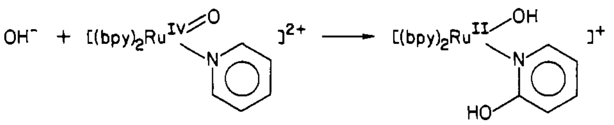
in this potential region, suggesting that hydroxypyridine type species may also appear as intermediates, at least, in the initial stage of ligand oxidation.

The decrease in Ru(III)/Ru(II) potential following ligand oxidation also helps to explain why the majority of reduced product is the reduced, unmodified complex. Following reduction via pyridyl group hydroxylation



the hydroxypyridine Ru(II) complex would be rapidly oxidized to Ru(III) by either $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ or $[(bpy)_2(py)Ru^{III}(OH)]^{2+}$, leading to unmodified, reduced complex product and further ligand oxidation of $[(bpy)_2(pyOH)Ru(O)]^+$.

Final Comments. A goal of this work was to evaluate the ability of polypyridyl ruthenium oxo complexes to act as oxidation catalysts in basic solution. It is clear that some catalyst loss occurs as a result of competitive ligand oxidation processes that are enhanced in regions of high pH. For example, $[(bpy)_2(py)Ru(O)]^{2+}$ is stable toward self-reduction in acidic or neutral solution for hours while at pH 13 the half-time for self-reduction is 2 min. Nonetheless, the rates observed here for the self-reduction processes are sufficiently slow that useful catalytic rate data can be obtained in basic solution[9] provided the substrate of interest is sufficiently reactive and/or present in large excess.

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Contribution from the Chemistry Department,
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Ammonia Scrambling as a Result of Chloride Photoaquation in Chloropentaamminerhodium(III)

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The ^{15}N-labeled compounds *cis*- and *trans*-$[Rh(NH_3)_4(^{15}NH_3)Cl]Cl_2$ have been prepared. The ammonia ligand that is photoaquated in aqueous perchloric acid solution at 13 °C as a result of ligand field excitation of labeled $Rh(NH_3)_5Cl^{2+}$ originates to an equal extent from axial and equatorial positions, implying that the axial ammonia is labilized four times as efficiently as the equatorial ammonia ligands. The axial/equatorial ammonia photoaquation ratio shows no significant temperature dependence up to 37 °C. Isotopic analyses of the ammonia that is photoaquated from labeled $Rh(NH_3)_5Cl^{2+}$ in acidic aqueous chloride solution showed that chloride photoaquation and subsequent photoanation result in ammonia scrambling.

Introduction

Ligand field excitation of hexacoordinated rhodium(III) ammine complexes leads to ligand labilization and, in aqueous solution, to photoaquation with relatively large, wavelength-independent quantum yields.[1,2] In complexes belonging to the pentaammine series, the ammonia that becomes substituted by water as a result of ligand field excitation can originate either from the axial position on the tetragonal axis or from an equatorial position. Such excited-state substitution reactions have high stereomobility,[3-5] and the product stereochemistry is not necessarily indicative of whether axial or equatorial ammonia is substituted:

$$Rh(NH_3)_5I^{2+} + H_3O^+ \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)I^{2+} + NH_4^+$$

$$Rh(NH_3)_5(CN)^{2+} + H_3O^+ \xrightarrow{h\nu} cis\text{-}Rh(NH_3)_4(H_2O)(CN)^{2+} + NH_4^+$$

However, for cyanopentaamminerhodium(III) a direct indication of specific equatorial photolabilization has been obtained by ^{15}N-labeling.[6] The ammonia photoaquation in this latter complex in which, notably, the heteroligand is the stronger field ligand, is thus occurring by a stereoretentive process. In order to establish the origin of the photolabilized ammonia in a pentaamminerhodium(III) complex containing a ligand of weaker field than ammonia, chloropentaamminerhodium(III) has been ^{15}N-labeled. The labeling procedures are reported here together with a photochemical investigation of the two substrates *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$.

Experimental Section

Materials. $[Rh(NH_3)_5Cl]Cl_2$ was prepared according to a published procedure,[7] 99% ^{15}N-enriched NH_4Cl was supplied by Amersham Int., and other reagents were of analytical grade.

Spectra. Electronic absorption spectra were recorded on a Cary Varian 219 spectrophotometer.

Isotopic Analysis. The ^{15}N isotopic abundance in the labeled compounds and in the photochemically liberated NH_3 was determined by optical emission analysis at the Physics Laboratory of the Royal Veterinary and Agricultural University. A detailed description of the analytical procedure may be found in ref 8.

Photolysis Experiments. Weighed amounts of the labeled compounds were dissolved in 50-mL aliquots of the appropriate acidic aqueous media. The resulting solutions were transferred to quartz tubes and irradiated with 350-nm light in a Rayonet RMR-500 photochemical reactor. The light intensity was approximately 3×10^{12} quanta mL^{-1} s^{-1}. The photolysis solutions were stirred magnetically and temperature was kept

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Table I. Fraction of Equatorial NH_3 Released during Ammonia Photoaquation[a] of $Rh(NH_3)_5Cl^{2+}$ in 0.010 M $HClO_4$

^{15}N enrichment of $Rh(NH_3)_5Cl^{2+}$							
av %	net % cis	net % trans	*T*, °C	mmol of $Rh(NH_3)_5Cl^{2+}$ [b]	mmol of NH_3 [c]	$Z(^{15}NH_3)$,[d] %	$\alpha_{eq}^{NH_3}$ [e]
9.81	(0.36)[f]	47.6	13	0.20	0.015	25.0	0.48
9.73	12.1	(0.36)[f]	13	0.20	0.020	6.1	0.49
10.8	(0.36)[f]	52.6	37	0.17	0.018	27.0	0.49

[a] λ_{irr} = 350 nm, irradiated for ~8 h. [b] Amount of $Rh(NH_3)_5Cl^{2+}$ photolyzed. [c] Amount of released NH_3 separated from photolysis solution. [d] ^{15}N percentage in separated NH_3. [e] Equatorial NH_3 photoaquated as a fraction of total NH_3 photoaquated. [f] Corresponding to natural $^{15}N/^{14}N$ ratio.

Table II. Isotopic Distribution in NH_3 Photoaquated[a] from *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ in 0.5 M NaCl at 13 °C

^{15}N enrichment of $Rh(NH_3)_5Cl^{2+}$			expected $Z(^{15}NH_3)$,[b] %			
av %	net % cis	net % trans	nonscrambling[d]	scrambling[e]	t_{irr},[c] h	$Z(^{15}NH_3)$[b] found, %
9.81	(0.36)[f]	47.6	24.5	11.4	4 1/2	11.6
9.81	(0.36)[f]	47.6	24.5	11.4	7	11.5
11.4	14.2	(0.36)[f]	7.1	10.9	8	11.4

[a] λ_{irr} = 350 nm. [b] ^{15}N-percentage in NH_3 separated from photolysis solution. [c] Irradiation time. [d] Calculated with $\alpha_{eq}^{NH_3}$ = 0.49; cf. Table I. [e] Calculated from eq 4 and 5. [f] Corresponding to natural $^{15}N/^{14}N$ ratio.

constant within ca. 2 °C by circulating thermostated water through a "finger" inside the photolysis solution. The exhaustively or nearly exhaustively photolyzed solutions (monitored by UV spectroscopy) were transferred quantitatively to distillation flasks. The excess acid was neutralized with NaOH and the solution was buffered with 3 g of $Na_2B_4O_7{\cdot}10H_2O$. By means of a gentle N_2 flow through the ice-cooled, light-protected solution for 7 h, the photoproduct NH_3 was separated from the reaction solution and trapped in standardized 0.004 M H_2SO_4. The amount of NH_3 thus separated was determined by electrochemical back-titration of the acid. The volume of the titrated solution was subsequently reduced to give a concentration of ca. 1 mg of nitrogen/mL, and the degree of ^{15}N enrichment was then determined.

Isotopic Labeling. The cis- and trans-labeling procedures were carried out as outlined in Figure 1, starting from unlabeled $[Rh(NH_3)_5Cl]Cl_2$.

***cis*-$[Rh(NH_3)_4(^{15}NH_3)Cl]Cl_2$.** $[Rh(NH_3)_5Cl]Cl_2$ was converted to *cis*-$[Rh(NH_3)_4(OH)(H_2O)]S_2O_6$ by published procedures.[7] A 220-mg (0.60 mmol) portion of the latter compound was dissolved together with 545 mg of 99% $^{15}NH_4Cl$ in 10.00 mL of 1.108 M aqueous NH_3 (natural $^{15}N/^{14}N$ ratio corresponding to 0.36% ^{15}N) plus 10.00 mL of 1.0 M $NaClO_4$ and heated in a sealed ampule at 85 °C for 6 h. The reaction mixture was subsequently mixed with 20 mL of 1.0 M HCl and kept at 100 °C for 5 min. The desired product was precipitated by slow cooling to 0 °C as fine bright crystals. These were filtered off and washed with ice-cold water, ethanol, and, finally, ether. Typical results are as follows. Yield: 100 mg (55%). UV spectrum $[(\lambda, \epsilon)_{max}]$: 348 nm, 98 L mol^{-1} cm^{-1}; 276 nm, 105 L mol^{-1} cm^{-1}. Total ^{15}N enrichment: calcd, 9.72%; found, 9.73 ± 0.05%.

***trans*-$[Rh(NH_3)_4(^{15}NH_3)Cl]Cl_2$.** $[Rh(NH_3)_5Cl]Cl_2$ was converted to *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ by published procedures.[9] The labeling procedure was the same as for the cis counterpart, starting with a 305-mg (0.60 mmol) portion of *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$. Typical results are as follows. Yield: 110 mg (60%). UV spectrum $[(\lambda, \epsilon)_{max}]$: 348 nm, 102 L mol^{-1} cm^{-1}; 276 nm, 109 L mol^{-1} cm^{-1}. Total ^{15}N enrichment: calcd, 9.71%; found, 9.81 ± 0.05%.

Results

The ^{15}N-labeled compounds *cis*- and *trans*-$[Rh(NH_3)_4(^{15}NH_3)Cl]Cl_2$ were prepared from $[Rh(NH_3)_5Cl]Cl_2$ by the route outlined in Figure 1. Both labeled compounds had UV spectra in agreement with that published for $[Rh(NH_3)_5Cl]Cl_2$.[10] In the actual labeling step, *cis*- and *trans*-$Rh(NH_3)_4(OH)_2^+$, respectively, were heated in a ^{15}N-enriched equimolar NH_3/NH_4^+ buffer at 85 °C for 6 h. These latter conditions are known to result in the formation of hydroxopentaamminerhodium(III) in a stereoretentive reaction.[11,12] The ^{15}N analyses of the labeled compounds confirmed that only 1 mol of enriched ammonia/mol of complex had entered the coordination sphere, which also indicated that exchange between coordinated and solution ammonia was insignificant. The stereoretentive course of the reaction was confirmed by the photochemical experiments (vide infra).

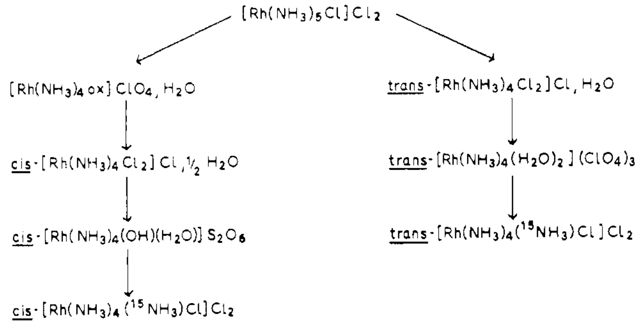
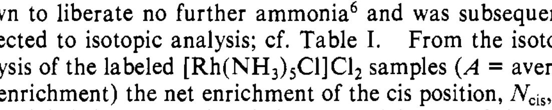


Figure 1. cis and trans ^{15}N labeling of $[Rh(NH_3)_5Cl]Cl_2$.

Ligand field excitation of chloropentaamminerhodium(III) in acidic solution results in substitution of either chloride or ammonia



$$Rh(NH_3)_5Cl^{2+} \xrightarrow{h\nu} \begin{cases} Rh(NH_3)_5(H_2O)^{3+} + Cl^- \\ Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3 \end{cases} \qquad (1)$$

and for water as the solvent, chloride aquation is the dominant reaction: $\Phi_{Cl^-} = 0.18 \pm 0.01$, $\Phi_{NH_3} = 0.02 \pm 0.01$ at 25 °C.[13] Portions of 0.20 mmol of either of the labeled compounds dissolved in 50 mL of 0.010 M $HClO_4$ were irradiated at 350 nm until the reactions of eq 1 had gone to completion. The NH_4^+ formed was separated from the reaction mixture by a procedure that was known to liberate no further ammonia[6] and was subsequently subjected to isotopic analysis; cf. Table I. From the isotopic analysis of the labeled $[Rh(NH_3)_5Cl]Cl_2$ samples (*A* = average ^{15}N enrichment) the net enrichment of the cis position, N_{cis}, for the cis-labeled compound and the net enrichment of the trans position, N_{trans}, for the trans-labeled compound, respectively, were calculated:[15]

$$N_{cis} = [(5A - 0.36)/4]\% \qquad (2)$$

$$N_{trans} = [5A - 0.36 \times 4]\% \qquad (3)$$

The equatorial ammonia as a fraction of the total ammonia photoaquated, $\alpha_{eq}^{NH_3}$, was calculated from the ^{15}N percentage found for the photoaquated ammonia, $Z(^{15}NH_3)$, together with the net enrichment percentages. The results may be found in Table I.

Chloride has been found to photoanate $Rh(NH_3)_5(H_2O)^{3+}$ in acidic aqueous chloride solution with relatively large, but strongly chloride ion concentration dependent quantum yields.[14] Thus, although ammonia photoaquation is the minor reaction path for

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(15) 0.36% is the natural ^{15}N abundance.

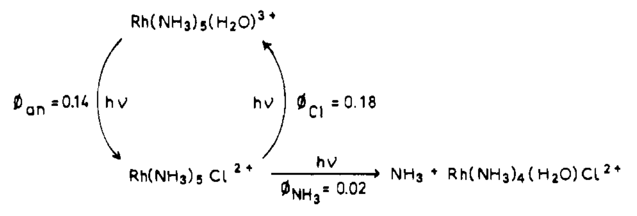

Figure 2. Photolysis of chloropentaamminerhodium(III) in 0.5 M chloride aqueous solution with quantum yields for ambient temperature conditions.[13,14]

$Rh(NH_3)_5Cl^{2+}$, the $Rh(NH_3)_5(H_2O)^{3+}$ formed in aqueous chloride solution in the principal photoreaction will subsequently photoanate, and the final photoproducts will be a cis and trans mixture of $Rh(NH_3)_4(H_2O)Cl^{2+}$; cf. Figure 2.[3-5] Portions of 0.07–0.15 mmol of either of the labeled compounds dissolved in 50 mL of 0.50 M NaCl (pH 2) were irradiated at 350 nm, and NH_4^+ was separated from the reaction mixture and analyzed as described above; cf. Table II.

Discussion

Almost equal fractions of equatorial and axial ammonia are labilized as a result of ligand field excitation of $Rh(NH_3)_5Cl^{2+}$, as can be seen from the results in Table I. The consistency between the results obtained for the two substrates *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ confirms that the labeling procedure employed is stereospecific, as was to be expected from the observation of retention of the absolute configuration in ammoniation of a series of optically active mixed-haloamine rhodium(III) complexes.[11]

Investigations using sensitization techniques and wavelength dependence of quantum yields have led to the conclusion that the photochemically reactive state for low-spin rhodium(III) amine complexes is the lowest energy triplet.[1,2] When pure O_h symmetry is lowered to the C_{4v} symmetry of the pentaammine complexes, the reactive ^3T state splits into ^3E and ^3A levels. In $Rh(NH_3)_5(CN)^{2+}$, in which the cyanide is the stronger field ligand, the ^3A triplet has the lower energy, corresponding to the one-electron 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 excitation is consequently concentrated in the equatorial plane. The ammonia photoaquated in $Rh(NH_3)_5(CN)^{2+}$ has, as should be anticipated on the basis of these arguments, been found to originate from the equatorial positions (>95%).[6]

In $Rh(NH_3)_5Cl^{2+}$ the heteroligand is the weaker field ligand, and the lowest energy triplet is ^3E with the σ-antibonding orbital along the z axis. Consequently, axial photolabilization is expected, and indeed the major photoreaction in aqueous solution is chloride aquation.[13] The photoaquated ammonia originates equally from the axial and the equatorial positions, and with the introduction of a simple statistical correction it appears that the axial ammonia is labilized four times as efficiently as the equatorial ammonia ligands. However, the occurrence of significant equatorial labilization suggests that the ^3A triplet component also plays a role in the photochemistry for $Rh(NH_3)_5Cl^{2+}$.

In the 1,4,8,11-tetraazacyclotetradecane complex *trans*-$Rh(cyclam)(CN)_2^+$ (D_{4h} symmetry), the ^3A level is of lower energy than the ^3E level, as in $Rh(NH_3)_5(CN)^{2+}$, but for the former macrocyclic complex the amine photoaquation is efficiently blocked by chelation.[16] Radiative deactivation and reaction are competitive pathways for the triplet states, and in agreement herewith, *trans*-$Rh(cyclam)(CN)_2^+$ showed surprisingly long-lived phosphorescence under ambient conditions. Furthermore, the phosphorescence lifetimes at room temperature showed a temperature dependence corresponding to an activation energy of 38 kJ mol^{-1}, and it was suggested[16] that a thermally activated internal conversion $^3A \rightarrow {}^3E$ was, at least in part, responsible for the observed temperature dependence, with ^3E as the emitting state. This interpretation, entailing partial equilibration between the two states, corresponds to a situation intermediate between the following extremes: (1) The two triplets are populated by intersystem crossing from the higher energy singlet states in the same ratio in which they subsequently are deactivated. (2) The two triplets are fully thermally equilibrated prior to deactivation. $Rh(NH_3)_5Cl^{2+}$, in which the ^3A level has the higher energy as depicted in Figure 3, shows the same equatorial/axial ammonia aquation ratio at 13 and 37 °C (cf. Table I), suggesting that there is no thermal equilibration between the ^3E and ^3A states. As judged from these observations, the internal conversion is slow compared to deactivation at ambient conditions for $Rh(NH_3)_5Cl^{2+}$, in contrast to what is the case for *trans*-$Rh(cyclam)(CN)_2^+$, in agreement with the dramatic difference in the phosphorescence lifetimes noted for the two complexes: τ = 14 ns for $Rh(NH_3)_5Cl^{2+}$ at 25 °C,[13] and τ = 8.0 μs for *trans*-$Rh(cyclam)(CN)_2^+$ at 22 °C.[16]

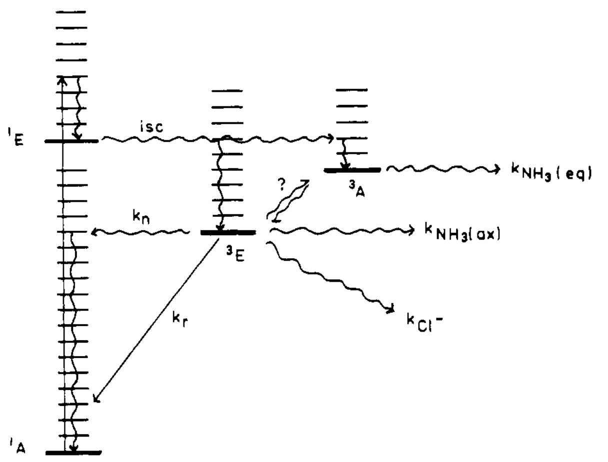

Figure 3. Simplified energy-level diagram for $Rh(NH_3)_5Cl^{2+}$: efficient intersystem crossing (isc) from initially populated excited singlet states (only the lowest energy excited singlet is shown for clarity) to reactive triplet states. k_n and k_r are rate constants for nonradiative and radiative deactivation, respectively. k_{NH_3} and k_{Cl^-} are rate constants for photosubstitution reactions.

Photoaquation of chloride in *cis*- and *trans*-dichlorotetraamminerhodium(III) and photochemical water exchange in *cis*- and *trans*-aquachlorotetraamminerhodium(III) lead to both cis and trans photoproducts in a ratio that is independent of the reactant stereochemistry and independent of whether the leaving ligand is chloride or water.[4,5] The observation of a product distribution independent of the leaving ligand provides evidence for a photoisomerization mechanism for rhodium(III) amine complexes in which the initial step is excited-state ligand dissociation. Furthermore, the observation of a product distribution independent of reactant stereochemistry indicates that the rearrangement between the pentacoordinate excited-state intermediates, *basal*- and *apical*-$Rh(NH_3)_4Cl^{2+*}$, generated from the cis and trans substrates, respectively, is fast compared to deactivation to the ground state.[3-5] The kinetic barrier between basal and apical excited-state intermediates depends on the nature of the ligands, and it has been suggested that this barrier increases with increasing average field of the five ligands to a point where deactivation to the ground state at ambient temperature is much faster than rearrangement.[17-19] $Rh(NH_3)_5^{3+*}$, which according to the dissociative model is an excited-state intermediate during the photochemical chloride aquation in chloropentaamminerhodium(III), has a high ligand field, and $Rh(NH_3)_5^{3+*}$ is, on the basis of these arguments, expected to behave like *cis*- and *trans*-$Rh(en)_2(NH_3)^{3+*}$,[20] for which little or no rearrangement was detected at 25 °C.[17,18]

If *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)^{3+*}$ are energetically separated by a barrier efficiently preventing rearrangement to each

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(20) en = ethylenediamine.

other, the ammonia photoaquated from *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ in aqueous chloride solution is expected to have the same ^{15}N enrichment as that photoaquated in a perchlorate medium. If, on the other hand, a complete scrambling of the five ammonia ligands in *cis*- and *trans*-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$ is occurring during the chloride photoaquation/photoanation cycle depicted in Figure 3, then the ^{15}N enrichment of the photoaquated ammonia $Z(^{15}NH_3)$ can be calculated from the following equations for the respective isomers:

cis-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$

$$Z(^{15}NH_3) = \frac{\Phi_{NH_3}}{\Phi_{Cl^-} + \Phi_{NH_3}}(\alpha_{eq}{}^{NH_3}N_{cis} + (1 - \alpha_{eq}{}^{NH_3}) \times 0.36) + \frac{\Phi_{Cl^-}}{\Phi_{Cl^-} + \Phi_{NH_3}}A \quad (4)$$

trans-$Rh(NH_3)_4(^{15}NH_3)Cl^{2+}$

$$Z(^{15}NH_3) = \frac{\Phi_{NH_3}}{\Phi_{Cl^-} + \Phi_{NH_3}}(\alpha_{eq}{}^{NH_3} \times 0.36 + (1 - \alpha_{eq}{}^{NH_3})N_{trans}) + \frac{\Phi_{Cl^-}}{\Phi_{Cl^-} + \Phi_{NH_3}}A \quad (5)$$

The values for $Z(^{15}NH_3)$ calculated for each experiment (the almost temperature-independent ratio $\Phi_{NH_3}/\Phi_{Cl^-} = 0.11$, taken from ref 13; and $\alpha_{eq}{}^{NH_3} = 0.49$, taken from Table I) are compared in Table II with the experimental values. The conclusion from these experiments is clear, viz. that during the photoaquation/photoanation cycle, the five ammonia ligands in $Rh(NH_3)_5Cl^{2+}$ are scrambled. Triplet $Rh(NH_3)_5{}^{3+}$ is, according to the dissociative model, an intermediate in both the photoaquation[13] and in the photoanation step,[14] and a complete scrambling or at least an almost complete scrambling is thus taking place during each step. This result suggests the generality of thermal equilibrium, at ambient temperature, between the pentacoordinated excited-state isomers of rhodium(III) amine complexes, independent of the strength of the five ligands.

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Registry No. $Rh(NH_3)_5Cl^{2+}$, 15379-09-6; Cl, 16887-00-6; NH_3, 7664-41-7.

Contribution from the Division of Earth and Physical Sciences,
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Spectrophotometric Investigations of the Octahedral-Tetrahedral Equilibria in Cobalt(II)-Thiocyanate Systems in Aqueous Methanol

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Received October 26, 1984

Spectrophotometric investigations of the complex formation equilibrium constants at constant ionic strength were carried out for Co(II)-SCN^- systems between 15 and 37 °C in aqueous methanol at water mole fractions between 0.03 and 1.00. At 25 °C, the logarithms of the stability constants in water are $\beta_1 = 1.077 \pm 0.022$, $\beta_2 = 1.735 \pm 0.028$, $\beta_3 = 1.988 \pm 0.051$, and $\beta_4 = -0.0794 \pm 0.0116$. As methanol is added to these systems, the equilibrium constants increase. In methanol (water mole fraction 0.03), the logarithms of the stability constants are $\beta_1 = 2.504 \pm 0.0095$, $\beta_2 = 5.720 \pm 0.017$, $\beta_3 = 7.021 \pm 0.134$, and $\beta_4 = 7.797 \pm 0.050$. At each solvent composition the enthalpy and entropy of complexation were determined for each successive complexation step. The first three complexes exist in the octahedral form, and the tetrakis complex exists in the tetrahedral form.

Introduction

Geometry changes involving a metal ion center can be important in simple inorganic systems as well as the more complex biochemical enzyme systems. We have been characterizing geometry changes in lanthanide salt systems as a function of solvent composition in aqueous methanol,[1] aqueous dimethyl sulfoxide (Me_2SO)[1] and aqueous *N,N*-dimethylformamide (DMF)[2] using the ultrasonic relaxation technique. Recently, we have demonstrated that significant chemical differences can be detected in aqueous methanol with ultrasonics between the high coordination number lanthanide(III) ions, which undergo coordination number changes in solution, and the chemically similar octahedral d-block transition-metal ion, scandium(III), which does not.[3] In aqueous Me_2SO, differences in behavior have been detected with the same cation, zinc(II), and two different ligands, chloride and nitrate.[4] An octahedral to tetrahedral change occurs at high water mole fractions at the zinc center as the third chloride adds to the bis complex, and this change is absent under similar concentrations in the zinc nitrate system, where only the one to one complex is detected by using ultrasonics.[4] No evidence for this structural change is apparent from the potentiometric investigations at constant ionic strength of the complex formation equilibrium constants in aqueous Me_2SO and aqueous DMF, where no abnormalities in behavior are detected in the region where the coordination number and geometry changes occur.[5,6] These observations led to this current investigation of the cobalt(II)-thiocyanate system where a kinetic study postulates the existence of an octahedral-tetrahedral geometry change, but where no equilibrium data exist as a function of solvent composition to determine if the effect can be detected by equilibrium measurements.

Swift utilized the temperature-jump relaxation technique in the study of the kinetics of the complexation reactions between Co(II) and Zn(II) with NO_3^- and SCN^- in water.[7] In the cobalt(II) nitrate system, Swift found that there was a relatively

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