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Reaction of Nitrosylpentaammineruthenium(II) with Ethylamine, Methylamine, and Hexaammineruthenium(III) Ion to Produce Dinitrogen Complexes

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Recent investigations on the nitrosyl ligand, NO^+, coordinated to ruthenium(II) have revealed a variety of interesting reactions.[1-5] In each of the reactions the proposed mechanism was nucleophilic attack at the coordinated nitrosyl by species such as hydroxide ion, hydrazine, hydroxylamine, and substituted anilines, with retention of the ruthenium–nitrogen bond. These reactions are analogous to the previously investigated reactions of the nitroprusside ion, $Fe(CN)_5NO^{2-}$, with nucleophiles such as OH^- and RS^-.[6]

Meyer[5] has reported that $Ru(2,2'\text{-bpy})_2Cl(NO)^{2+}$ reacts with substituted anilines to form ruthenium(II) complexes containing diazonium ion ligands. This paper reports on the reaction of nitrosylpentaammineruthenium(II) ion, $Ru(NH_3)_5NO^{3+}$, with aliphatic amines (methyl and ethyl) in aqueous solution and with hexaammineruthenium(III) ion, $Ru(NH_3)_6^{3+}$, in aqueous 1 M base.

Experimental Section

Chemicals and Equipment. Ruthenium trichloride hydrate (Alfa-Ventron), aqueous methylamine (J. T. Baker, 40%), aqueous ethylamine (Matheson Coleman and Bell, 70%), and argon gas (Matheson, prepurified) were used as received. Nitrosylpentaammineruthenium(II) trichloride monohydrate was prepared by the method of Gleu and Buddecker[7] and its purity established by comparison of its UV–visible spectrum with that in the literature.[8] Hexaammineruthenium(III) tribromide was prepared as described by Fergusson and Love.[9] Dinitrogenpentaammineruthenium(II) dibromide was prepared the method of Allen and Senoff.[10] Aquopentaammineruthenium(II) was generated by treating $[Ru(NH_3)_5Cl]Cl_2$, prepared by literature methods,[11] with Zn/Hg in aqueous CF_3COOH. Dowex 50W-X4 resin was pretreated by the method of Taube and Deutsch[12] to remove UV-absorbing impurities. Infrared spectra were obtained on a Perkin-Elmer 257 spectrophotometer and UV–visible spectra on Cary Model 14 and 15 spectrophotometers. A Corning Model 10C pH meter and a Varian Model T-60 NMR spectrometer were also used.

Product Studies. Weighed amounts of solid $[Ru(NH_3)_5NO]Cl_3$ (~0.3 mmol) were added to 100 mL of aqueous methylamine (~2 M), ethylamine (~1.1 M), or methylamine hydrochloride (~1.75 M) and allowed to stand until no further color change occurred (4–15 h). Addition of excess KBr, KI, or $NaBF_4$ (~10 g) produced pale yellow precipitates which were collected by filtration, washed successively with 95% ethanol and ether, and air-dried. Yields (after recrystallization) of about 60% were obtained (based on $[Ru(NH_3)_5N_2]X_2$ products). In some cases, the amine solutions were adjusted to pH 11 by addition of 12 M HCl prior to the reaction. The course of the reaction appeared to be identical under nitrogen, argon, or air.

Reaction between $[Ru(NH_3)_5NO]Cl_3$ (~10^{-5} mol) and $Ru(NH_3)_6Br_3$ (~10^{-4} mol) was carried out by dissolving the two complexes in 1 mL of H_2O, degassing the solution with argon, and adding an equal volume of 2 M NaOH. The reaction was monitored by removing 50-μL aliquots, diluting, and running the UV spectrum. After 40 min, the addition of saturated $NaBF_4$ precipitated the product, which was treated as described above.

Results and Discussion

Product of Reaction between $Ru(NH_3)_5NO^{3+}$ and RNH_2 (R = CH_3 or C_2H_5). The infrared spectra of the solid products formed in the reaction of methyl- and ethylamines with $Ru(NH_3)_5NO^{3+}$ in basic (pH ≥ 10) solution showed a strong peak, assignable to a N≡N stretch, at 2110 cm^{-1}, while the strong infrared stretch of the coordinated NO^+ at 1904 cm^{-1} disappeared. The electronic spectra of the reaction products in aqueous solution showed a single strong absorption (λ_{max} 221 nm, ϵ ~17 200 $M^{-1}\ cm^{-1}$ based on $[Ru(NH_3)_5N_2]X_2$) in contrast to the starting material which exhibited weak absorptions (λ_{max} 460 nm, ϵ 16.4 $M^{-1}\ cm^{-1}$ and λ_{max} 300 nm, ϵ 67.2 $M^{-1}\ cm^{-1}$). This spectral evidence is indicative of a reaction at the coordinated NO ligand. When methylamine hydrochloride (pH ~5) was used as a reactant, the product isolated showed IR and UV peaks only attributable to a $Ru(NH_3)_5NO^{2+}$ species, thus suggesting that the deprotonated amine, RNH_2, is one of the reactive species. Changing the environment from air to N_2 or argon had no effect on the reaction or reaction products.

The absence of a nitrosyl peak at ~1850 cm^{-1} serves to eliminate the possibility of the reaction

$$2Ru(NH_3)_5NO^{3+} + 2OH^- \rightarrow Ru(NH_3)_5N_2^{2+} + Ru(NH_3)_4(OH)NO^{2+} + 2H_2O \qquad (1)$$

which has been reported by Bottomley.[3] Further verification that reaction 1 did not occur came from an experiment in which $Ru(NH_3)_5NO^{3+}$ was treated with aqueous OH^- under conditions used in the amine reactions. The electronic and infrared spectra of the solid isolated after 24 h showed absorptions characteristic only of the $Ru(NH_3)_5NO^{3+}$ ion. Finally, a spectrophotometric study of yield (at 221 nm based on ϵ ~17 200 $M^{-1}\ cm^{-1}$ for $Ru(NH_3)_5N_2^{2+}$) in the amine reaction indicated a >90% conversion to product, while reaction 1 predicts a 50% maximum yield.

The preceding results indicated that a reaction between the amine and $Ru(NH_3)_5NO^{3+}$ ion had occurred, but positive identification of the product could not be made from this data. Two possibilities were considered: First, on the basis of the observations of Meyer,[5] was a diazonium complex $Ru(NH_3)_5N_2R^{3+}$; second, on the basis of the observations of Bottomley,[1-3] was the $Ru(NH_3)_5N_2^{2+}$ complex. Product identity was established by comparing chromatographic behavior, NMR spectral properties, and reactivity toward $Ru(NH_3)_5H_2O^{2+}$ with that of authentic $Ru(NH_3)_5N_2^{2+}$.

The chromatographic properties of the reaction products and of independently prepared $Ru(NH_3)_5N_2^{2+}$ were studied on a Dowex 50W-X4 cation-exchange resin, eluting with 1.2 M NaCl.[13] The compounds exhibited identical elution properties, indicating that they both have the same charge and are probably both $Ru(NH_3)_5N_2^{2+}$. The NMR spectra of the BF_4^- salts of the reaction products exhibited resonances at 2.66 and 3.42 ppm (from Me_4Si) with integrated intensities of 4:1, respectively. These resonances, in agreement with the literature values for $Ru(NH_3)_5N_2^{2+}$,[14a] are attributable to protons on the four cis ammonias and single trans ammonia in the dinitrogen complex. No evidence for a third resonance, attributable to the protons on an alkyl group, was found. Finally, when the reaction products were treated with $Ru(NH_3)_5H_2O^{2+}$, the product obtained exhibited electronic (λ_{max} 262 nm, ϵ 48 000 $M^{-1}\ cm^{-1}$) and infrared spectral properties ($\nu_{N\equiv N}$ 2060 cm^{-1}, weak, indicative of a symmetrically bound binuclear ion) of $[Ru(NH_3)_5]_2N_2^{4+}$, a binuclear pentaammineruthenium(II) complex with a bridging dinitrogen ligand.[14]

This evidence proves unequivocally that the reaction of $Ru(NH_3)_5NO^{3+}$ with methyl- and ethylamine yields $Ru^{II}(NH_3)_5N_2^{2+}$ under conditions used in this study. The formation of the dinitrogen complex under an argon atmosphere further establishes that the N_2 ligand is derived from the solution reactants rather than from atmospheric nitrogen. The probable net reaction is, therefore

$$Ru(NH_3)_5NO^{3+} + 2RNH_2 \rightarrow Ru^{II}(NH_3)_5N_2^{2+} + ROH + RNH_3^+ \qquad (2)$$

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Product of Reaction between $Ru(NH_3)_5NO^{3+}$ and $Ru(NH_3)_6^{3+}$. When $Ru(NH_3)_5NO^{3+}$ was reacted with $Ru(NH_3)_6^{3+}$, a peak at 262 nm was observed growing as a function of time. The infrared and electronic spectra of the isolated solid product exhibited properties characteristic of $[Ru(NH_3)_5]_2N_2^{4+}$.[14] Quantitative studies on the reaction solution, on the basis of an ϵ of 48 000 M^{-1} cm^{-1} at 262 nm for $[Ru(NH_3)_5]_2N_2^{4+}$, showed >95% conversion of $Ru(NH_3)_5NO^{3+}$ to product. Previous workers have shown[15,16] that, in 1 M base, $Ru(NH_3)_6^{3+}$ acts as a nucleophile for carbonyl groups, with the amidopentaammineruthenium(III) complex being the reactive species.

The overall reaction may be written as

$$Ru(NH_3)_6^{3+} + Ru(NH_3)_5NO^{3+} + OH^- + X^- \rightarrow [Ru(NH_3)_5]_2N_2^{4+} + 2H_2O + X \tag{3}$$

where X^- represents an unidentified reducing agent and X its oxidation product. Aqueous alkaline solutions have been implicated as the reducing agent in the reaction of $Ru(NH_3)_6^{3+}$ with diones[15] and in the reduction of $Ru(1,10\text{-phen})_3^{3+}$ to $Ru(1,10\text{-phen})_3^{2+}$,[17] suggesting that the solvent may play a role in reaction 3.

Although our observations do not provide the basis for a detailed mechanism, some general statements, on the basis of the observations of Meyer,[5] the chemistry of the nitroprusside ion,[6] and the known rapid hydrolysis of aliphatic diazonium ions, can be made: (1) The reaction involves the interaction of the electrophilic NO^+ ligand and the nucleophilic NH_2 group of the free amine. (2) Water is eliminated to form a coordinated diazonium ligand. (3) The coordinated diazonium ligand decomposes to yield the observed ruthenium product. The proposed reaction scheme is analogous to the diazotization of primary amines with nitrous acid. It is also consistent with the mechanism proposed by Meyer for the diazotization of $Ru(2,2'\text{-bpy})_2ClNO^+$ by substituted anilines.[5b] With the addition of a step involving the external reductant, the mechanism for the reaction of $Ru(NH_3)_5NO^{3+}$ with $Ru(NH_3)_6^{3+}$ probably exhibits the same general features as those described above.

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Registry No. $[Ru(NH_3)_5NO]^{3+}$, 37874-79-6; $Ru(NH_3)_6^{3+}$, 18943-33-4; CH_3NH_2, 74-89-5; $C_2H_5NH_2$, 75-04-7; $Ru(NH_3)_5N_2^{2+}$, 19504-40-6; $[Ru(NH_3)_5]_2N_2^{4+}$, 25754-89-6.

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