Concomitant Photoaquation–Photo-isomerization of *cis*-Dichlorotetra-amminerhodium(III), *cis*-$[Rh(NH_3)_4Cl_2]^+$

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Summary Photolysis of the lowest ligand field (LF) band of aqueous *cis*-$[Rh(NH_3)_4Cl_2]^+$ leads cleanly to the formation of *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ as the only detectable product with a quantum yield of 0·33 mol einstein^{-1}.

Quantitative mechanistic treatment of the photosubstitution pathways of transition-metal complexes resulting from ligand field (LF) excitation must be concerned not only with quantum yield for the ligand labilization pathways but also with the stereochemical consequences of photoexcitation. For example, photoisomerization simultaneous with photoaquation is well characterized for chromium(III) halogenoamine complexes [*e.g.*, equation (1)].† In contrast, analogous *trans*-rhodium(III) complexes {*trans*-$[RhA_4X_2]^+$,

$$trans\text{-}[Cr(en)_2(NH_3)Cl]^{2+} + H_2O \xrightarrow[546\text{ nm}]{h\nu} cis\text{-}[Cr(en)_2(H_2O)Cl]^{2+} + NH_3 \quad (1)$$

where A_4 is cyclam, $(en)_2$, or $(NH_3)_4$} undergo photoaquation of X^- with retention of configuration,[2] while the only *cis* Rh^{III} complexes studied[3] have chelating ligands which are not amenable to isomerization or which, it might be argued,[3b,4] display secondary reactions that rationalize any isomerizations observed. Here we report the photochemistry resulting from LF excitation of *cis*-$[Rh(NH_3)_4Cl_2]^+$ and demonstrate unambiguously that photoisomerization may be concomitant with ligand photoaquation from a Rh^{III} halogenoamine complex.

Spectra of the *cis*-$[Rh(NH_3)_4Cl_2]^+$ photolysis solutions (pH 3, aq. $HClO_4$) initially shows monotonic absorption changes. Photolysis at 365 nm of this complex (λ_{max} at 360 and 298 nm, ϵ = 126 and 108 mol^{-1} l cm^{-1}, respectively)[5] leads to the following spectral shifts. The lower energy band shifts to longer wavelength while the higher energy band shifts to shorter wavelength with isosbestic points maintained at 292 and 268 nm throughout the photolysis. The final product spectrum with maxima at 392 and 283 nm (ϵ = 44 and 107 mol^{-1} l cm^{-1}, respectively) matches that of *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ prepared by the stereoretentive thermal aquation[6] of *trans*-$[Rh(NH_3)_4Cl_2]^+$. Minimal pH differences between the irradiated solutions and analogously treated unirradiated solutions indicate that ammonia photoaquation is at most very minor [$\Phi(NH_3)$

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† Abbreviations are: en = ethylenediamine; cyclam = 1,4,8,11-tetra-azacyclotetradecane.

< 0·02 mol einstein^{-1}]. In addition the monotonic absorbance changes at all wavelengths demonstrate that the expected thermally stable intermediates such as *trans*-$[Rh(NH_3)_4Cl_2]^+$ (λ_{max} 415 nm) and *cis*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ (353 nm) are not formed in significant yields. Thus the photoreaction can be attributed to aquation of chloride concomitant with isomerization to the *trans*-configuration [equation (2)]. Also noteworthy are the qualitative observations, first, that since the product solution is stable to the photolysis conditions, secondary photoaquation of NH_3 or Cl^- from *trans*-$[Rh(NH_3)_4(H_2O)Cl]^{2+}$ is only very minor, and second, that both *cis*-$[Rh(NH_3)_4(H_2O)_2]^{3+}$ and [*cis*-$Rh(NH_3)_4(H_2O)Cl]^{2+}$ undergo efficient isomerization to their respective *trans* analogues when irradiated at 365 nm.

$$cis\text{-}[Rh(NH_3)_4Cl_2]^+ + H_2O \xrightarrow[365\text{ nm}]{h\nu} trans\text{-}[Rh(NH_3)_4(H_2O)Cl]^{2+} \quad (2)$$

The quantum yield for equation (2), calculated from spectral changes, is 0·33 ± 0·03 mol einstein^{-1}. This value is surprisingly close to that (0·37) measured[3a] for chloride aquation from *cis*-$[Rh(cyclam)Cl_2]^+$ induced by irradiating the lowest LF band. The latter reaction proceeds with retention of configuration presumably because of the difficulty inherent in interconverting the cyclam ligand between the *cis* and *trans* configurations. {A value of 0·38 mol einstein^{-1} has also been estimated for the photoisomerization quantum yield for *cis*-$[Rh(en)_2Cl_2]^+$; however, this value is ambiguous given the uncertainties regarding the products of the photoreaction[3b]}. Unlike the case[1] for Cr^{III} where inhibiting the simultaneous rearrangement reduces the photoaquation quantum yield by several orders of magnitude, inhibiting stereo rearrangement has little apparent effect with the Rh^{III} complexes. Thus it appears that the rearrangement occurs subsequent to the chloride aquation, perhaps the rearrangement of a pentaco-ordinate intermediate formed by photodissociation of Cl^-.

Previous workers[7] have found *trans*-$[Rh(NH_3)_4(H_2O)Br]^{2+}$ and *trans*-$[Rh(NH_3)_4(H_2O)I]^{2+}$ as the principal products from LF excitation of the respective halogenopenta-amine complexes and have assumed that the aquated NH_3 originated in the *trans* position. This proposal is consistent with several theoretical treatments arguing labilization along the weakest field ligand axis.[8] However, the present results suggest strongly that the *trans* configuration may be expected regardless of whether a *cis* or a *trans* NH_3 were photoaquated and demonstrate clearly the need for definitive product studies identifying the sites from which photoaquated NH_3 originates.

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