligand field excitation can be summarized as follows:

***cis*- and *trans*-$[Rh(tn)_2Cl_2]^+$.** Exhaustive photolyses of either isomer of the dichloro complex in 10^{-3} M $HClO_4$ lead to the same photoproduct distribution. A numerical analysis of the UV spectra showed the product to be a cis/trans mixture of $[Rh(tn)_2(H_2O)Cl]^{2+}$. The isomeric ratio was independent of the stereochemistry of the reacting dihalo complex but dependent on the wavelength of irradiation, indicating a product photostationary state. This was proven by irradiation of solutions of either isomer of $[Rh(tn)_2(H_2O)Cl]^{2+}$ made by dissolution of the dithionate salts. The quantum yields for the interconversion of the aqua chloro complexes in 10^{-3} M $HClO_4$ (eq 1) were determined in this direct manner at five different

$$cis\text{-}[Rh(tn)_2(H_2O)Cl]^{2+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} trans\text{-}[Rh(tn)_2(H_2O)Cl]^{2+} \qquad (1)$$

wavelengths of irradiation. No wavelength dependence was noted for the quantum yields. In addition the quantum yields in aqueous 0.10 M $HClO_4$ + 0.90 M $NaClO_4$ did not vary from those determined in 10^{-3} M $HClO_4$. The experimental results are presented in Table III. The cis/trans ratio in the photostationary state is related to the isomerization quantum yields by eq 2,[23] where ϵ_{trans}^{irr} and ϵ_{cis}^{irr} are the molar absorption

$$\frac{C_{cis}^{\infty}}{C_{trans}^{\infty}} = \left(\frac{\Phi_{tc}}{\Phi_{ct}}\right)\left(\frac{\epsilon_{trans}^{irr}}{\epsilon_{cis}^{irr}}\right) \qquad (2)$$

coefficients at the wavelength of irradiation (cf. Figure 1). The isomeric distributions calculated from the product spectra agree well with those calculated from eq 2 as seen in Table IV.

Table III. Photoisomerization Quantum Yields[a] for Aquahalobis(1,3-propanediamine)rhodium(III) Complexes in Aqueous 10^{-3} M $HClO_4$ at 25 °C

	Φ_{ct}	Φ_{tc}
$cis\text{-}[Rh(tn)_2(H_2O)Cl]^{2+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} trans\text{-}[Rh(tn)_2(H_2O)Cl]^{2+}$ [b]	0.538 ± 0.012	0.059 ± 0.004
$cis\text{-}[Rh(tn)_2(H_2O)Br]^{2+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} trans\text{-}[Rh(tn)_2(H_2O)Br]^{2+}$ [c]	0.55 ± 0.02	0.025 ± 0.004

[a] cis to trans photoisomerization quantum yield, Φ_{ct}, and trans to cis photoisomerization quantum yield, Φ_{tc}, in mol einstein^{-1}. [b] λ_{irr} = 313, 334, 366, 405, and 436 nm; a total of 17 experiments. [c] λ_{irr} = 366, 405, and 436 nm; a total of six experiments.

The quantum yields for the chloride photoaquation in the dichloro complexes were calculated at 382 nm where the two photoproducts have an isosbestic point (cf. Figure 1). The quantum yields (also wavelength independent) are listed in Table V, and the composition of the photostationary state is given in Table IV.

***cis*- and *trans*-$[Rh(tn)_2Br_2]^+$.** The photochemical behavior of the bromo complexes was similar to that of the chloro analogues and the same experimental approach was used. The quantum yields for the photoisomerization

$$cis\text{-}[Rh(tn)_2(H_2O)Br]^{2+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} trans\text{-}[Rh(tn)_2(H_2O)Br]^{2+} \qquad (3)$$

are listed in Table III. The compositions of the cis/trans photostationary state at three different wavelengths are presented in Table IV in comparison with those calculated from eq 2. The bromide photoaquation quantum yields given in Table V for the dibromo complexes were calculated at the *cis*-/*trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$ isosbestic point at 403 nm (cf. Figure 1).

Emission Spectra and Emission Lifetimes. The emission spectra of *cis*- and *trans*-$[Rh(tn)_2X_2]^+$ (X = Cl, Br) were measured in ambient-temperature aqueous solution. These spectra had approximately the same maxima but larger band widths than the corresponding spectra previously obtained for the solid perchlorate salts of the same complexes in KBr presses at 77 K.[26]

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Table IV. Photostationary States for *cis*- and *trans*-Aquachlorobis(1,3-propanediamine)rhodium(III) and Aquabromobis(1,3-propanediamine)rhodium(III) Ions at 25 °C in Aqueous 10^{-3} M Perchloric Acid Solution[a]

		cis-/trans- $[Rh(tn)_2(H_2O)Cl]^{2+}$ photostationary state			*cis-/trans-* $[Rh(tn)_2(H_2O)Br]^{2+}$ photostationary state	
λ_{irr}, nm	reacting complex	% trans obsd[b]	% trans calcd[c]	reacting complex	% trans obsd[b]	% trans calcd[c]
313	*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	87	88.7			
	cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	87				
334	*cis*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	95	96.2			
	trans-$[Rh(tn)_2Cl_2]^+$	96				
	cis-$[Rh(tn)_2Cl_2]^+$	95				
366	*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	94	95.9	*cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$	98	99.1
	cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	95		*cis*-$[Rh(tn)_2Br_2]^+$	98	
	cis-$[Rh(tn)_2Cl_2]^+$	95				
405	*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	75.7	74.8	*trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$	94	95.4
	cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	75.6		*cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$	93	
	trans-$[Rh(tn)_2Cl_2]^+$	75.5		*trans*-$[Rh(tn)_2Br_2]^+$	91	
	cis-$[Rh(tn)_2Cl_2]^+$	76.3		*cis*-$[Rh(tn)_2Br_2]^+$	95	
436	*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$	68	70.8	*trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$	92	92.1
	cis-$[Rh(tn)_2(H_2O)Cl]^{2+}$	69		*cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$	89	
	trans-$[Rh(tn)_2Cl_2]^+$	68		*trans*-$[Rh(tn)_2Br_2]^+$	88	
				cis-$[Rh(tn)_2Br_2]^+$	91	

[a] Most of the experiments were repeated in 0.10 M $HClO_4$ + 0.90 M $NaClO_4$ with identical results. [b] Calculated from spectral analysis of exhaustively photolyzed solutions. [c] Calculated from % trans = 100/(1 + *r*), where $r = (\Phi_{tc}\epsilon_{trans}^{irr}/\Phi_{ct}\epsilon_{cis}^{irr})$; cf. ref 10 and 23.

Table V. Quantum Yields for Halide Dissociation and Phosphorescence Lifetimes for Dichloro- and Dibromobis(1,3-propanediamine)rhodium(III) Ions in Aqueous 10^{-3} M $HClO_4$ at 25 °C

complex ions	Φ_X, mol einstein^{-1}	τ, ns
trans-$[Rh(tn)_2Cl_2]^+$	0.080 ± 0.004[a]	1.4 ± 0.1
cis-$[Rh(tn)_2Cl_2]^+$	0.56 ± 0.02[b]	0.9 ± 0.1
trans-$[Rh(tn)_2Br_2]^+$	0.055 ± 0.002[c]	0.67 ± 0.07
cis-$[Rh(tn)_2Br_2]^+$	0.64 ± 0.04[d]	0.30 ± 0.05

[a] λ_{irr} = 334, 405, and 436 nm; a total of eight experiments. [b] λ_{irr} = 334, 366, and 405 nm; a total of six experiments. [c] λ_{irr} = 405 and 436 nm; a total of six experiments. [d] λ_{irr} = 366, 405, and 436 nm; a total of six experiments.

Room-temperature phosphorescence lifetimes of the lowest energy LF triplet excited states are listed in Table V. Analysis of the luminescence decay profiles indicated two emission components: one short (<100 ps) and the other longer lived and red shifted relative to the former. Similar properties have been reported for haloamminerhodium(III) complexes, with the faster element attributed to fluorescence from incompletely relaxed singlet LF excited states.[24]

The observed emission intensities of the bis(1,3-propanediamine) complexes in fluid solution were comparable to those previously noted for the tetraammine analogues, suggesting emission quantum yields in the range $10^{-6} > \Phi_{em} > 10^{-7}$.[24]

Discussion

Excitation of the halo(amine)rhodium(III) multiplicity allowed LF transitions $^1T_1 \leftarrow {}^1A_1$ and $^1T_2 \leftarrow {}^1A_1$ (pseudooctahedral symmetry assumed) results via internal conversion/intersystem crossing, in population of the thermally equilibrated lowest triplet state. Previous investigations using wavelength-dependence and sensitization techniques[29] concluded that halopentaamminerhodium(III) complexes form the lowest energy LF triplet states with quantum yield approximately unity ($\Phi_{isc} \sim 1$) and that these are the states responsible for the majority of the observed photoreactivity.[30]

The quantum yields for the various triplet deactivation processes may be described by eq 4, where k_x is the excited state

$$\Phi_i = \Phi_{isc}\frac{k_i}{k_x + k_r + k_n} \tag{4}$$

rate constant for ligand substitutions and k_r and k_n are the rate constants for radiative and nonradiative deactivation, respectively.[16] The phosphorescence lifetime, τ, may also be expressed in terms of the triplet-state relaxation rate constants (eq 5).

$$\tau = (\sum_i k_i)^{-1} \tag{5}$$

The luminescence efficiency is small ($\Phi_{em} < 10^{-6}$), and consequently $k_r \ll k_x + k_n$, allowing the evaluation of k_x and k_n from halide-substitution quantum yields and lifetimes measured under identical conditions (Table V). The rate constants determined for *cis*- and *trans*-$[Rh(tn)_2X_2]^+$ (X = Cl, Br) are summarized in Table VI along with those of the tetraammine analogues.[15]

Even minor changes in ligand properties have proven to have a strong influence on the excited-state dynamics. The two closely related tetraamine complexes *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ and the ethylenediamine analogue *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ thus respond differently to light.[19] *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ forms a cis/trans photostationary state whereas *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ photoisomerizes completely to its trans counterpart. This difference can, however, be attributed either to differences in the electronic properties of the N ligator (en is known to be a significantly stronger σ donor than NH_3) or by the strain introduced by the chelate ring in the excited state. In contrast, NH_3 and tn have very similar σ-donor properties as evidenced by the spectral data for several transition-metal complexes[17,20] including those in Table VII. Thus, any differences noted between the photobehavior of tn and NH_3 complexes can be attributed to chelation and steric effects.

Examination of Table VI shows that the excited-state chloride dissociation rate is marginally lower for *trans*-$[Rh(tn)_2Cl_2]^+$ than for *trans*-$[Rh(NH_3)_4Cl_2]^+$, whereas the opposite is observed for the cis counterparts. Furthermore, in both amine series chloride dissociation is faster for the cis stereochemistry (in the tn complexes by 1 order of magnitude). The nonradiative deactivation rates for all four chloro com-

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Table VI. Calculated Rate Constants (s^{-1}) for Ligand Dissociation and Nonradiative Deactivation from the Lowest Energy Ligand Field Excited States for Dihalobis(1,3-propanediamine)rhodium(III) and Dihalotetraamminerhodium(III) Complexes in Dilute Aqueous Solution at 25 °C

	bis(1,3-propanediamine)[a]		tetraammine[b]		
complex	k_X[c]	k_n	k_X[c]	k_{NH_3}	k_n
trans-$[RhA_4Cl_2]^+$	$(5.7 \pm 0.4) \times 10^7$	$(6.6 \pm 0.5) \times 10^8$	$(8 \pm 1) \times 10^7$	$\leqslant 1.1 \times 10^7$	$(5 \pm 1) \times 10^8$
cis-$[RhA_4Cl_2]^+$	$(6.2 \pm 0.6) \times 10^8$	$(4.9 \pm 1.2) \times 10^8$	$(3.0 \pm 0.6) \times 10^8$	$(1.0 \pm 0.2) \times 10^7$	$(5 \pm 2) \times 10^8$
trans-$[RhA_4Br_2]^+$	$(8.2 \pm 1.0) \times 10^7$	$(1.4 \pm 0.2) \times 10^9$	$(6.3 \pm 0.7) \times 10^7$	$\leqslant 1.3 \times 10^8$	$(6.0 \pm 0.5) \times 10^8$
cis-$[RhA_4Br_2]^+$	$(2.1 \pm 0.4) \times 10^9$	$(1.2 \pm 0.7) \times 10^9$	$(2.4 \pm 0.3) \times 10^8$	$(6.4 \pm 0.8) \times 10^7$	$(7 \pm 1) \times 10^8$

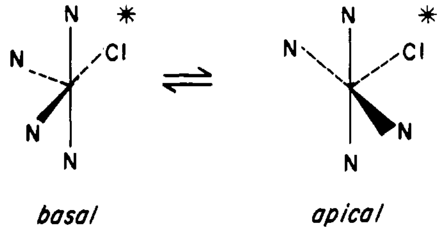
[a] $A_4 = (tn)_2$; this work. [b] $A_4 = (NH_3)_4$.[15] [c] k_X is the halide dissociation rate constant (X = Cl, Br).

Table VII. Emission and Absorption Spectra for Bis(1,3-propanediamine)- and Tetraamminerhodium(III) Complexes[a]

	bis(1,3-propanediamine)[b]				tetraammine[c]			
	emission[d]			absorption[e]	emission[d]			absorption[e]
complex	ν_{max}	$\Delta\nu_{1/2}$	ν_{0-0}[f]	ν_{max}	ν_{max}	$\Delta\nu_{1/2}$	ν_{0-0}[f]	ν_{max}
trans-$[RhA_4Cl_2]^+$	1.34	0.24	1.65	2.39	1.37	0.31	1.77	2.41
cis-$[RhA_4Cl_2]^+$	1.35	0.27	1.70	2.83	1.42	0.29	1.79	2.78
trans-$[RhA_4Br_2]^+$	1.32	0.17	1.54	2.27	1.36	0.26	1.70	2.27
cis-$[RhA_4Br_2]^+$	1.38	0.26	1.71	2.72	1.41	0.31	1.81	2.65

[a] Energies in μm^{-1}. [b] $A_4 = (tn)_2$; from ref 26 and Table I. [c] $A_4 = (NH_3)_4$.[27,28] [d] Emission: ca. 2% in KBr pellets at 77 K. [e] Absorption: lowest energy ligand field band. Dilute aqueous solution at 298 K. [f] Calculated from $\nu_{0-0} = \nu_{max} + 1.29\Delta\nu_{1/2}$.

plexes in question are identical within experimental uncertainties, and these observations together imply that the tn chelate does not introduce any strain that promotes either vibrionic coupling to the solvent, resulting in faster nonradiative deactivation, or dissociation of a chloro ligand. The excited-state rearrangement following ligand dissociation in the ammonia complexes was recently shown to achieve thermal equilibrium prior to deactivation.[10,31]



Since the excited-state lifetimes and deactivation rates are very similar for the two complex series, a similar equilibration is also expected to precede deactivation for the tn complexes. The composition of the *cis*-/*trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$ photostationary state is a result of two factors: the ratio between the molar absorptivities of the two isomers at the wavelength of irradiation and the quantum yield ratio Φ_{tc}/Φ_{ct} (cf. eq 2). The latter reflects the excited-state preference for either stereochemistry, which should be very sensitive to crowding by bulky ligands and/or bond strain resulting from chelation. For the photoisomerization reaction shown by eq 6 the

$$cis\text{-}[Rh(NH_3)_4(H_2O)Cl]^{2+} \underset{h\nu}{\overset{h\nu}{\rightleftarrows}} trans\text{-}[Rh(NH_3)_4(H_2O)Cl]^{2+} \quad (6)$$

quantum yields are $\Phi_{ct} = 0.52 \pm 0.01$ and $\Phi_{tc} = 0.064 \pm 0.003$ mol einstein^{-1},[31] quite similar to those found in the present study for the tn analogues (cf. Table III). Consequently, the Φ_{tc}/Φ_{ct} ratio gives no indication of any effect of the $-(CH_2)_3-$ linking the N ligators together.

More significant effects are noted for the bromo complexes. Bromide dissociation is accelerated for both stereochemistries of the tn complexes relative to the NH_3 complexes. *trans*-$[Rh(tn)_2Br_2]^+$ has a rate of bromide dissociation slightly higher than *trans*-$[Rh(NH_3)_4Br_2]^+$, but notably the opposite was observed for the *trans*-dichloro complexes. Furthermore, for the *cis*-dibromo complexes the bromide dissociation rate is close to 1 order of magnitude larger for the tn complex than for the NH_3 complex. In the cis complexes, having approximate D_{4h} symmetry with the N–N axis defined as the z axis, the lowest energy ligand field state has the one-electron configuration $(d_{xz})^2(d_{yz})^2(d_{xy})^1(d_{x^2-y^2})^1(d_{z^2})^0$ with excitation concentrated in the xy plane. For *cis*-$[Rh(NH_3)_4Br_2]^+$ ammonia and bromide dissociation occur in a 1:4 ratio, whereas solely bromide dissociation is observed for *cis*-$[Rh(tn)_2Br_2]^+$. The spectroscopic model of Vanquickenborne and Ceulemans[11] predicts that both complexes should labilize the amine and bromide ligands, yet chelation clearly inhibits the former.[32] The excitation in both of these complexes distorts the excited-state geometries along the (equatorial) N–Br axes, but whereas the distortion is released through two reaction channels in the NH_3 complex, only bromide dissociation is appreciable for the tn complex. The increased excited-state distortion resulting from the blocking of the N ligator by chelation results in a larger Stokes shift for the cis tn complex (Table VII) and, more significantly, promotes bromide dissociation. The coordination sphere is crowded by the relatively bulky tn ligands and the voluminous bromide ligands.[35] These steric effects facilitate dissociation of the adjacent bromides. The quantum yield ratio for the photoisomerizations of *cis*-/*trans*-$[Rh(tn)_2(H_2O)X]^{2+}$ according to eq 1 and 2 is in keeping herewith (bromide, $\Phi_{tc}/\Phi_{ct} = 0.045$; chloride, $\Phi_{tc}/\Phi_{ct} = 0.11$), indicating a different excited-state preference for the two halide series.

In conclusion, the comparison of the photobehavior of the two series of rhodium(III) halo amine complexes shows that chelation blocks amine photoaquation and that crowding in the coordination sphere, which is of special significance for

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the cis stereochemistry, accelerates excited-state dissociation of bromide ligands but not of the smaller chloride ligands.

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Registry No. *trans*-$[Rh(tn)_2Cl_2]^+$, 52795-66-1; *trans*-$[Rh(tn)_2Cl_2]Cl$, 92186-50-0; *cis*-$[Rh(tn)_2Cl_2]^+$, 65437-15-2; *trans*-$[Rh(tn)_2(H_2O)Cl]^{2+}$, 92282-21-8; *trans*-$[Rh(tn)_2(H_2O)Cl]S_2O_6$, 92282-23-0; *cis*-$[Rh(tn)_2(H_2O)Cl]^{2+}$, 92186-40-8; *cis*-$[Rh(tn)_2(H_2O)Cl]S_2O_6$, 92186-42-0; *trans*-$[Rh(tn)_2(OH)Cl]^+$, 92186-44-2; *cis*-$[Rh(tn)_2(OH)Cl]^+$, 92282-25-2; *trans*-$[Rh(tn)_2Br_2]^+$, 65394-34-5; *trans*-$[Rh(tn)_2Br_2]Br$, 92186-51-1; *cis*-$[Rh(tn)_2Br_2]^+$, 65437-17-4; *trans*-$[Rh(tn)_2(H_2O)Br]^{2+}$, 92282-22-9; *trans*-$[Rh(tn)_2(H_2O)Br]S_2O_6$, 92282-24-1; *cis*-$[Rh(tn)_2(H_2O)Br]^{2+}$, 92186-41-9; *cis*-$[Rh(tn)_2(H_2O)Br]S_2O_6$, 92186-43-1; *trans*-$[Rh(tn)_2(OH)Br]^+$, 92186-45-3; *cis*-$[Rh(tn)_2(OH)Br]^+$, 92282-26-3; *trans*-$[Rh(tn)_2Cl(OSO_2CF_3)]OSO_2CF_3$, 92186-47-5; *trans*-$[Rh(tn)_2Br(OSO_2CF_3)]OSO_2CF_3$, 92186-49-7.

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Electrochemistry and Photochemistry of Silver(II) Complexes of Macrocyclic Amines

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Silver(II) complexes of macrocyclic polyamines undergo both thermal and photochemical reduction reactions in a variety of solvents. Cyclic voltammetric and rotating disk electrode studies in acetonitrile have been used to assess the thermodynamics of reduction of silver(I) species and hence the possible use of silver(II) macrocyclic amine complexes in a silver purification process. Preliminary photochemical experiments have shown that photoreduction occurs without ligand decomposition but that quite subtle changes in ligand structure have a marked influence on the photosensitivity of the silver(II) complexes.

The stabilization of metals in high oxidation states by strongly basic ligands is a familiar phenomenon and is exemplified in the readily observed chemistry of silver(II) and silver(III) when coordinated to N-donor ligands.[1-4] However, in the particular case of saturated, macrocyclic tetraamine ligands it appears that this stabilization is only such as to render silver(I) and silver(II) of comparable stability, so that the position of the disproportionation equilibrium

$$2Ag(I) \rightleftharpoons Ag(0) + Ag(II)$$

is significantly solvent dependent.[4,5] This observation suggested to us that macrocyclic amines might well be of practical use in silver recovery and purification through a process closely analogous to one that has been thoroughly investigated for copper.[6] Thus, the equilibrium lies to the right in water but to the left in ethanenitrile (acetonitrile), so that it would appear feasible to dissolve crude silver in a solution of silver(II) in acetonitrile containing a small amount of water and then to remove acetonitrile by distillation until disproportionation occurs.

$$\begin{aligned} Ag(crude) + Ag^{II}L^{2+} &\xrightarrow{CH_3CN/H_2O} 2Ag^{I}(CH_3CN)_2^{+} + L \\ &\xrightarrow{H_2O} Ag(pure) + Ag^{II}L^{2+} \end{aligned}$$

True utility for such a process would require considerable thermal stability of the complexes with respect to ligand dissociation and possible ligand oxidation[4,7-10] by silver(II). We have chosen to investigate the properties of silver(I) and silver(II) complexes of macrocyclic tetraamines and one macrobicyclic hexaamine through conventional electrochemical methods, including among the ligands species that were expected to differ considerably in their redox stability. As preliminary observations established marked photosensitivity for the various silver(II) compounds, discussion of basic aspects of their photochemistry is included in this report.

Experimental Section

1. Instrumentation. ^1H NMR (60 MHz) and ^{13}C NMR (21.115 MHz) spectra were run on Hitachi R-24B and Bruker WP80 instruments, respectively. All shifts are quoted relative to internal or external tetramethylsilane, 4,4-dimethyl-4-silapentanesulfonate (^1H) and dioxane (^{13}C) being used as internal references in aqueous media. Infrared and UV/visible spectra were recorded on Perkin-Elmer 283 and HP 8450A instruments, while fluorescence excitation and emission spectra were recorded on a Perkin-Elmer 650-40 spectrofluorimeter. EI mass spectra were obtained on an HP 5986 instrument at 70 eV.

ESR spectra were recorded on a Varian 4500-10A spectrometer equipped with an X-band microwave source, a 9-in. magnet, and 100-KHz field modulation. Aqueous solutions of Fremy's salt (g = 2.0055) were used as calibrant. The system for electrochemical measurements was constructed from a PAR Model 175 Universal Programmer and Model 173 potentiostat, with a platinum rotating disk electrode, active surface area $(6.162 \pm 0.001) \times 10^{-6}$ m^2, set in Teflon support. Saturated NaCl/calomel (aqueous media) and $Ag/AgNO_3$, 10^{-2} dm^{-3} (dry acetonitrile), were used as reference electrodes.

An IL 153 atomic absorption spectrophotometer was used for Ag analyses. C,H,N, analyses were performed by the Canadian Microanalytical Service, Vancouver, BC.

2. Solvent Purification and Basic Chemicals. All aqueous solutions were prepared from deionized, distilled water and, when necessary,

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