Aqueous Solution Phosphorescence Lifetimes of *cis*- and *trans*-Amminebis(ethylenediamine)chlororhodium(III). Effect of Coordination Geometry on Excited State Deactivation

D. Magde[a] and L. H. Skibsted[b]

[a]Department of Chemistry, University of California at San Diego, La Jolla, California 92093, USA and
[b]Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark.

Magde, D. and Skibsted, L. H., 1987. Aqueous Solution Phosphorescence Lifetimes of *cis*- and *trans*-Amminebis(ethylenediamine)chlororhodium(III). Effect of Coordination Geometry on Excited State Deactivation. – Acta Chem. Scand., Ser. A 41: 208–212.

The room-temperature phosphorescence lifetimes of amminebis(ethylenediamine)chlororhodium(III) depend strongly on the coordination geometry and were found, using a mode-locked laser and time-correlated single-photon detection, to be 2.1(1) and 13.0(5) ns for the *cis*- and *trans*-isomers, respectively. From the lifetimes combined with the photoaquation quantum yields, triplet excited state ammonia- and chloride dissociation rate constants and non-radiative deactivation rate constants were evaluated, and are discussed in relation to the same kinetic parameters for triplet pentaamminechlororhodium(III).

Photoaquation quantum yields for hexacoordinate d^6 electronic configuration aminehalorhodium(III) complexes combined with phosphorescence lifetimes measured under identical ambient solution conditions have allowed the evaluation of rate constants for the individual processes deactivating the photoreactive state.[1–4] The photoreactive state has been identified as the lowest energy ligand field triplet $(t_{2g})^5(e_g)^1$ state, and investigations of series of complexes in which the nature of reacting and non-reacting ligands, as well as stereochemistry, have been systematically varied have revealed that certain patterns of reactivity for this state can be recognized and accounted for in terms of electronic and steric ef-

fects similar to those normally invoked to rationalize ground state chemistry.[5–7] As a continuation of our investigations of the photophysics of aminehalorhodium(III) complexes, we have determined the excited state lifetimes for the isomeric amminebis(ethylenediamine)chlororhodium(III) ions in order to understand the photophysical background for the significant differences noted in the photoaquation reactions of the two isomers.

Experimental

Materials. cis- and *trans*-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$ were prepared from *cis*-[Rh(en)$_2$Cl$_2$]Cl$_{\frac{1}{2}}$(ClO$_4$)$_{\frac{1}{2}}$[8]

Table 1. Ligand field spectra of the *cis*- and *trans*-amminebis(ethylenediamine)chlororhodium(III) nitrate samples used for the photophysical investigations.[a]

	$\lambda_{max}(\varepsilon)$[b]	$\lambda_{min}(\varepsilon)$[b]
cis-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$	343(150),275(189)	320(130),250(92)
trans-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$	343(99), 275(140)	324(89), 252(88)

[a]In 0.50 M HClO$_4$ plus 0.50 M NaClO$_4$, cf. Ref. 10. [b]λ in nm, ε in l mol^{-1} cm^{-1}.

and *trans*-[Rh(en)$_2$Cl$_2$]NO$_3$,[7] respectively, by the method of Johnson and Basolo,[9] and were reprecipitated twice from 6 M nitric acid (8 ml per g of compound) by addition of ethanol. The UV-visible spectrum (Table 1) did not change between first and second reprecipitation, and agreed with the spectra obtained for *cis*-[Rh(en)$_2$(NH$_3$)Cl]Cl$_2$ and *trans*-[Rh(en)$_2$(NH$_3$)Cl](CF$_3$SO$_2$O)$_2$,[10] respectively, for which satisfactory analyses (C, H, N, Cl, S) were obtained. The purity of both nitrate salts was checked by high-performance ion-exchange chromatography (Waters HPLC system with a M6000 A solvent delivery unit, a U6K universal injector and a Merck-Hitachi L-3000 UV/VIS Diodearray Detector), using a TSKgel SP-5PW column and 0.20 M Na$_2$SO$_4$ (pH $\approx$ 5) as eluent, with a flow of 1.0 ml min^{-1}. This chromatographic procedure gave an efficient separation of complexes with different charge and an efficient isomeric separation. No impurities could be detected in *cis*-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$, whereas *trans*-[Rh(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$ was found to contain 4 % of the *cis*-isomer and no other impurities.

Phosphorescence lifetimes were measured using time-correlated single-photon methods, as previously described in detail[7] apart from the changes needed to provide an excitation pulse at a shorter wavelength and a lower repetition rate. The same mode-locked argon ion laser, operating at 514.5 nm, was used to pump a mode-locked synchronous dye laser operating at 688 nm, the output of which was frequency doubled in a 20 mm KD*P crystal to provide excitation pulses at 344 nm.

The dye laser was cavity dumped at 8 MHz, both to increase the pulse peak power so as to improve frequency doubling, and to reduce the repetition rate in order to facilitate measurement of the relatively long lifetime of one of the compounds in the present study.

Results and discussion

In aqueous solution at ambient temperature, *cis*- and *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ show a very broad diffuse phosphorescence in the red, with emission intensities comparable to those previously noted for other aminehalorhodium(III) complexes (Φ_{ph} < 10^{-6}),[5-7] and with decay curves that can be described by a single exponential function convoluted with the excitation function[7] (see Figs. 1 and 2). The instrument response (or "excitation" function) was well separated from the phosphorescence, as may be seen in Fig. 3 for the shorter lived of the isomers.

The lifetimes were found to be 13.0(5) ns for *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$, which is very close to the value of 14.2(1.0) ns previously measured for [Rh(NH$_3$)$_5$Cl]$^{2+}$,[1] whereas a lifetime of 2.1(1) ns was found for *cis*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ (Table 2). The lifetime of the *cis* isomer is significantly shorter than that of two other pentaaminechloro complexes and is close to those found for *cis*- and *trans*-[Rh(en)$_2$Cl$_2$]$^+$.[7] However, neither of these tetraamine complexes nor any hydrolysis products could be detected by the sensitive chromatographic method employed, thereby establishing the significant difference between the phosphorescence lifetimes of *cis*- and *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$.
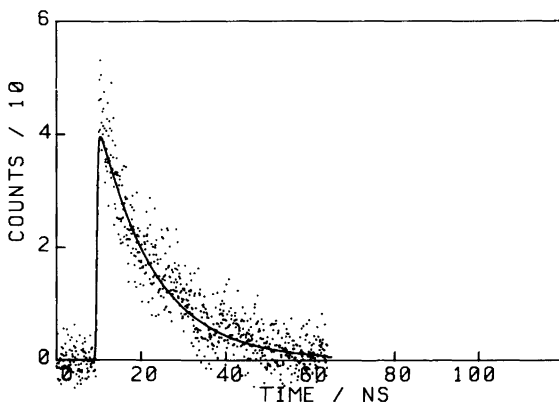

Fig. 1. Phosphorescence decay for *trans*-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ in aqueous solution. Excitation wavelength 344 nm. Solid line is the best fit of an exponential convoluted with the excitation function.
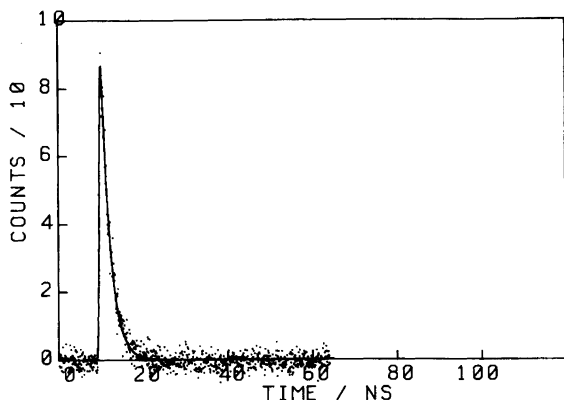
Fig. 2. Phosphorescence decay for
cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$
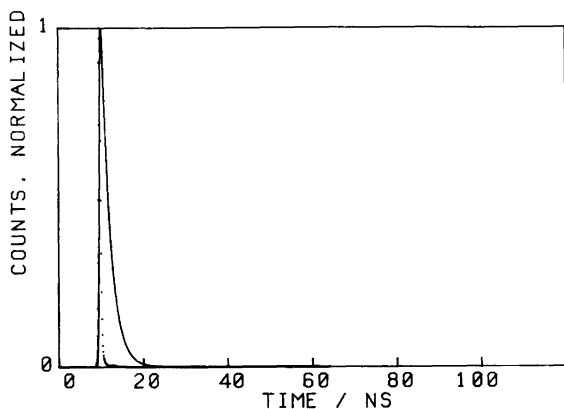in aqueous solution (cf. Fig. 1).

Fig. 3. Normalized phosphorescence decay for
cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ (solid line) compared to
instrument response (dotted line).

As noted in the introduction and discussed in detail elsewhere,[3,5-7] the photoreactive state (chloride and ammonia ligand photoaquation, cf. Table 2) is identical to the emitting state. This allows calculation of the rate constants for the excited state chloride and ammonia dissociation, and for the excited state non-radiative deactivation, from the relationships given in the footnotes to Table 3. For [Rh(NH$_3$)$_5$Cl]$^{2+}$, the ammonia that becomes substituted by water can originate from either the axial or an equatorial position, and it has been shown by ^{15}N-labelling[12] that the yields of the equatorial and axial ammonia are very similar, thus allowing the assignment of the individual rate constants for the axial and equatorial ammonia ligands given in Table 3.

Table 2. Phosphorescence lifetimes and photoaquation quantum yields for pentaamminechlororhodium(III) and cis- and trans-amminebis(ethylenediamine)chlororhodium(III) in dilute aqueous solution at 25 °C.

Complex	τ/ns	Φ_{Cl^-} /mol einstein^{-1}	Φ_{NH_3} /mol einstein^{-1}
[Rh(NH$_3$)$_5$Cl]$^{2+}$ [a]	14.2(1.0)	0.15(1)	0.04(1)
cis-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ [b]	2.1(1)	0.075(3)	0.0041(7)
trans-[Rh(en)$_2$(NH$_3$)Cl]$^{2+}$ [b]	13.0(5)	0.075(3)	0.057(1)

[a]Refs. 1 and 11. [b]Present work and Ref. 10.

210

Table 3. Rate constants for chloride[a] and ammonia[a] dissociation and non-radiative deactivation[b] from the lowest energy ligand field excited state for pentaamminechlororhodium(III) and for *cis*- and *trans*-amminebis (ethylenediamine)chlororhodium(III) in dilute aqueous solution at 25 °C.

Complex	k_{Cl^-}/s^{-1}	$k_{NH_3}^{eq}/s^{-1}$	$k_{NH_3}^{ax}/s^{-1}$	k_n/s^{-1}
$[Rh(NH_3)_5Cl]^{2+}$	$1.6(1)\cdot10^7$	$1.4(1)\cdot10^6$	$1.4(1)\cdot10^6$	$5.7(4)\cdot10^7$
cis-$[Rh(en)_2(NH_3)Cl]^{2+}$	$3.5(4)\cdot10^7$	$1.5(2)\cdot10^6$		$4.7(5)\cdot10^8$
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	$5.8(2)\cdot10^6$		$4.5(2)\cdot10^6$	$6.7(3)\cdot10^7$

[a]Calculated from experimental data of Table 2: $k_x = \Phi_x \tau^{-1}$. [b]$k_n = \tau^{-1} - \Sigma k_x$.

The lowest energy triplet is, for all three pentaamine complexes in question, a ^3E state with the σ-antibonding orbital along the tetragonal axis, and in agreement herewith, the major ligand labilization is observed to take place from this axis (Fig. 4).[12-14] For *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$, chloride dissociation is the only axial reaction path available, since axial amine photoaquation is blocked by chelation;[6] yet $k_{Cl^-} = 3.5 \cdot 10^7$ s^{-1} is greater than the rate constant for the overall axial ligand dissociation in each of $[Rh(NH_3)_5Cl]^{2+}$ and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$, for which $k_{Cl^-} + k_{NH_3}^{ax}$ are 1.7 and 1.0 $\cdot$ 10^7 s^{-1}, respectively. The occurrence of significant equatorial photolabilization in the pentaamines in which this latter reaction path is available (i.e. not blocked by chelation) suggests that higher energy states play a role (^3A triplet components have been suggested[12]). For *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$, $k_{NH_3}^{eq}$ is 1.5 $\cdot$ 10^6 s^{-1}, and is larger than $k_{NH_3}^{eq}$ for $[Rh(NH_3)_5Cl]^{2+}$ (0.4 $\cdot$ 10^6 s^{-1}, when corrected for the number of equivalent leaving ligands) by a factor of 4. The *cis* isomers of tetraaminerhodium(III) complexes have been found to have larger excited state distortion that their *trans* analogues, as evidenced by a larger Stokes shift for the *cis* complexes.[5,6] This distortion is released through both ligand dissociation and vibronic coupling to solvent molecules, rendering both of these reaction paths more efficient. The present series of pentaamine complexes is especially interesting, since a small perturbation of the coordination sphere has this effect of enhancing reactivity both on the axial and equatorial positions, despite their inherent difference in reactivity. In particular, it is noteworthy that such minor changes in the coordination geometry also have the noted effect on the vibronic coupling: $k_n \approx 5 \cdot 10^7$ s^{-1} for $[Rh(NH_3)_5Cl]^{2+}$ and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$, and $k_n \approx 5 \cdot 10^8$ s^{-1} for *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$. This latter photophysical process is a competitor to ligand dissociation, and the remarkable difference in reactivity between the two triethylenetetraamine complexes *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ with respect to chloride photoaquation may stem from similar differences in the efficiency of the non-radiative deactivation.[15,16]

References

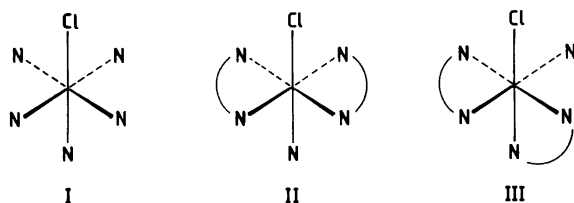1. Bergkamp, M. A., Brannon, J., Magde, D., Watts, R. J. and Ford, P. C. *J. Am. Chem. Soc. 101* (1979) 4549.

Fig. 4. Aquation of ligands on the tetragonal axis is the major photoreaction in $[Rh(NH_3)_5Cl]^{2+}$ (I), *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$ (II) and *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$ (III).

2. Bergkamp, M. A., Watts, R. J. and Ford, P. C. *J. Am. Chem. Soc. 102* (1980) 2627.

3. Sexton, D. A., Skibsted, L. H., Magde, D. and Ford, P. C. *J. Phys. Chem. 86* (1982) 1758.

4. Frink, M., Sexton, D. A., Magde, D. and Ford, P. C. *Inorg. Chem. 23* (1984) 1238.

5. Sexton, D. A., Skibsted, L. H., Magde, D. and Ford, P. C. *Inorg. Chem. 23* (1984) 4533.

6. Skibsted, L. H., Hancock, M. P., Magde, D. and Sexton, D. A. *Inorg. Chem. 23* (1984) 3735.

7. Skibsted, L. H., Hancock, M. P., Magde, D. and Sexton, D. A. *Inorg. Chem. 26* (1987) 1708.

8. Hancock, M., Nielsen, B. and Springborg, J. *Inorg. Synth. 24* (1986) 220.

9. Johnson, S. A. and Basolo, F. *Inorg. Chem. 1* (1962) 925.

10. Mønsted, L., Mønsted, O. and Skibsted, L. H. *To be published.*

11. Frink, M. E. *Thesis,* University of California at Santa Barbara, Santa Barbara 1984.

12. Skibsted, L. H. *Inorg. Chem. 24* (1985) 3791.

13. Vanquickenborne, L. G. and Ceulemans, A. *Inorg. Chem. 17* (1978) 2730.

14. Vanquickenborne, L. G. and Ceulemans, A. *Coord. Chem. Rev. 48* (1983) 157.

15. Martins, F. and Sheridan, P. S. *Inorg. Chem. 17* (1978) 2822.

16. Martins, F. and Sheridan, P. S. *Inorg. Chem. 17* (1978) 3631.