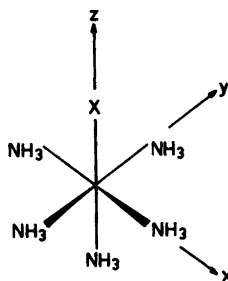


Specific Equatorial Photolabilization of Ammonia in Cyanopentaamminerhodium(III)

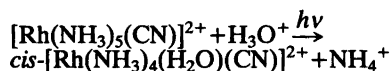
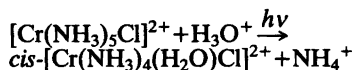
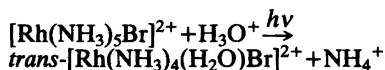
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In octahedral complexes belonging to the pentaammine series two different ammonia ligands can be distinguished, and the ammonia which becomes substituted by water as a result of ligand field excitation in aqueous solution can be either



in the axial position on the unique tetragonal axis or in an equatorial position. The product stereochemistry found for such reactions¹⁻³



is not, however, indicative of whether axial or equatorial ammonia is substituted, owing to the high stereomobility of such excited state reactions.⁴⁻⁶

trans-[Rh(en)₂(NH₃)Br]²⁺ has been used as a model for [Rh(NH₃)₅Br]²⁺, and the observation that ammonia, rather than ethylenediamine (en), photoaquates in the mixed amine complex was considered indicative of axial labilization also in the pentaammine complex [Rh(NH₃)₅Br]²⁺.¹ A more direct proof of axial labilization and, consequently, of photoisomerization was provided by the use of isotopic labelling in [Cr(NH₃)₅Cl]²⁺.² In both of the complexes in which axial labilization has been identified, the heteroligand has been the weaker field ligand. In order to establish the origin of the photolabilized ammonia in a pentaammine complex containing a ligand of greater ligand field strength than ammonia, we have ¹⁵N-labelled *trans*-NH₃ in [Rh(NH₃)₅(CN)]²⁺ and report here the result of an isotopic analysis of the ammonia released during photoaquation.

trans-[Rh(NH₃)₄Cl(CN)]⁺ was heated in a ¹⁵N-enriched (2.69 %) aqueous NH₃/NH₄⁺ buffer solution, and the enrichment of the complex was confirmed by a ¹⁵N/¹⁴N analysis of the isolated and recrystallized [Rh(NH₃)₅(CN)]Cl₂. The ¹⁵N/¹⁴N analysis showed that only one mol of enriched ammonia per mol of complex had entered the coordination sphere, indicating that exchange between coordinated and solution ammonia was insignificant. Since thermal substitution of ammonia for chloride at Rh(III) centers is stereoretentive,⁷⁻⁹ scrambling among the five ammonia ligands was excluded. Thus, the procedure employed resulted in specific *trans*-labelling:

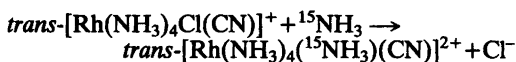


Table 1. Fraction of equatorial NH₃ released during photoaquation of [Rh(NH₃)₅(CN)]²⁺ in aqueous 0.10 M HClO₄ calculated from isotopic analysis of NH₃ released from 2.69 % ¹⁵N *trans*-enriched [Rh(NH₃)₅(CN)]²⁺.

λ_{irr} nm	[Rh(NH ₃) ₅ (CN)] ²⁺ ^a μmol	NH ₃ ^b μmol	¹⁵ N %	Equatorial NH ₃ ^c
254	9.6	8.4	0.46	0.96
254	9.6	8.8	0.43	0.97
254	9.6	8.9	0.46	0.96
313	8.9	9.3	0.54	0.93

^a Amount of [Rh(NH₃)₅(CN)]²⁺ photolyzed. ^b Amount of released NH₃ separated from photolysis solution. ^c Equatorial NH₃ released as a fraction of total released NH₃.

2 mM solutions of the ^{15}N *trans*-enriched $[\text{Rh}(\text{NH}_3)_5(\text{CN})]\text{Cl}_2$ in aqueous 0.10 M HClO_4 were irradiated with 254 or 313 nm monochromatic light until at least 90 % was converted to *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})]^{2+}$ (as monitored by UV-spectroscopy). 254 nm excitation (1E , $^1B_2 \leftarrow ^1A_1$; C_{4v} symmetry) was found to result in the same photoproducts, *viz.* *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})]^{2+}$ and NH_4^+ , with the same photoreaction quantum yield, 0.10 ± 0.01 mol/einstein at 25 °C, as the previously investigated 3 excitation at 313 and 334 nm (1E , $A_2 \leftarrow ^1A_1$). NH_4^+ was separated from the reaction mixture by a procedure (*vide infra*) which was known to liberate no further ammonia, and was subsequently subjected to $^{15}\text{N}/^{14}\text{N}$ analysis.

With the present experimental design, a natural $^{15}\text{N}/^{14}\text{N}$ ratio corresponding to 0.36 % ^{15}N is expected in the photoaquated ammonia from equatorial labilization, whereas 2.69 % is indicative of axial labilization. Experimental results are found in Table 1. The observed $^{15}\text{N}/^{14}\text{N}$ ratios are only slightly greater than corresponding to 0.36 % and indicate that as much as 96 ± 1 % of the ammonia separated from the reaction mixture originates from equatorial positions. From these results we conclude that photolabilization in $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$ takes place almost exclusively in the equatorial plane.

In Rh(III) low-spin complexes the photochemically reactive state has been identified as the lowest ligand field excited state.^{4,5} In $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$ this triplet state is 3A_2 , corresponding to the configuration $(d_{xz}, d_{yz})^4 (d_{xy})^1 (d_{x^2-y^2})^1 (d_{z^2})^0$, and the σ -antibonding e_g orbital eventually populated as a result of ligand field excitation is therefore located in the x - y plane. Labilization is consequently expected to occur among the four equatorial ammonia ligands.³ In the more detailed theoretical treatment by Vanquickenborne and Ceulemans^{10,11} for d^6 (Rh(III)) and d^3 (Cr(III)) complexes, excited state bond indices $I^*(\text{ML})$ are calculated from spectroscopic σ - and π -parameters for metal-ligand bonds and provide a quantitative indication of which ligand becomes labilized. $I^*(\text{ML})$ calculated for the individual bonds in $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$ clearly predicts equatorial labilization,^{3,11} in agreement with the qualitative arguments presented above and, which is more significant, in agreement with our experimental observations. These results therefore serve as an important verification of the predictive power of the Vanquickenborne-Ceulemans model for a C_{4v} complex with the strong field ligand in an axial position.

It should also be noted that despite the common photoproduct stereochemistry, the

photoaquated ammonia originates from different coordination sites in the two octahedral pentaammine complexes in which the stereochemical origin has been established by direct experiment. In $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ axial ammonia is preferentially labilized, whereas equatorial ammonia is almost exclusively labilized in $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$. These results are both accommodated within Adamson's photochemical rules,¹² which are based empirically on the relative strength of the ligand field, and they are also well understood on the basis of more recent theories,^{4,5} as discussed above for $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$.

Isotopic labelling. A 125 mg portion of *trans*- $[\text{Rh}(\text{NH}_3)_4(\text{CN})\text{Cl}]\cdot 1\frac{1}{2} \text{H}_2\text{O}$, prepared and purified as described previously,³ was dissolved together with 125 mg of 96.3 % ^{15}N NH_4Cl (VEB Berlin Chemie, GDR) in 7.70 ml of 12.1 M aqueous NH_3 (natural $^{15}\text{N}/^{14}\text{N}$ ratio corresponding to 0.36 %) and the solution was maintained at 90 °C in the dark under reflux for 75 min. The product, which precipitated upon slow cooling to room temperature, was filtered off and recrystallized from aqueous HCl. Yield 100 mg (83 %). The UV spectrum was identical to that previously reported³ for $[\text{Rh}(\text{NH}_3)_5(\text{CN})]\text{Cl}_2$. Calculated ^{15}N enrichment: 0.748 %. Found: 0.755 %.

Photolysis experiments. The quantum yield for the photoreaction of $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$ resulting from 254 nm irradiation was determined by experimental and numerical procedures outlined previously,¹³ using an Oriel 6035 low-pressure Hg-Ar penlight equipped with an Oriel 6041 short-wave filter. The exhaustive or nearly exhaustive photolyses were performed with ≈ 10 μmol samples of enriched $[\text{Rh}(\text{NH}_3)_5(\text{CN})]\text{Cl}_2$ dissolved in 5.00 ml of 10^{-1} M HClO_4 in a Rayonet RMR-500 photochemical reactor with an RMA-400 Merry-Go-Round Unit (254 nm), or in the Spindler and Hoyer optical train described previously (313 nm).¹³ After quantitative transfer of the photolyzed solution to a distillation flask, the excess acid was neutralized with NaOH and the solution buffered with 0.5 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. By means of a gentle N_2 flow through the solution for 8 h, the photoproduct NH_3 was separated from the other principal photoproduct, *cis*- $[\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CN})]^{2+}$, and trapped in standardized 10^{-2} M HCl. The amount of NH_3 thus separated was determined by titration, and the $^{15}\text{N}/^{14}\text{N}$ ratio was subsequently determined.

Isotopic analysis. The $^{15}\text{N}/^{14}\text{N}$ ratio in the labelled compound and in the photochemically liberated NH_3 was determined by optical emission analysis at the Physics Laboratory of the Royal Veterinary and Agricultural University.

The analytical procedure (a detailed description is found in Ref. 14) involved a Dumas destruction of the material.

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