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The Reaction of Aquopentaammineruthenium(II) Cation with Hydrazoic Acid

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The reaction of hydrazoic acid with $[Ru^{II}(NH_3)_5H_2O]^{2+}$ yields ammonia, nitrogen gas, and ruthenium(III) complexes. The ammonia formed is found coordinated to the oxidized ruthenium, since $[Ru(NH_3)_6]^{3+}$ is a reaction product. This species is isolated and characterized as the perchlorate salt of its sulfate ion pair, $[Ru(NH_3)_6](SO_4)ClO_4$. A possible mechanism for the decomposition reaction is discussed.

Introduction

Interest in the interaction of the azide ion with transition metal complexes has led to a variety of azide ion decomposition reactions. The one electron reduction of transition metals (Ce(IV),[1] Co(III),[2] Mn(III),[3] Ru(III)[4]) by azide ion, to yield 1.5 mol of N_2/mol of azide ion, is well documented. The decomposition of Ru(III) coordinated azides has been proposed to proceed *via* a coordinated nitrene intermediate.[4]

A nitrene intermediate is also proposed[5] for the acid decomposition of the azide ligand in $[Ir(NH_3)_5N_3]^{2+}$. Reduction of the Ir(III) ion does not occur, but evidence for an electrophilic nitrene intermediate has been observed.

Different behavior has been reported for the reaction of azide ion with one-electron reducing agents (Cr(II),[6,7] V(II),[7] Co(II),[8] Ni(I)).[8] Both chromous and vanadous ion reduce the azide ion to N_2 and NH_3, and one of the products of the chromous reaction is $[Cr(NH_3)(H_2O)_5]^{3+}$.

Our general interest in the field of azide ion decomposition reactions led us to investigate the reaction of $[Ru(NH_3)_5H_2O]^{2+}$, another strong reducing agent, with the azide ion. We wish to report on the decomposition of the azide group to NH_3 and N_2, and of the identification of $[Ru(NH_3)_6]^{3+}$ as a reaction product.

Experimental Section

Preparation of Aquopentaammineruthenium(II) Cation.—A solution of $[Ru^{II}(NH_3)_5H_2O]^{2+}$ was prepared by zinc amalgam reduction of $[Ru^{III}(NH_3)_5Cl]Cl_2$. The chloride ligand was labilized when the ruthenium was reduced to the divalent state, so the resulting solution was predominantly the water substituted product, $[Ru^{II}(NH_3)_5H_2O]^{2+}$.[9] The following operations were done in deareated solutions under an argon blanket.

Freshly prepared zinc amalgam (1–2 g) was dropped into an aqueous solution of $[Ru(NH_3)_5Cl]Cl_2$ (0.29 g, 1.0 mmol in 15–20 ml H_2O). Three drops of concentrated H_2SO_4 were added to the solution, and the bubbling solution was allowed to stand at room temperature for 45–60 min. The product was used immediately.

Reaction of Hydrazoic Acid with Aquopentaammineruthenium(III) Cation.—Standard Schlenk tube and syringe techniques were used to ensure exclusion of air. The $[Ru(NH_3)_5H_2O]^{2+}$ solution was filtered from the zinc amalgam into a previously deareated aqueous solution of sodium azide (0.49 g, 0.75 mmol). Immediate effervescence was observed. The addition of 3–4 drops of 4 *M* H_2SO_4 was often necessary to keep the reaction mixture acidic—an orange solution and a fluffy $Zn(OH)_2$ precipitate signaled when such acid was needed.

Separation of Hexaammineruthenium(III) Sulfate Perchlorate.—The reaction mixture was allowed to react at room temperature for 4 hr before it was filtered into an aqueous solution of $LiClO_4$ (0.5 g in 10 ml H_2O). The white precipitate which formed was collected by filtration (in the atmosphere), washed with cold water, ethanol, and acetone, and air dried; yield 0.16 g (40% based on total Ru). *Anal.* Calcd for $[Ru(NH_3)_6](SO_4)ClO_4$: N, 21.08; H, 4.55; SO_4^{2-}, 24.09. Found: N, 20.67; H, 4.65; SO_4^{2-}, 24.16.

Ion-Exchange Chromatography.—Whatman CM-32 cation-exchange resin was prepared as prescribed by the manufacturer in the lithium form and packed into a 12-in. column. The reaction mixture was concentrated to a volume of 5 ml and was loaded onto the column. Using dilute $LiClO_4$ (0.01 *M*) as eluent, and controlling the flow rate to 1 ml/min, the sample required about 3 hr to descend the column. Small fractions (3 ml) were collected and their electronic spectra recorded.

Gas Evolution Measurements.—The quantitative gas evolution measurements were performed with standard vacuum line techniques, as reported elsewhere.[4]

Ultraviolet and Infrared Spectra.—The ultraviolet spectra were recorded on a Hitachi Perkin Elmer 124 double beam spectrophotometer, using 1-cm quartz cells. Infrared spectra in the region 4000–400 cm^{-1} were recorded on a Perkin Elmer 457 spectrophotometer calibrated against polystyrene. Spectra were taken as Nujol mulls between KBr plates.

Elemental Analyses.—Nitrogen, hydrogen, and sulfate analyses were performed by Mr. G. M. J. Powell of the University of Kent at Canterbury (England).

Results

Reaction of Hydrazoic Acid with Aquopentaammineruthenium(III) Cation.—The addition of sodium azide to an acidic solution of $[Ru^{II}(NH_3)_5H_2O]^{2+}$ causes the immediate evolution of gas and a rapid color change from orange to pale yellow. The electronic spectrum (Figure 1) of the resulting acidic solution is complex and does not correspond to the spectrum of any single ruthenium(II)- or ruthenium(III)-ammine species. The intense bands in the ultraviolet region, characteristic of monomeric (220 nm) or dimeric (260 nm) Ru(II)-dinitrogen species,[4] are not observed. The spectrum remains unchanged when the solution is exposed to the air.

Gas evolution measurements showed that when excess $[Ru(NH_3)_5H_2O]^{2+}$ is added to sodium azide, 1.0 mol of nitrogen is released per mole of azide ion initially present. (Ceric ion oxidation of sodium azide yields 1.5 mol of nitrogen per mole of azide ion.) In the reaction of $[Ru(NH_3)_5H_2O]^{2+}$ with azide ion, the

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[1] C. F. Wells and M. Husain, *J. Chem. Soc. A*, 2891 (1969).

[2] C. F. Wells and D. Mays, *ibid.*, 2175 (1969); A. Hamm and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *ibid.*, **7**, 1876 (1968); R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *ibid.*, **9**, 1590 (1970).

[3] M. A. Suwyn and R. E. Hamm, *ibid.*, **6**, 2150 (1967); G. Davies, L. I. Kirschenbaum, and K. Kustin, *ibid.*, **8**, 663 (1969).

[4] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

[5] B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *ibid.*, **94**, 3786 (1972).

[6] M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

[7] R. G. Linck, *Inorg. Chem.*, **11**, 61 (1972).

[8] W. C. Kaska, C. Sutton, and E. Serros, *Chem. Commun.*, 100 (1970).

[9] P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

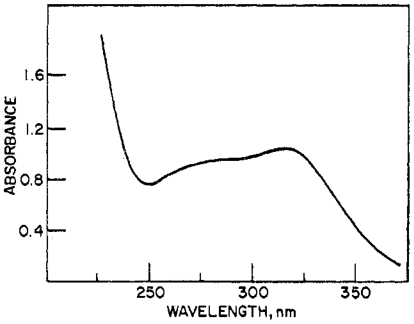

Figure 1.—Spectrum of solution after reaction of $[Ru(NH_3)_5H_2O]^{2+}$ and sodium azide (pH 1).

unaccounted for nitrogen atom does not enter the solution as free ammonia, hydrazine, or hydroxylamine, for sensitive qualitative tests found no evidence of these species.[10]

The reaction solution contains the products $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_6]^{3+}$. The two complexes were partially separated by ion-exchange chromatography, but were more simply separated by fractional crystallization. Addition of lithium perchlorate solution to the reaction mixture (which had been made acidic with sulfuric acid) precipitated the hexaammineruthenium(III) cation as $[Ru(NH_3)_6](SO_4)ClO_4$. The product remaining in solution was primarily $[Ru(NH_3)_5H_2O]^{3+}$, identified by its electronic spectrum (Figure 2). Neutralization of this solution led to the immediate, reversible, formation of $[Ru(NH_3)_5OH]^{2+}$ with its characteristic, intense ultraviolet spectrum.[11] Attempts to isolate $[Ru(NH_3)_5H_2O](ClO_4)_3$ yielded a white solid contaminated with $[Ru(NH_3)_5Cl]^{2+}$ cation.

The amount of $[Ru(NH_3)_5H_2O]^{3+}$ generated in this reaction was measured by neutralizing the reaction solution, and measuring the absorption at 295 nm, characteristic of $[Ru(NH_3)_5OH]^{2+}$ (λ_{max} 295 nm, ϵ 2100 M^{-1} cm^{-1}).[11] The absorption of $[Ru(NH_3)_6]^{3+}$ at 295 nm is small compared to the intense absorption of $[Ru(NH_3)_5OH]^{2+}$ so that by the careful reaction of measured amounts of $[Ru^{II}(NH_3)_5H_2O]^{2+}$ and sodium azide the stoichiometry of the reaction could be studied.

The maximum yield of $[Ru(NH_3)_5OH]^{2+}$ attained from this reaction is 50% of the initial concentration of $[Ru^{II}(NH_3)_5H_2O]^{2+}$; atmospheric oxygen generates twice as much $[Ru^{III}(NH_3)_5OH]^{2+}$ from $[Ru^{II}(NH_3)_5H_2O]^{2+}$ as azide ion does.

The $[Ru^{II}(NH_3)_5H_2O]^{2+}:N_3^-$ ratio in the stoichiometry of this section could also be monitored by measuring the amount of $[Ru^{III}(NH_3)_5OH]^{2+}$ produced. The yield of $[Ru^{III}(NH_3)_5OH]^{2+}$ increased as the azide ion concentration increased, until the azide ion concentration was 0.5 of the initial $[Ru^{II}(NH_3)_5H_2O]^{2+}$ concentration (Figure 3). Neither the introduction of atmospheric oxygen nor the addition of excess azide ion increased the yield of $[Ru^{III}(NH_3)_5OH]^{2+}$ after the N_3^-:Ru(II) ratio had passed 1:2. When the azide ion concentration was less than that prescribed by the 1:2 ratio, the presence of unoxidized Ru(II) was noted.

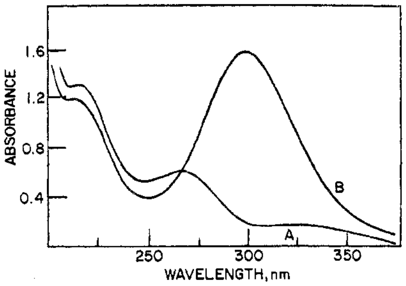

Figure 2.—Spectrum of reaction solution after separation of $[Ru(NH_3)_6](SO_4)ClO_4$. Curve A is due to $[Ru(NH_3)_5H_2O]^{3+}$ (pH 1); addition of NaOH gives curve B, due to $[Ru(NH_3)_5OH]^{2+}$ (pH 6).

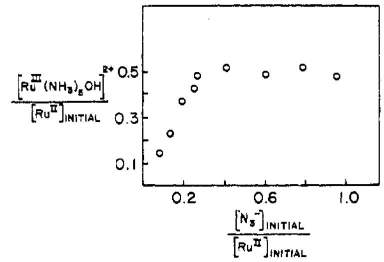

Figure 3.—Analysis of stoichiometry of reaction between $[Ru(NH_3)_5H_2O]^{2+}$ and azide ion. This graph measures the amount of $[Ru^{III}(NH_3)_5OH]^{2+}$ generated in the reaction as a function of the initial azide ion concentration and shows that only half of the ruthenium atoms form $[Ru^{III}(NH_3)_5OH]^{2+}$ in the reaction. The concentration of $[Ru^{III}(NH_3)_5OH]^{2+}$ was measured by its intense absorbance at 295 nm.

This was indicated by the immediate growth of the $[Ru^{III}(NH_3)_5OH]^{2+}$ ultraviolet spectrum upon introduction of air.

The overall stoichiometry of the reaction can then be written

$$2[Ru^{II}(NH_3)_5H_2O]^{2+} + 3H^+ + N_3^- \longrightarrow [Ru(NH_3)_5H_2O]^{3+} + [Ru(NH_3)_6]^{3+} + N_2 + H_2O \quad (1)$$

Isolation and Identification of Hexaammineruthenium(III) Sulfate Perchlorate.—Attempts to use ion-exchange chromatography to separate reaction products were only partially successful. The yellow-brown sample band spread to a width of 4–5 cm after descending the column, and the initial fractions gave electronic spectra corresponding to pure $[Ru(NH_3)_6]^{3+}$ (λ_{max} 275 nm).[12] The intense absorption at 295 nm due to $[Ru(NH_3)_5OH]^{2+}$ contaminated all but the first few fractions, however, until at the tail of the sample band, pure $[Ru(NH_3)_5OH]^{2+}$ was eluted from the column.

A clean separation could be effected by fractional crystallization. In the presence of sulfate ion, the addition of perchlorate ion precipitated the hexaammineruthenium(III) sulfate ion pair as the perchlorate salt, $[Ru(NH_3)_6](SO_4)ClO_4$. Isolation of such an ion paired species is an unusual phenomenon, and its identification is based upon the following data.

Elemental analyses fit the proposed formulation (Experimental Section). The complex is paramagnetic, with $\mu_{eff} = 1.96$, a typical value for a low-spin Ru(III)–ammine complex.[13] The electronic spectrum (λ_{max}

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[10] F. Fiegl, "Spot Tests in Inorganic Analysis," 5th ed, translated by Ralph E. Oesper, Elsevier, New York, N. Y., 1958, pp 235–247.

[11] T. Eliades, R. O. Harris, and P. Reinsalu, *Can. J. Chem.*, **47**, 3823 (1969).

[12] J. N. Armor and H. Taube, *Inorg. Chem.*, **10**, 1570 (1971).

[13] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

TABLE I

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR THE INFRARED ABSORPTIONS OF THE COMPLEXES $[Ru(NH_3)_6](SO_4)ClO_4$, $[Ru(NH_3)_6]Cl_3$, K_2SO_4, AND $KClO_4$ BETWEEN 4000–400 CM^{-1} [a]

Assignment	$[Ru(NH_3)_6]SO_4ClO_4$	$[Ru(NH_3)_6]Cl_3$[b]	SO_4^{2-}[c]	ClO_4^-[c]
$\nu(NH)$	3350–3100[d]	*d*		
$\delta(NH_3)_{deg}$	1630 s, br	1612 s, br		
$\delta(NH_3)_{sym}$	1340 s	1362 m, 1338 s, 1316 vs		
$\rho(NH_3)$	850 s, br	788 s		
$\nu(RuN)$	450 w	464 w, 452 w		
$\nu_1(SO_4^{2-})$	970 vw		983 vw	
$\nu_1(ClO_4^-)$	935 vw			935 vw
$\nu_3(SO_4^{2-}, ClO_4^-)$	1080 br		1105	1050–1170
$\nu_4(ClO_4^-)$	626 s			630
$\nu_4(SO_4^{2-})$	615 sh		611	

[a] Abbreviations: s, strong; vs, very strong; br, broad; w, weak; vw, very weak; sh, shoulder. [b] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967). [c] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970. [d] Region of broad absorption.

275 nm, ϵ 485 M^{-1} cm^{-1}) is similar to the spectrum reported for $[Ru(NH_3)_6]Cl_3$ (λ_{max} 274 nm, ϵ 473 M^{-1} cm^{-1}).[12]

The infrared spectrum of $[Ru(NH_3)_6](SO_4)ClO_4$ also supports the proposed formulation (Table I). Of particular interest is the marked difference in the NH_3 rocking vibration (850 cm^{-1}), for this is the most sensitive of the NH_3 deformations to the effects of the outer ligands.[14] The increased frequency of the NH_3 rocking mode for $[Ru(NH_3)_6](SO_4)ClO_4$ is indicative of increased hydrogen bonding to the outer ions.[15]

The infrared absorptions due to the sulfate and perchlorate ions overlap extensively, but the very weak absorptions at 935 and 970 cm^{-1} can be assigned to the symmetric stretching vibration (ν_1) of the perchlorate and sulfate ions, respectively.[16] No splitting of the intense ν_3 absorption (1090 cm^{-1}), which would indicate coordination of the sulfate, was observed, nor were any peaks observed which would indicate bonding of the sulfate ion to the ammine nitrogens.[5] Thus it is concluded that both the sulfate and perchlorate ions maintain approximate T_d summetry in $[Ru(NH_3)_6](SO_4)ClO_4$.

Addition of barium ion to a cold solution of freshly dissolved $[Ru(NH_3)_6](SO_4)ClO_4$ led to the immediate precipitation of $BaSO_4$. Recrystallization of $[Ru(NH_3)_6](SO_4)ClO_4$ from a cold solution of NH_4Br yielded the yellow solid $[Ru(NH_3)_6]Br_3$ which gave a negative test for sulfate. These results confirm that the sulfate ion is not strongly bound to the ruthenium or to the coordinated ammines, and that it is best considered as a free ion in the outer coordination sphere of the hexaammineruthenium(III) cation.

Discussion

The two-electron reaction of hydrazoic acid with ruthenium(II), as observed here, has also been reported using Cr(II)[6,7] and V(II).[6] The reaction products were also nitrogen gas, ammonia, and 2 equiv of oxidized metal complexes in the trivalent state. In the chromous reaction approximately half of the resulting chromic complexes contained a Cr–N bond,[6] reminiscent of the formation of $[Ru(NH_3)_6]^{3+}$ in eq 1. This suggests that a similar mechanism may be involved in all of these noncomplementary reactions between hydrazoic acid and one-electron reducing agents.

A plausible mechanism for the reaction of hydrazoic acid with $[Ru(NH_3)_5H_2O]^{2+}$ may be similar to that proposed by Linck[7] for the reaction of HN_3 with $Cr^{2+}{}_{aq}$. The experimental results reported here are consistent with the reaction scheme illustrated by eq 2–5.

$$[(NH_3)_5RuH_2O]^{2+} + HN_3 \longrightarrow [(NH_3)_5RuN_3H]^{2+} + H_2O \quad (2)$$

$$[(NH_3)_5RuN_3H]^{2+} \longrightarrow [(NH_3)_5RuNH]^{2+} + N_2 \quad (3)$$

$$[(NH_3)_5RuNH]^{2+} + H^+ \longrightarrow [(NH_3)_5RuNH_2]^{3+} \quad (4)$$

$$[(NH_3)_5RuNH_2]^{3+} + [Ru(NH_3)_5H_2O]^{2+} + H^+ \longrightarrow [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_5H_2O]^{3+} \quad (5)$$

The initial coordination of hydrazoic acid (eq 2) is consistent with the known substitution lability of $[Ru^{II}(NH_3)_5H_2O]^{2+}$, and the fact that all of the ammonia generated in the reaction is coordinated. No ammonia could be found free in the solution, so the formation of a Ru–N bond must precede cleavage of an N–N bond in the azide group. Once formed, this Ru–N bond remains intact throughout the reaction.

The decomposition of the coordinated hydrazoic acid, with the release of a molecule of nitrogen gas, is represented in eq 3. The following reactions (eq 4 and 5) of protonation and redox to yield the ruthenium(III) products need not take place in the sequence shown, and no attempt was made in this work to investigate the details of these processes.

The interesting question to ask is, what is the nature of the proposed active intermediate $[(NH_3)_5RuNH]^{2+}$? Similar intermediates have been proposed for the reactions of $[Ru(NH_3)_5N_3]^{2+}$ and of $[Ir(NH_3)_5N_3]^{2+}$ with acid. The intermediates in these reactions were formulated[4,5] as the coordinated nitrene species $[(NH_3)_5Ru^{III}\text{–}\ddot{N}H]^{3+}$ and $[(NH_3)_5Ir\text{–}\ddot{N}H]^{3+}$, respectively. The formulations were made on the basis of the electrophilic reactions of the coordinated nitrene. For example, in the absence of efficient trapping agents the ruthenium(III)–nitrene system couples to form the known bridged species (eq 6), whereas the iridium(III)–nitrene reacts with hydrochloric acid to form the chloramine derivative (eq 7).

$$2[(NH_3)_5Ru^{III}\text{–}NH]^{3+} \longrightarrow [(NH_3)_5Ru^{II}\text{–}N_2\text{–}Ru^{II}(NH_3)_5]^{4+} + 2H^+ \quad (6)$$

$$[(NH_3)_5Ir^{III}\text{–}NH]^{3+} + HCl \longrightarrow [(NH_3)_5Ir^{III}\text{–}NH_2Cl]^{3+} \quad (7)$$

In contrast to this nitrene behavior, it is clear that the species $[(NH_3)_5RuNH]^{2+}$ (eq 3) reacts as a nucleo-

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[14] G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 3313 (1957).

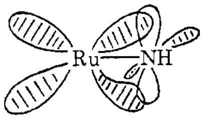
[15] A. Nakahara, Y. Saito, and M. Kobayashi, *ibid.*, **78**, 3295 (1956).

[16] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970.

phile (eq 4 and 5). Thus the coordinated NH group in this complex reacts as a coordinated imido group, $-\underset{\cdot\cdot}{\ddot{N}}H^{2-}$, and not as a coordinated nitrene, $-\ddot{N}H$. It should be noted that the imido and the nitrene formulations are, in fact, valence resonance structures, as shown by

$$\underset{\text{coordinated imido}}{[(NH_3)_5Ru^{IV}-\underset{\cdot\cdot}{\ddot{N}}H]^{2+}} \longleftrightarrow \underset{\text{coordinated nitrene}}{[(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}}$$

These two structures show an electron pair localized either on the nitrogen (imido) or on the ruthenium (nitrene). The electron delocalization representation, with appropriate orbital overlap, is given by



This pictorial representation is preferable to the above valence bond designations, and suggests a structure somewhere between the extreme imido and nitrene forms. The experimental results show that this species reacts as a nucleophile, indicating that there is a fairly high electron density at the nitrogen atom of the intermediate. The electron delocalization stabilization of such a species may be responsible for the thermal reaction of certain azido metal complexes with acid,[4,5] as well as their photochemical reactions,[17] to yield molecular nitrogen.

Returning to the reaction scheme proposed (eq 2–5), the species involved can be represented in accordance with eq 3a–5a.

$$[(NH_3)_5Ru^{II}N_3H]^{2+} \longrightarrow [(NH_3)_5Ru^{IV}-\underset{\cdot\cdot}{\ddot{N}}H]^{2+} + N_2 \quad (3a)$$

$$[(NH_3)_5Ru^{IV}-\underset{\cdot\cdot}{\ddot{N}}H]^{2+} + H^+ \longrightarrow [(NH_3)_5Ru^{IV}-\ddot{N}H_2]^{3+} \quad (4a)$$

$$[(NH_3)_5Ru^{IV}-\ddot{N}H_2]^{3+} + [Ru^{II}(NH_3)_5H_2O]^{2+} + H^+ \longrightarrow [Ru^{III}(NH_3)_6]^{3+} + [Ru^{III}(NH_3)_5H_2O]^{3+} \quad (5a)$$

Under the conditions of the experiments in this investigation, the stoichiometry of the reaction was established to be that shown by eq 1. This means the proposed intermediate reacts (eq 4a) as the imido nucleophile and not as its valence resonance equivalent, the nitrene $[(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}$. It would be of interest to attempt this reaction in the presence of a high concentration of a strong nucleophile to determine if any of the nitrene behavior can be detected, but this was not done. However, the reactions[12] when oxygen is passed through a solution containing $[Ru(NH_3)_6]^{3+}$ and sulfur nucleophiles to produce $[Ru(NH_3)_5NHSO_3]^+$ may involve a nucleophilic attack on the nitrogen of the coordinated nitrene in the resonance system $[(NH_3)_5Ru^{IV}-\underset{\cdot\cdot}{\ddot{N}}H]^{2+} \leftrightarrow [(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}$. Additional studies are required to resolve the questions of reaction mechanisms in these systems, but it will be important in such investigations to keep in mind that the intermediate species may behave either as a nucleophile (imido) or an electrophile (nitrene).

Acknowledgment.—We thank Professor R. D. Gillard for helpful discussions and for the use of his laboratory to do the "last" experiment. We thank Professor R. G. Pearson for his help and we also thank Mr. T. R. Weaver for his help and Dr. L. Engelhardt for the magnetic measurement. The ruthenium used was loaned to us by the Matthey Bishop Co. and the project was supported by a grant from the National Science Foundation.

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[17] J. L. Reed, F. Wang, and F. Basolo, *J. Amer. Chem. Soc.*, in press.

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The Proton Nuclear Magnetic Resonance Determination of the Methanol Exchange Rate of the Monothiocyanate Complex of Cobalt(II)

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Proton nmr was used to measure the methanol exchange rate from the cis and trans coordination sites of the $Co(CH_3OH)_5NCS^+$ ion by line-shape analysis of the methyl resonance of the coordinated methanol. The exchange contributions to the transverse relaxation times of the cis and trans methanols were found to be equal. The exchange contribution to the transverse relaxation time of the methyl resonance of the bulk methanol was measured and the result compared to the value predicted on the basis of the bound solvent relaxation data. From these measurements it was concluded that the methanol exchanged from each type of coordination site without internal rearrangement of the complex, and the cis and trans exchange rates were equal. The value for the solvent exchange rate constant per coordinated methanol molecule at 25° is 2.4×10^6 sec^{-1}. The corresponding values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 11.7 kcal mol^{-1} and 9.9 eu, respectively. Data describing the natural line widths and chemical shifts of the coordinated solvent are also included.

Introduction

Summaries of current theories concerning the mechanisms of substitution reactions of labile transition metal ions can be found in many recent reviews.[1] Detailed mechanistic information concerning substitution reactions of labile octahedral transition metal complexes has generally been limited to a few ions exhibiting comparatively slow reaction rates. For reactions involving substitution of coordinated solvent molecules, the reaction rate appears to be controlled by the rate of dissociation of the bound solvent molecule rather than by the rate of bond formation with the

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[1] (a) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970); (b) A. McAuley and J. Hill, *Quart. Rev., Chem. Soc.*, **23**, 18 (1969).