Acta Chemica Scandinavica A 37 (1983) 647-657

# Aqueous Solution Photochemistry of *cis*- and *trans*-Diaquabis(ethylenediamine)rhodium(III) Ions and Their Conjugated Bases. Photoisomerization and Photostationary States and Their Correlation with Spectroscopic Properties

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Upon ligand field excitation the *cis*-diaquabis(ethylenediamine)-rhodium(III) ion isomerizes to the corresponding *trans*-complex with a quantum yield of 0.27 mol/Einstein in acidic 1.0 M perchlorate aqueous solution at 25 °C. Under the same conditions the *trans*-isomer appears photoinert. The aquahydroxobis(ethylenediamine)rhodium(III) ions photoisomerize *trans* to *cis* with a quantum yield of 0.61 mol/Einstein and *cis* to *trans* with 0.048 mol/Einstein, whereas the dihydroxo species are photoinert. The photoisomerization has been investigated in the pH region 0 to 12 and the composition of the *cis*/*trans*-photostationary states is described quantitatively as a function of pH. The ethylenediamine complexes differ qualitatively in their photochemical properties from the analogous, previously investigated ammonia complexes, and this difference is discussed in relation to the $\sigma$-donor strength of the amine ligands.

According to recent theories[1-4] on ligand-field (LF) excited states of rhodium(III) and other $d^6$ low-spin complexes, the stereochemical consequences of LF photosubstitution reactions are related to the nature of the ligand field of the pentacoordinate intermediate generated by ligand dissociation from a hexa-coordinate triplet excited state. This intermediate is capable of *apical*/*basal* rearrangements prior to deactivation to the ground state and trapping by a solvent molecule. In this context, the observation that tetraamminerhodium(III) complexes undergo *cis* to *trans* photoisomerizations,[2-5] *i.e.*,

$$cis\text{-}[Rh(NH_3)_4Cl_2]^+ + H_2O \xrightarrow{h\nu} trans\text{-}[Rh(NH_3)_4(H_2O)Cl]^{2+} + Cl^-$$

as well as *trans* to *cis* photoisomerizations,[6,7] *i.e.*,

$$trans\text{-}[Rh(NH_3)_4(OH)Cl]^+ + H_2O \xrightarrow{h\nu} cis\text{-}[Rh(NH_3)_4(OH)_2]^+ + H^+ + Cl^-$$

can be explained by the relative energies of the *apical* and *basal* triplet excited-state isomers of the pentacoordinate intermediate. MO calculations suggest[1-4] that the isomer with the weakest $\sigma$-donor ligand in the apical position has the lowest energy. Thus, in accordance with the proposed $\sigma$-donor strength series $OH^- > NH_3 > H_2O > Cl^-$, the more stable excited-state intermediates in the two above-mentioned photoreactions would be *apical*-$[Rh(NH_3)_4Cl]^{2+\,*}$ and *basal*-$[Rh(NH_3)_4(OH)]^{2+\,*}$, respectively.

The photochemical behaviour of *cis*- and *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ confirms that water and ammonia have comparable $\sigma$-donor strengths and that the energy separation between *basal*- and *apical*-$[Rh(NH_3)_4(H_2O)]^{3+\,*}$ is small, as LF excitation of *cis*- or *trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ leads to a *cis*/*trans*-photostationary state,[7]

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$$cis\text{-}[Rh(NH_3)_4(H_2O)_2]^{3+} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} trans\text{-}[Rh(NH_3)_4(H_2O)_2]^{3+}$$

Substitution of ammonia with other amine ligands in diaquatetraaminerhodium(III) complexes is expected to influence the *apical/basal* excited-state equilibrium in accordance with the water amine $\sigma$-donor strength difference. The composition of the *cis/trans* photostationary states should therefore correlate with the amine $\sigma$-donor strength and in principle be predictable from the LF spectra.

An investigation of the photochemistry of a series of diaquatetraminerhodium(III) complexes in which the amine $\sigma$-donor strength is systematically varied is therefore of importance in the evaluation of excited-state properties and processes of rhodium(III) complexes and of $d^6$ low-spin complexes in general. As the first part of such studies we here report the results for the *cis*- and *trans*-diaquabis(ethylenediamine)rhodium(III) ions and their conjugated bases.

## EXPERIMENTAL

*Matrials.* The ethylenediamine (en=1,2-diaminoethane) complex *cis*-$[Rh(en)_2(H_2O)(OH)]S_2O_6$ was prepared from *cis*-$[Rh(en)_2Cl_2]Cl_{1/2}(ClO_4)_{1/2}$ by a literature method.[8,9,16] The precursor to *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$, *trans*-$[Rh(en)_2Cl_2]NO_3$, was also prepared by a (somewhat modified) literature method.[8] Other chemicals were of analytical grade.

*Synthesis.* *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$, for which several methods of preparation have been suggested,[10–13] was prepared and purified by the following method. A 400 mg portion of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 1.0 g of HgO were dissolved in 60 ml of 0.33 M $HClO_4$ and heated at reflux for 2 h. Then the volume was reduced to 15 ml by evaporation and the resulting solution cooled in ice. 10 M NaOH was added slowly until pH≈10 and the precipitated HgO was removed by filtration through a G-4 sintered glass filter. While kept at ≈0 °C, pH was adjusted by addition of 5 M $HClO_4$ to ≈6. The product formed, crude *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$, was filtered off, washed with ice-cold water and subsequently with 96 % ethanol then ether. The crude product (yield 300 mg) was dissolved in 0.8 ml of 1 M HBr and the resulting solution was filtered through a G-4 sintered glass filter. 0.8 ml of an ice-cold saturated aqueous LiBr solution was added in order to precipitate *trans*-$[Rh(en)_2(H_2O)_2]Br_3$. Yield of this compound after washing with ice-cold absolute ethanol was 270 mg. After dissolving the product in 1.0 ml of boiling water, 1.0 ml of a saturated, aqueous $LiClO_4$ solution was immediately added and pH adjusted to≈6 with 0.2 M NaOH. After cooling in ice for 2 h, a 200 mg yield of *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ was filtered off and washed as before. This product was reprecipitated twice by dissolution in 1.0 ml of 0.5 M $HClO_4$ and subsequent adjustment of pH to≈6 with 2 M NaOH. After cooling in ice for 2 h the product was filtered off, washed with ice-cold water, then with 96 % ethanol and finally with ether. A third reprecipitation did not change the absorption spectrum. Yield 160 mg (30 %). Anal. C, H, N, Cl.

*Absorption spectra.* Electronic spectra were recorded on a Zeiss DMR 21 or 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 a 1.0 M $(H,Na)(ClO_4,OH)$ medium, the definition $pH= -\log[H^+]$ was used throughout by using standardized perchloric acid in 1.0 M $NaClO_4$ as pH standards.

*Photolyses.* The optical train consisted of the light source, an Osram HBO 100/2 high pressure mercury lamp, a light condenser, a heat filter (a 5 cm water-filled cell), an interference filter, a precision shutter connected to an electronic timer and lenses focusing the light into the thermostatted photolysis cell. All optical parts and cells were of quartz (Spindler und Hoyer, Göttingen, GFR). Photolyses were carried out with monochromatic light (312 or 334 nm) at 25±0.5 °C. Light intensities were determined by standard ferrioxalate actinometry.[7,17]

For all the complex ions under investigation, experiments were made to ensure that no significant thermal reactions ("dark reactions") occurred during photolysis.

*Calculation of quantum yield.* The calculations of quantum yields were based on spectral changes at four different wavelengths in principle by Method B of Ref. 7 with some minor modifications.[19] The molar absorptivities at the monitoring wavelengths $\lambda_{mon}$ are given in Table 3 for the relevant complex ions.

## RESULTS

The results reported here are a quantitative description of the aqueous solution ligand field excitation photochemistry of *cis*- and *trans*-

*Table 1.* $pK_a$ value for *cis*- and *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ in aqueous solution.

| $pK_{a,1}$ | $pK_{a,2}$ | Medium | $t$/°C | Ref. |
|---|---|---|---|---|
| *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ | | | | |
| 4.43 | 7.81 | 0.20 M $NaNO_3$ | ≈20 | 10 |
| 4.37 | 7.64 | 1.0 M $NaClO_4$ | 26.4 | 11 |
| 4.33 | 7.72 | 0.5 M $NaClO_4$ | 25 | 13 |
| 4.47 | 7.91 | 1.0 M $NaClO_4$ | 25.0 | This work[a] |
| *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ | | | | |
| 5.82 | 7.98 | 0.01 M $NaClO_4$ | 25 | 15 |
| 6.09 | 8.08 | 0.5 M $NaClO_4$ | 25 | 15 |
| 6.34 | 8.24 | 1.0 M $NaClO_4$ | 25.0 | 16[a] |

[a] Values used in the present study.

$[Rh(en)_2(H_2O)_2]^{3+}$ and their conjugated bases in a 1.0 M perchlorate medium at 25 °C. Also reported is an improved preparation and purification procedure for *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ and the $pK_a$ values of this complex together with the electronic spectra determined in aqueous 1.0 M $(H,Na)(ClO_4,OH)$ solution in comparison with the same characteristics for the *cis*-isomer.

*Acid dissociation and ligand field spectra.* Weighed amounts of *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ (between 0.02 and 0.05 mmol) were dissolved in 25.00 ml of 0.00200 M $HClO_4$ plus 1.00 M $NaClO_4$ and titrated with 0.0200 M NaOH in 0.98 M $NaClO_4$. $pK_{a,1}$ and $pK_{a,2}$ were calculated by standard numerical procedures[18] from 8 full titration curves (estimated standard deviation on the $pK_a$-values 0.02) and are com-

*Table 2.* UV-visible absorption spectra of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ and conjugated bases. [$\lambda$ in nm ($\varepsilon$ in l $mol^{-1}cm^{-1}$)].

| $\lambda_{max}(\varepsilon_{max})$ | $\lambda_{min}(\varepsilon_{min})$ | Medium | Ref. |
|---|---|---|---|
| *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ | | | |
| 342 ( 64), 262(148) | | pH=2 | 10 |
| 351 ( 61.6), 274(138) | | 0.02 M $HClO_4$, 1.0 M $NaClO_4$ | 11 |
| 342 ( 66), 272(125) | | 0.1 M $HClO_4$ | 12 |
| 350 ( 60), 274(130) | | 0.01 M $HClO_4$ | 13 |
| 352 ( 58.4), 274(130) | 330(51.5), 251(96) | 0.10 M $HClO_4$, 0.90 M $NaClO_4$ | This work[a] |
| *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ | | | |
| 337 ( 88), 270(158) | | pH=6 | 10 |
| 343 ( 89), 282(154) | | | 13 |
| 344 ( 87), 284(149) | 326(79), 244(59) | 1.0 M $NaClO_4$, pH=6.2 | This work[a] |
| *trans*-$[Rh(en)_2(OH)_2]^{+}$ | | | |
| 346 ( 99), 297(130) | | 0.7 M NaOH | 14 |
| 336 ( 94), 289(154) | | pH=11 | 10 |
| 338 (136), 290(136) | | 0.1 M NaOH | 12 |
| 344 ( 99), 296(134) | | 0.01 M NaOH | 13 |
| 344 ( 97), 295(132) | 327(91), 244(48) | 0.04 M NaOH, 0.96 M $NaClO_4$ | This work[a] |

[a] *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ dissolved in the media quoted.

*Table 3.* Spectral characteristics of *cis*- and *trans*-diaquabis(ethylenediamine)rhodium(III) ions and their conjugated bases in aqueous 1.0 M (Na,H)($ClO_4$,OH) [$\lambda$ in nm ($\varepsilon$ in l $mol^{-1}cm^{-1}$)].

| Complex ion[a] | $\lambda_{max}(\varepsilon_{max})$ | $\lambda_{irr}(\varepsilon_{irr})$ | $\lambda_{mon}(\varepsilon_{mon})$[d] |
|---|---|---|---|
| *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ | 318(175), 271(137) | 312(166), 334(142) | 320(174), 330(155) 340(120) |
| *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ [b] | 323(203), 280(161)[c] | 312(196), 334(192) | 320(209), 330(202) 340(170) |
| *cis*-$[Rh(en)_2(OH)_2]^{+}$ | 329(179), 278.5(171) | 312(150), 334(177) | 320(170), 330(179) 340(166) |
| *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ | 352(58.4), 274(130) | 312( 71), 334( 52) | 320( 58), 330( 52) 340( 55) |
| *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ [b] | 344( 87), 284(149) | 312(100), 334( 82) | 320( 83), 330( 80) 340( 86) |
| *trans*-$[Rh(en)_2(OH)_2]^{+}$ | 344( 97), 295(132) | 312(109), 334( 97) | 320( 95), 330( 92) 340( 97) |

[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=½($pK_{a,1}+pK_{a,2}$); for the dihydroxo complexes: 0.04 M NaOH, 0.96 M $NaClO_4$. [b] $\lambda_{max}(\varepsilon_{max})$ reported is that measured for a mixture at pH=½($pK_{a,1}+pK_{a,2}$), whereas $\lambda_{irr}(\varepsilon_{irr})$ and $\lambda_{mon}(\varepsilon_{mon})$ has been corrected for the presence of the diaqua and the dihydroxo species. [c] Shoulder. [d] $\lambda_{mon}$ are the wavelengths used in the calculations of quantum yields and of the composition of photostationary states and $\varepsilon_{mon}$ are the molar absorptivities at these wavelengths.

pared in Table 1 with literature values for the same compound and for its *cis*-isomer. In Table 2, $\lambda_{max}$ ($\varepsilon_{max}$) and $\lambda_{min}$ ($\varepsilon_{min}$) for the ligand field spectra of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$, of *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ and of *trans*-$[Rh(en)_2(OH)_2]^{+}$ are compared with the available literature data.

cis- *and* trans-*$[Rh(en)_2(H_2O)_2]^{3+}$ photoreactions.* LF photolysis of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ in aqueous acidic 1.0 M perchlorate solution ($[H^+]\geq 0.010$ M) led cleanly and efficiently to *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$. 6.00 ml of a 2.124 · $10^{-3}$ M solution of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ in 0.10 M $HClO_4$, 0.90 M $NaClO_4$ exhaustively photolyzed ($\lambda_{irr}$=334 nm, light intensity $I_0$=9.08 · $10^{-7}$ Einstein/min over a front window of 3.5 $cm^2$, 7 h of irradiation, 25 °C) had the following spectral characteristics: $\lambda_{max}$ ($\varepsilon_{max}$)=352 nm (58.9 l/mol cm); 274(127); $\lambda_{min}(\varepsilon_{min})$=330 (52.0); 251 (93) which within experimental uncertainties are identical with the spectral characteristics of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ under the same conditions, see Tables 2 and 3. An analysis of the product spectrum (4 characteristic wavelengths, see Table 3) showed that no more than 0.6 % of the *cis*-isomer was left in the product solution. Isosbestic points at 358, 290, 278 and 258 nm were maintained throughout the photolysis, see Fig. 1. The photoreaction of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ under the present conditions is thus a clean isomerization without any detectable competing or secondary reactions of thermal or photochemical nature.

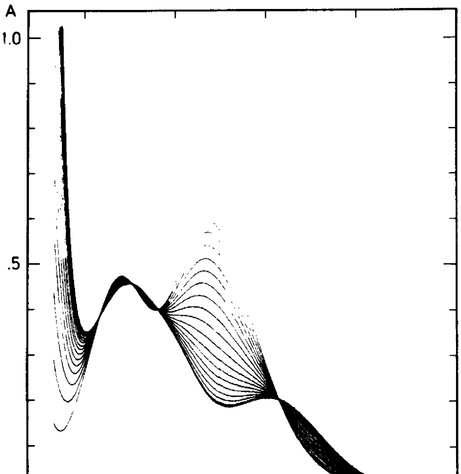


*Fig. 1.* Absorption spectra recorded during 334 nm photolysis at 25 °C of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ ($\lambda_{max}$=318 and 271 nm) in 0.10 M $HClO_4$ plus 0.90 M $NaClO_4$ to give *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ ($\lambda_{max}$=352 and 274 nm), see Results.

*Table 4*. Photoisomerization quantum yields for *cis*- and *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ and their conjugated bases in aqueous 1.0 M (Na,H) ($ClO_4$,OH) at 25 °C.

| Complex ion | Principal photoproduct | $\lambda_{irr}$/nm | pH | $\Phi$/mol Einstein$^{-1}$ | Number of exp. |
|---|---|---|---|---|---|
| *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ | *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ | 334 | 0.0 | 0.27±0.01 | 2 |
| | | 334 | 1.0 | 0.26±0.01 | 4 |
| | | 312 | 1.0 | 0.26±0.01 | 3 |
| | | 334 | 2.0 | 0.28±0.01 | 2 |
| *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ | *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ | 334 | 1.0 | <0.002 | 2 |
| *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ | *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ | 334 | 8.25$^a$ | 0.052$^{b,c}$ | 1 |
| | | 334 | 8.37$^a$ | 0.048$^{b,c}$ | 1 |
| | | 334 | 8.48$^a$ | 0.043$^{b,c}$ | 1 |
| *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ | *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ | 334 | 6.1–6.2$^a$ | 0.62±0.04$^c$ | 5 |
| | | 312 | 6.1–6.2$^a$ | 0.59±0.02$^c$ | 2 |
| *cis*-$[Rh(en)_2(OH)_2]^{+}$ | *trans*-$[Rh(en)_2(OH)_2]^{+}$ | 334 | 12.6 | <0.002 | 2 |
| *trans*-$[Rh(en)_2(OH)_2]^{+}$ | *cis*-$[Rh(en)_2(OH)_2]^{+}$ | 334 | 12.6 | <0.002 | 2 |

[a] Initial pH, see Results. [b] Corrected for photoreaction of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$. [c] Calculated on the basis of the light absorbed by the complex ion mentioned.

Evaluation of quantum yields was made from spectral changes and the results (experiments at three different acid concentrations and two different wavelengths of irradiation) are seen in Table 4. No acid concentration or wavelength dependence was observed and an average value of $\Phi=0.27\pm0.01$ mol/Einstein was calculated for the *cis* to *trans* photoisomerization.

LF photolysis of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ under the same conditions as the *cis*-isomer resulted in very minor spectral changes and a generous upper limit of $\Phi=0.002$ mol/Einstein for a *trans* to *cis* photoisomerization was estimated.

The *cis*/*trans* ratio in the product solutions after exhaustive photolysis was <0.006 as calculated from the product spectrum (see above) and <0.003 as calculated from $(\varepsilon^{irr}_{trans}\,\Phi_{trans})/(\varepsilon^{irr}_{cis}\,\Phi_{cis})$ (see Ref. 7), and it was concluded that whereas *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ photoisomerizes efficiently to the *trans*-isomer, *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ is photoinert (except for the possibility of photochemical water exchange[17]).

cis- *and* trans-*$[Rh(en)_2(OH)_2]^+$ photoreactions.* Long term LF photolysis of either dihydroxobis(ethylenediamine)rhodium(III) ion in aqueous 0.04 M NaOH, 0.96 M $NaClO_4$ led to minor and uncharacteristic spectral changes and these changes did not indicate any photoisomerization. The photoisomerization quantum yield presented in Table 4 for the dihydroxo species are estimated upper limits.

cis- *and* trans-*$[Rh(en)_2(H_2O)(OH)]^{2+}$ photoreactions.* Aqueous 1.0 M $NaClO_4$ solutions of *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ showed a very high photoreactivity, whereas *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ were but moderately photoreactive. This indicated a different photochemical behavior for the aquahydroxo complex ions in comparison to both the diaqua and to the dihydroxo complex ions.

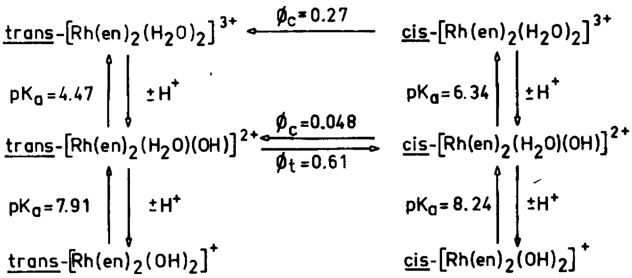
A 9.95 $10^{-4}$ M *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ solution with pH=6.00 was photolyzed with 312 nm monochromatic light until no further spectral changes were observed. Throughout the photolysis isosbestic points at 259, 292, and 366 nm were maintained. The product solution had a pH value of 7.00 and the following spectral characteristics: $\lambda_{max}(\varepsilon_{max})=322$ nm (180 l/mol cm), $\lambda_{sh}(\varepsilon_{sh})=280$ (139), and $\lambda_{min}(\varepsilon_{min})=246$ (83). An analogous experiment with the *cis*-isomer (initial pH=7.30) gave a product solution with pH=7.16 and $\lambda_{max}(\varepsilon_{max})=322$ nm (201 l/mol cm), $\lambda_{sh}(\varepsilon_{sh})=280$ (164), and $\lambda_{min}(\varepsilon_{min})=247$ (110). Both the spectral and pH changes in these two experiments indicated *trans* to *cis* photoisomerization for the *trans*-isomer and *cis* to *trans* photoisomerization for the *cis*-isomer. Numerical analysis of the product solution absorption spectra in combination with solution pH's at this and different $\lambda_{irr}$ demonstrated the photoproduct to be solely $[Rh(en)_2(H_2O)(OH)]^{2+}$ in a *cis*/*trans* photostationary state, both isomers in thermal acid/base equilibria with the corresponding diaqua and dihydroxo complex ions.

Quantum yields for the *trans* to *cis* photoisomerization process were determined from photolysis of *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ solutions with initial pH=½(p$K_{a,1}$+p$K_{a,2}$). At pH=6.19 the aquahydroxo ion fraction of the *trans*-isomer is 0.963 and $\delta_{(H_2O)(OH)}$, the light fraction absorbed by this ion, is 0.970 at 334 nm and 0.966 at 312 nm, respectively, as calculated from eqn. (1):

$$\delta_{(H_2O)(OH)}=\frac{\varepsilon^{irr}_{(H_2O)(OH)}[H^+]K_{a,1}}{\varepsilon^{irr}_{(H_2O)_2}[H^+]^2+\varepsilon^{irr}_{(H_2O)(OH)}[H^+]K_{a,1}+\varepsilon^{irr}_{(OH)_2}K_{a,1}K_{a,2}} \quad (1)$$

where $\varepsilon^{irr}$ are the molar absorptivities of the different complex ions at the wavelength of irradiation. The quantum yield for the *trans* to *cis* isomerization, $\Phi^{(H_2O)(OH)}_{trans}$, had the value 0.61 mol/Einstein (Table 4) as calculated from spectral changes correcting for both inner filter effects and for *cis* to *trans* photoisomerization, *cf.* Method B of Ref. 7.

In order to separate the photoreaction of *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ from that of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$, photolysis experiments to establish the *cis* to *trans* photoisomerization of the aquahydroxo ion as well as to determine the quantum yield of this process were carried out at pH≥8.25. At pH=8.25 the light fractions absorbed for the three *cis*-species calculated from eqn. (1) and the two analogous formulas are $\delta_{(H_2O)_2}=0.005$, $\delta_{(H_2O)(OH)}=0.512$, and $\delta_{(OH)_2}=0.483$, respectively. The observed quantum yield corrected for *trans* to *cis* photoisomerization was $\Phi^{obs}_{cis}=0.0232$ mol/Einstein at pH=8.25. Correcting this value by eqn. (2).



*Scheme 1.*

$$\Phi_{cis}^{(H_2O)(OH)} = \frac{\Phi_{cis}^{obs} - \Phi_{cis}^{(H_2O)_2}\delta_{(H_2O)_2} - \Phi_{cis}^{(OH)_2}\delta_{(OH)_2}}{\delta_{(H_2O)(OH)}} \quad (2)$$

the value $\Phi_{cis}^{(H_2O)(OH)}=0.052$ reported in Table 4 was obtained.

cis/trans-*Photostationary states. trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$, *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$, and *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ are each photoreactive with respect to isomerization and the quantum yields for these photoreactions are shown in Scheme 1. The difference in photoreactivity of the different acid/base-forms of the two isomers leads to photostationary states in which the *cis*/*trans* composition depends on the product solution pH.

Solutions of either *cis*- or *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ in 1.0 M $NaClO_4$ were adjusted to different pH and photolyzed at 334 nm until no further spectral changes were observed. The *cis*-fraction in the exhaustively photolyzed solutions, $\omega_{cis}$, was calculated for each experiment by the previously published method[7] from a combination of the pH-value and the absorption spectrum of the product solution. In Fig. 2 the experimentally observed *cis*-fractions as a function of pH are compared to that functionality predicted from the quantum yields of Scheme 1, from the molar absorptivities at 334 nm (Table 3), and from the $pK_a$-values of the complex ions (Table 1). The experimental points for $\omega_{cis}$ are seen to agree within experimental uncertainties with the predicted curve. For comparison, the function predicted assuming the photoisomerization quantum yield of *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ to be zero, is also shown in Fig. 2. In accordance with the result mentioned above, it is seen that the *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ ion indeed is photoactive with respect to isomerization.

## DISCUSSION

The following discussion will focus mainly on the differences between the photochemical behavior of the bis(ethylenediamine)rhodium(III) complexes and that of the previously investigated[7] tetraamminerhodium(III) complexes. Special emphasis will be placed on the kinetics and the thermodynamics of the excited state rearrangement processes suggested by the theoretical model for the photoisomerization reactions.

In Table 5 the reaction quantum yields for the photoprocesses of the two series of diaquatetra-

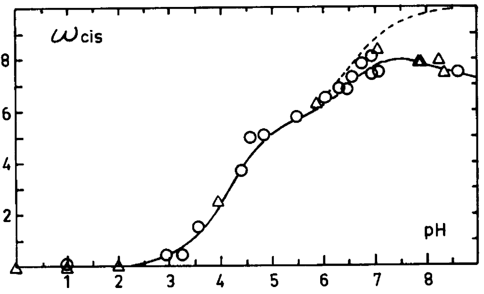


*Fig. 2.* $\omega_{cis}$, the *cis*-fraction in the photostationary state, after exhaustive photolysis of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$, $\Delta$, or of *trans*-$[Rh(en)_2(H_2O)_2]^{3+}$, 0, at 334 nm in 1.0 M $(Na,H)ClO_4$ at 25 °C as a function of product solution pH. The full line is calculated from the independently determined parameters: the quantum yields for the photoisomerization processes (Scheme 1), and the molar absorptivities at 334 nm (Table 3), in combination with the $pK_a$-values of the *cis*- and *trans*-species (Table 1). The broken line is calculated from the same parameters as the full line but assuming that the photoisomerization quantum yield for *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ is zero.

*Table 5.* Comparison between the photoisomerization quantum yields for bis(ethylenediamine)rhodium(III) and the corresponding tetraamminerhodium(III) complexes in aqueous 1.0 M perchlorate solution at 25 °C.

| Photoreaction | Bis(ethylenediamine)[a] $\Phi$ in mol. Einstein$^{-1}$ | Tetraammine[b] $\Phi$ in mol Einstein$^{-1}$ |
|---|---|---|
| *cis*-$[RhA_4(H_2O)_2]^{3+} \xrightarrow{h\nu}$ *trans*-$[RhA_4(H_2O)_2]^{3+}$ | 0.27 | 0.072 |
| *cis*-$[RhA_4(H_2O)(OH)]^{2+} \xrightarrow{h\nu}$ *trans*-$[RhA_4(H_2O)(OH)]^{2+}$ | 0.048 | [c] |
| *cis*-$[RhA_4(OH)_2]^{+} \xrightarrow{h\nu}$ *trans*-$[RhA_4(OH)_2]^{+}$ | [c] | [c] |
| *trans*-$[RhA_4(H_2O)_2]^{3+} \xrightarrow{h\nu}$ *cis*-$[RhA_4(H_2O)_2]^{3+}$ | [c] | 0.012 |
| *trans*-$[RhA_4(H_2O)(OH)]^{2+} \xrightarrow{h\nu}$ *cis*-$[RhA_4(H_2O)(OH)]^{2+}$ | 0.61 | 0.59 |
| *trans*-$[RhA_4(OH)_2]^{+} \xrightarrow{h\nu}$ *cis*-$[RhA_4(OH)_2]^{2+}$ | [c] | [c] |

[a] $A_4$=(en)$_2$; present work. [b] $A_4$=$(NH_3)_4$; from Ref. 7. [c] Photoisomerization not detected.

aminerhodium(III) complexes and their conjugated bases are compared. There is a qualitative difference between the two amine series. The *cis/trans*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ ions photoisomerize to each other forming a product photostationary state in contrast to the *cis/trans*-$[Rh(en)_2(H_2O)_2]^{3+}$ ions of which only the *cis*-isomer is active with respect to photoisomerization. Notably, the situation for the aquahydroxo species is totally reversed from that for the diaqua species, as only the *trans*-isomer of the $[Rh(NH_3)_4(H_2O)(OH)]^{2+}$ ions photoisomerizes, whereas both *trans*- and *cis*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ are photoactive isomerizing to a common *cis/trans* photostationary state. None of the four dihydroxo complexes show, however, any significant photoactivity. The consequences of the different photochemical properties of the two series of aminerhodium(III) complexes on the photoproduct solution composition are depicted in Fig. 3. The *cis/trans* photostationary state as a function of pH illustrates the behavioral crossover.

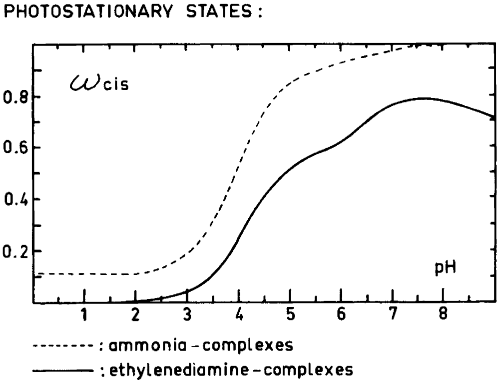
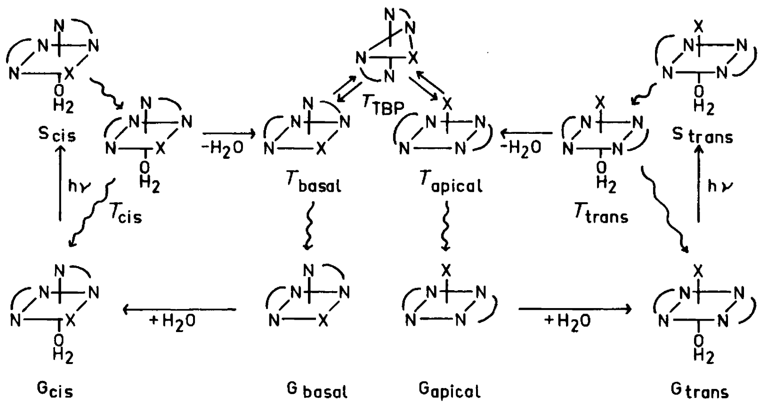


*Fig.3.* Comparison between $\omega_{cis}$, the *cis*-fraction in the photostationary state, as a function of pH for the tetraamminerhodium(III) ($\lambda_{irr}$=350 nm, Ref. 7) and the bis(ethylenediamine)rhodium(III) complexes ($\lambda_{irr}$=334 nm, present work) in 1.0 M (Na,H)$ClO_4$ at 25 °C.

The photoisomerization reactions of dihalotetraminerhodium(III) complexes proceed *via* ligand substitution, *i.e.*[5,20]

$$cis\text{-}[Rh(en)_2Cl_2]^{+} + H_2O \rightarrow trans\text{-}[Rh(en)_2(H_2O)Cl]^{2+} + Cl^{-} \qquad (3)$$

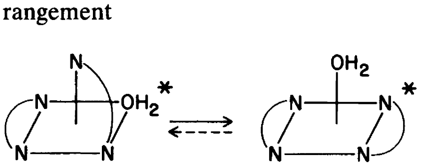
with the initial chemical reaction suggested[1-4] to be ligand dissociation for the lowest triplet excited state populated by efficient intersystem crossing from the higher singlet excited state originally generated in the excitation process. Photoisomerization of aquaaminerhodium(III)



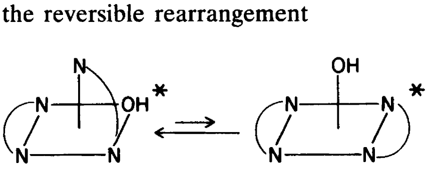
Scheme 2: N⌒N = ethylenediamine; X = $H_2O$, OH

complexes is analogous to the photoisomerization of the dihalotetraamine complexes initiated by dissociation of a water ligand as recently shown for *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ by isotopic labelling.[17] The dissociative mechanism, which now draws support from several different types of experiments,[2,17,21-24] appears to be generally operating for this type of photoreactions of $d^6$ low spin complexes. The ensuing discussion of the photoisomerization of diaqua- and aquahydroxotetraaminerhodium(III) complexes will be held within the framework outlined by this model.[1-4]

The reaction sequences responsible for photoisomerization (Scheme 2) of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ (X=$H_2O$) and of *cis* and *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ (X=OH) follow the initial excitation of the ground state molecules $G_{cis}$ or $G_{trans}$ to their singlet excited states $S_{cis}$ or $S_{trans}$, respectively. The intersystem crossing generates the corresponding triplet excited states $T_{cis}$ or $T_{trans}$, from which deactivation to the parent ground states competes with the dissociation of an $H_2O$ to form the triplet square pyramidal pentacoordinated intermediates $T_{basal}$ or $T_{apical}$, respectively. The rearrangement between $T_{basal}$ and $T_{apical}$ proceeds *via* the high energy, trigonal bipyramidal intermediate $T_{TBP}$, also in a triplet state. Deactivation of $T_{basal}$ or $T_{apical}$ leads to the square pyramidal pentacoordinate ground states $G_{basal}$ or $G_{apical}$, which being coordinately unsaturated react with a solvent molecule giving the photoproducts *cis* or *trans*-$[Rh(en)_2(H_2O)X]^{n+}$, respectively. The energy difference between the *basal* and *apical* square pyramidal triplets is essentially a function of the σ-donor strengths of the five ligator atoms, as the stronger σ-donors have a strong site preference for a basal position.[1-4] Given the σ-donor strength series[25] $\sigma_{OH^-} > \sigma_{saturated\ amine} > \sigma_{H_2O} > \sigma_{Cl^-}$, the photoisomerization of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ is a result of the excited state rearrangement


(4)

whereas the photoisomerizations of *cis*- and *trans*-$[Rh(en)_2(H_2O)(OH)]^{2+}$ are the result of the reversible rearrangement


(5)

In this context it is important to note that the excited state lifetimes of these intermediates are in the nsec region and therefore by several orders of magnitude too short-lived to attain excited state acid/base equilibrium with the medium.[7]

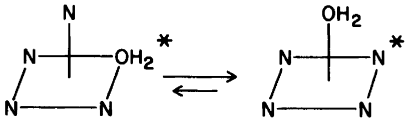
The calculations based on the spectroscopic parameters have proved successful in the prediction of the stereochemical consequences of photochemical ligand exchange reaction[2,5-7] including water exchange reactions.[17] They also offer an explanation for the observed differences between the photoisomerization of the tetraam-

*Table 6.* Energy of the lowest multiplicity allowed ligand field transition ($^1T_{1g} \leftarrow {}^1A_{1g}$, pseudo octahedral symmetry assumed) for *cis*-[Rh(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ and *cis*-[Rh(en)$_2$(H$_2$O)$_2$]$^{3+}$ and their conjugated bases.

| | Energy in kK | |
|---|---|---|
| | Bis(ethylenediamine)[a] | Tetraammine[b] |
| *cis*-[RhA$_4$(H$_2$O)$_2$]$^{3+}$ | 31.4 | 30.7 |
| *cis*-[RhA$_4$(H$_2$O)(OH)]$^{2+}$ | 31.0 | 30.4 |
| *cis*-[RhA$_4$(OH)$_2$]$^{+}$ | 30.4 | 29.9 |

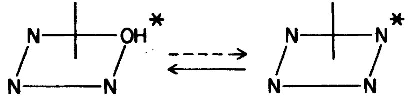
[a] A$_4$=(en)$_2$, present work. [b] A$_4$=(NH$_3$)$_4$, Ref. 7.

mine- and bis(ethylenediamine)rhodium(III) complexes. The energies of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition (pseudo octahedral symmetry assumed, Table 6) indicates that ethylenediamine is a stronger field ligand than ammonia for this class of compounds, and given that the $\pi$-bonding properties of the two ligands appear identical,[25] the ethylenediamine ligand must be a significantly stronger $\sigma$-donor than ammonia. The more detailed $\sigma$-order of the relevant donors is therefore $\sigma_{OH^-} > \sigma_{en} > \sigma_{NH_3} > \sigma_{H_2O}$. Consequently, the energy difference between the *basal* and *apical* isomers of eqn. (4) must be greater than the analogous energy difference for eqn. (6) in which N=NH$_3$:



(6)

The small energy difference in eqn. (6) allows the coexistence of both isomers for the aquatetaammine intermediate, whereas the *apical*-aquabis(ethylenediamine) intermediate, is energetically favored over its *basal* counterpart. Another consequence of the $\sigma$-donor strength order is that the energy difference between the two isomers of eqn. (7) is greater than the corresponding energy difference of eqn. (5):



(7)

In this case the *basal*-hydroxotetraammine is energetically favored over the *apical* isomer, whereas the *basal* and the *apical* isomers of the hydroxobis(ethylenediamine) species have comparable energy. These qualitative predictions for the reactions of eqns. (4) – (7), made on the basis of spectroscopic parameters, are in agreement with the observed pattern of photoisomerizations.

Despite the success and the predictive power of the purely spectroscopic model,[1,4] other aspects of the excited state properties and processes have to be taken into account. For example, the arguments presented above do not allow any corrections of the energetics due to the chelate effect present in the ethylenediamine but not in the ammonia complexes. Since the energy difference between products and reactants in the reactions of eqns. (4) – (7) is apparently very small, any such perturbation in these systems might alter the relative energies of the isomers. However, comment on this point must await the results of investigations of complexes with chelating amines having $\sigma$-donor properties comparable to the $\sigma$-donor properties of ammonia.

The relative rates of deactivation of the *basal* and *apical* triple intermediates may also have some influence upon the product distribution.[2,21] For example, photolysis of *cis*-[Ir(en)$_2$Cl$_2$]$^+$ leads to a 10:1 *cis–trans* mixture of the [Ir(en)$_2$(H$_2$O)Cl]$^{2+}$ ions significantly different from the 100 % *trans* product of *trans*-[Ir(en)$_2$Cl$_2$]$^+$ photolysis.[26] In contrast both *trans*- and *cis*-[Rh(en)$_2$Cl$_2$]$^+$ give solely[5] *trans*-[Rh(en)$_2$(H$_2$O)Cl]$^{2+}$ as the photoproduct. These differences have been[26] attributed to the larger spin-orbit coupling present in the Ir(III) complexes, making the direct deactivation of [Ir(en)$_2$Cl]$^{2+\,*}$ intermediates faster than rearrangement. Thus, the product ratio indicates that the *basal*-[Ir(en)$_2$Cl]$^{2+\,*}$ intermediate deactivates about an order of magnitude faster than *basal* to *apical* rearrangement. For the Rh(III) analogs, rearrangement is apparently much faster relative to deactivation and the same photoproduct distribution is found for both ions.[24] Consistent with this is the observation that a reexamination of the photoreactions of *cis*- and *trans*-$[Rh(NH_3)_4ClX]^{n+}$ (X=Cl or $H_2O$) shows that the $[Rh(NH_3)_4Cl]^{2+*}$ intermediate generated from either *cis*-$[Rh(NH_3)_4Cl_2]^+$ or *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ undergoes direct deactivation at a rate about one-fifth on the rearrangement rate.[17]

One should keep in mind that not only the relative energies of the *apical* and *basal* excited state intermediate isomers but also the energy barrier for their isomerization are functions of the ligand fields. Thus, it is notable that photoaquation of chloride from *cis*- and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$ or photolysis of *cis*- or *trans*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ led to little photoisomerization[5,23] at 25 °C, although substantially greater isomerization was noted when *cis*-$[Rh(en)_2(NH_3)(H_2O)]^{3+}$ was photolyzed at 50 °C. The interpretation offered was that the average ligand field of the $[Rh(en)_2(NH_3)]^{3+*}$ intermediate increased the kinetic barrier for isomerization to a point where deactivation is much faster at 25 °C.[23] In this context, it is interesting that the photoisomerization of *cis*-$[Rh(en)_2(H_2O)_2]^{3+}$ goes with a moderately large quantum yield. Although the extent of isomerization relative to deactivation of the *basal*-$[Rh(en)_2(H_2O)]^{3+*}$ excited state intermediate is as yet unknown (this depends on determining the extent of water photoexchange relative to photoisomerization), these results indicate that the apparent similarity of $NH_3$ and $H_2O$ in their influence on the relative energies of the square pyramidal isomers is not as great in determining the activation barrier for rearrangements.

*Acknowledgements.* This research was supported by grants from the Danish Natural Science Research Council and by a NATO Research Grant. The authors with to thank Bodil Øby and Jacob Ventegodt for technical assistance, Dr. Karen Kaas for writing the computer program, and Dr. M. P. Hancock for helpful advice. We also thank Johnson Matthey for the loan of the rhodium used in these studies.

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Received December 16, 1983.