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Studies of Substitution Reactions of Aquopentaammineruthenium(II)

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The specific rates for the substitution in $(NH_3)_5RuOH_2^{2+}$ for pyridine, ammonia, pyrazine, isonicotinamide, 3-picoline, 2,6-lutidine, acetonitrile, cyanoacetate ion, and imidazole at 25° were measured as 9.3×10^{-2}, 5.5×10^{-2}, 5.6×10^{-2}, 10.5×10^{-2}, $\sim 3 \times 10^{-3}$, $< 4.3 \times 10^{-5}$, 30.2×10^{-2}, 1.2, and 20×10^{-2} M^{-1} sec^{-1}, respectively. Paths corresponding to the reactions of the protonated forms were identified for pyridine, isonicotinamide, and imidazole, and the specific rates observed are 3.1×10^{-3}, 3.6×10^{-3}, and 2.7×10^{-3} M^{-1} sec^{-1}, respectively. Activation energies for a large group of neutral, unhindered ligands are in the range 16.8 ± 1.5 kcal mol^{-1}. Measurements of the rate of loss of pyridine and of NH_3 from $(NH_3)_5Ru(py)^{2+}$ and $Ru(NH_3)_6^{3+}$ have led to estimates of the equilibrium constant for the reaction of the two bases with Ru(II). Those in turn have led to an estimate of *ca.* 5 kcal mol^{-1} extra stabilization resulting from the fact that pyridine is a π acid.

Ruthenium(II) in the aquoammine complex and even in the hexaammine displays unusual reactivity in respect to both substitution[2-4] and redox processes.[5] This background of chemical behavior was sufficient incentive for the present study which was devoted to extending our knowledge of the substitution reaction of aquopentaammineruthenium(II).

We have concerned ourselves with the kinetics of complex formation with a variety of nitrogen-containing heterocyclic ligands[6]—for these unsaturated ligands back-bonding is an important factor in the interaction[7]—as well as with the saturated ligand NH_3. For the heterocyclic ligands, we were interested in examining the effect of substituents adjacent to the nitrogen in causing steric interference and in the possibility that a path for substitution might be observed involving the protonated ligand. The principle of detailed balancing applied in the context of the observation[4] that removal of pyridine[8] from pyridinepentaammineruthenium(II) requires that the reverse path involving pyH^+ reacting with $(NH_3)_5RuOH_2^{2+}$ must exist. But in the absence of information on the value of the equilibrium constant for the reaction, the principle provides no guarantee that the path in question will actually be observable, and it is left for experiment to decide whether the rate for the reverse reaction can be measured. We have succeeded in measuring the rate at which pyH^+ converts $(NH_3)_5RuOH_2^{2+}$ to the pyridine complex, and the information thus gained, together with improved data on the rate of the reaction of $(NH_3)_5Rupy^{2+}$ with H^+, has led to a value of the equilibrium constant governing the reaction of py with $(NH_3)_5RuOH_2^{2+}$. Again, using a kinetic method, the equilibrium constant for the reaction of NH_3 with $(NH_3)_5RuOH_2^{2+}$ has been measured. The two results on affinity, one with a saturated and the other with an unsaturated ligand, have led to an estimate of the contribution of back-bonding to the interaction of Ru(II) with py, at least to the extent that the total interaction is separable into two contributions.

Experimental Section

Chemicals and Reagents. All chemicals were of the highest quality available. It was found to be essential to purify the N-heterocyclic ligands so as to observe the intrinsic kinetic behavior. Organic reagents were filtered through Millipore 0.45 μHAWPO47 filtration disks to remove solid particles. Ultrapure 2,6-lutidine was prepared starting with Matheson Coleman and Bell practical grade LX-410. After distillation, enough of the 143–144° fraction was treated to two cycles of the Eastman Kodak purification scheme[9] to produce 1 kg of purified product. For each cycle 1000 g of the 2,6-lutidine of bp 143–144° was mixed with 200 g of ethyl *p*-toluenesulfonate (MCB technical grade) and refluxed for 1 hr and cooled. The liquid phase was decanted and was distilled, without fractionation, to remove remaining pyridinium tosylate salts. The distillate was redistilled over 100 g of CaH_2 (MCB 94% 4–40 mesh) to eliminate ethanol and trace amounts of ethyl *p*-toluenesulfonate. Two purification cycles were necessary to eliminate species which showed absorbance in the visible region when brought into reaction with $(NH_3)_5RuOH_2^{2+}$. By means of gas chromatography the major impurity in the original material was found to be 3-picoline.

2-Picoline was never fully purified. A sample purified by simple distillation, distillation through a 6-ft column of glass beads, and spinning-band distillation at 130.0° was found to contain enough pyridine to cause complications in the measurements, though the pyridine content was less than 0.1%.[10]

Pyridine and 3-picoline reagents (MCB) were purified by fractional distillation.

Pyrazine and 2-methylpyrazine (Aldrich Puriss grade), imidazole (MCB), and acetonitrile (MCB Spectral Quality) were used as supplied.

Isonicotinamide as supplied by City Chemical Corp., New York, N. Y., contained an oxidant for Ru(II). Two recrystallizations and two treatments with activated charcoal were needed to remove the troublesome impurity. Sodium cyanoacetate, sodium chloroacetate, and sodium acetate were produced by neutralizing the corresponding acids. Trifluoromethylsulfonic acid was used as supplied by 3M Co. Hydrochloric acid from three sources was used (B&A, J. T. Baker Analyzed reagent, and Titrisol of E. Merck, Darmstadt, Germany) with no difference in the results.

Zinc amalgam was used to reduce solutions of $VO(ClO_4)_2$, $Cr(ClO_4)_3$, $(NH_3)_6RuCl_3$, and $(NH_3)_5RuCl_3$ to V(II), Cr(II), $(NH_3)_6Ru^{2+}$, and $(NH_3)_5RuOH_2^{2+}$, respectively. Solutions were deoxygenated with Ar before adding Zn(Hg). Hexaammineruthenium(III) chloride was prepared by Armor's procedure[11] and $(NH_3)_5RuCl_3$ by the method of Vogt, Katz, and Wiberley,[12] starting with $(NH_3)_6RuCl_3$ as supplied by Johnson Matthey Chemicals, Ltd. In the electrochemical measurements, a second source of $(NH_3)_6RuCl_3$ was used,

(1) To whom correspondence should be addressed.

(2) Reaction with N_2: D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, 89, 5706 (1967); D. E. Harrison, E. Weissberger, and H. Taube, *Science*, 159, 320 (1968).

(3) Reaction with N_2O: J. Armor and H. Taube, *J. Amer. Chem. Soc.*, 91, 6874 (1969).

(4) Proton assisted removal of nitrogen bases: P. C. Ford, J. Kuempel, and H. Taube, *Inorg. Chem.*, 7, 1976 (1968).

(5) Oxidation by ClO_4^-: J. Endicott and H. Taube, *Inorg. Chem.*, 4, 437 (1965).

(6) Some of our measurements overlap those of R. J. Allen and P. C. Ford, *Inorg. Chem.*, 11, 679 (1972).

(7) P. C. Ford, DeF. P. Rudd, R. G. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968).

(8) Abbreviations: py, pyridine; pz, pyrazine; 2-pic, 2-picoline; 3-pic, 3-picoline; isoam, isonicotinamide; lu, 2,6-lutidine; *o*-phen, 1,10-*o*-phenanthroline; 2-mepz, 2-methylpyrazine; imz, imidazole.

(9) J. A. Cathcart and D. D. Reynolds, *J. Amer. Chem. Soc.*, 73, 3504 (1951).

(10) Shown by gas chromatography and by microwave analysis. We are grateful to Dr. Lee Sharpin of Hewlett-Packard Corp. for doing the microwave analyses.

(11) J. N. Armor, Ph.D. Thesis, Stanford University, 1970.

(12) L. H. Vogt, J. L. Katz, and S. B. Wiberley, *Inorg. Chem.*, 4, 1157 (1965).

the material being supplied by J. N. Armor, and some of the rate data were checked using a sample of $(NH_3)_5RuCl_3$ supplied by R. G. Gaunder.

Vanadyl perchlorate was prepared by the method of Rossotti and Rossotti.[13] Chromium(III) perchlorate was prepared and standardized by the sequence given by Zanella.[14] Sodium, potassium, lithium, and ammonium chlorides were weighed as salts and the solutions standardized with $AgNO_3$ using Ag–AgCl *vs.* calomel electrodes. Sodium thiocyanate (B&A) was recrystallized twice from water after millipore filtration of the original solution.

Isonicotinamidepentaammineruthenium(II) in solution was prepared from a known concentration of $(NH_3)_5RuOH_2^{2+}$ in chloride medium as well as by dissolving the perchlorate salt (supplied by R. Magnuson, who followed Gaunder's[6] synthesis). Measurements on the two preparations agreed in showing ϵ at 478 nm to be $1.19 \times 10^4\ M^{-1}\ cm^{-1}$ and the maximum absorption to be at 481 nm. The value of ϵ measured by us is some 10% higher than that reported by Armor and Taube.[15] For some experiments it was necessary to prepare a complex free from ligand. In such cases, an excess of ligand was used to bring about conversion of $(NH_3)_5RuOH_2^{2+}$ to the desired complex, and following the conversion, ion-exchange separation in an inert atmosphere yielded the complex in solution.

Argon (Liquid Carbonic Co., 99.995% pure) was used as blanketing gas. It was deoxygenated by passing it through scrubbing towers containing chromous ion, through a water rinse scrubber, and, when volatile reactant was used, through a solution containing the reagent in question at the same concentration as in the experimental solution. An all-glass line was used to conduct the gas.

Electrochemical Measurements. An H-shaped apparatus having the compartments separated by glass frits and having one fitted with a stopcock to control the stream of Ar was used. In the oxygen-free compartment a Pt foil electrode was mounted in a rubber stopper which carried an additional glass access port covered with a septum. The port provided for exit of the Ar gas through a syringe needle. For titrations a Teflon needle attached to a Gilmont microburet of 1.500-ml capacity was inserted through a pipet dropper bulb and attached at the port. The buret assembly was flushed with many cycles of Ar and deoxygenated reagent before use. Measurements were made in KCl of total ionic strength 1.00.

For the pyridinepentaammineruthenium(II)–pyridinepentaammineruthenium(III) couple, the Ru(II) complex was prepared *in situ* in a 0.01 *M* pyridine–0.01 *M* pyridinium chloride–KCl solution. After reaction of pyridine with $(NH_3)_5RuOH_2^{2+}$ was complete, excess free pyridine was neutralized with deoxygenated HCl. Titration was carried out with 5.00×10^{-3} *M* Ce(IV) ($\mu = 1.00$ ($HClO_4$)). The middle compartment contained 1.00 *M* KCl–1.00×10^{-3} *M* HCl and the reference compartment 1.00 *M* KCl–1.00×10^{-3} *M* HCl saturated with freshly prepared and washed AgCl. A silver wire dipping in the chloride medium served as the reference Ag–AgCl electrode. Measurements were made with the Beckman Expandomatic pH meter, standardized with a Weston cell at 1.018 V. The junction potential for the cell was measured by four titrations in KCl medium using the value of the $(NH_3)_6Ru^{III}$–$(NH_3)_6Ru^{II}$ couple determined by Meyer.[16]

Titrating $(NH_3)_5RuOH_2^{3+}$ (1.00×10^{-4} *M*) with Cr^{2+} ([Cr(II)] = 4.91×10^{-3} *M*, $[H^+] = 1.55 \times 10^{-3}$ *M*, $\mu = 1.00$ (KCl–HCl)) the junction potential E_j was calculated as 0.085 and 0.088 V; on titrating $(NH_3)_6Ru^{2+}$ (1.00×10^{-4} *M*) with Ce(IV) ([Ce(IV)] = 5.00×10^{-3} *M*, $[HClO_4] = 1.00$ *M*) E_j was calculated as 0.075 V. The last value was selected as applying to the titrations for the determination of the reduction potential, which were done with Ce(IV).

Ion-Exchange Methods. AG 50W-X2 resin (Bio-Rad Inc.) was cleaned by methods described in the literature.[17] For it to be suitable for use in spectrophotometric measurements under exacting conditions, it was found to be necessary to treat the resin just prior to use with HCl, acetone, 95% ethanol, water, and NaCl(aq) washes. Decomposition of the resin apparently occurs even in the absence of air and light. By maintaining a continuous flow of an eluting solution, the level of contaminants absorbing as far into the uv region as 224 nm could be kept very low.

Special columns were used to make possible separations in an inert atmosphere.

(13) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 9, 1177 (1955).
(14) A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, 93, 7166 (1971).
(15) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 92, 6170 (1970).
(16) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).
(17) E. A. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

Kinetic Measurements. Solutions were made up in a Zwickel flask immersed in a constant-temperature bath, and after adding the last reagent, the solution was discharged by Ar pressure into a spectrophotometer cell, fitted with two stopcocks. The progress of the reaction was followed by repetitive scans as a function of time or by following the change in absorbance at a single wavelength.

The absorbance data were obtained under pseudo-first-order conditions and were given to computer storage and analyzed on simple first-order programs. They were also plotted graphically to see if curvature was evident. Least-squares averaging was handled by a program of J. Malin using a 50% confidence limit. The traces when the stopped-flow apparatus[18] was used were analyzed by a separate program of Malin's.

When secondary reactions interfered with the determination of A_∞, the Guggenheim treatment of the data was used. Slopes as drawn by eye were tested on sample plots against least-squares computer analysis with agreement within 1%.

The temperature of the cell compartment of the Cary 14 spectrophotometer was controlled by circulating water from a Forma constant-temperature bath, allowance being made for the temperature difference between bath and the cell contents.

Competitive Reactions. For the most of the systems, the ruthenium(II)–ligand complex absorbs strongly in a wavelength region conveniently removed from the d–d absorptions of Ru(II) or absorptions peculiar to the ligand. But in several cases it was difficult to follow the substitution by a direct spectrophotometric method. In such instances pyrazine was added, the course of reaction then being followed by observing the absorption of the product species $(NH_3)_5Ru(pz)^{2+}$ at 472 nm (ϵ $1.34 \times 10^4\ M^{-1}\ cm^{-1}$) as it is formed competitively with the complex of the ligand of interest. The reactions of $(NH_3)_5RuOH_2^{2+}$ with imidazole, ammonia, 2,6-lutidine, and thiocyanate ion were followed in this way.

The principle of the method is the following: when [Ru(II)] $\ll$ [ligand] or [pz], the pseudo-first-order specific rate in a particular experiment is given by $k_{pz}[pz] + k_L[L]$. The derivation is shown in the Appendix. Since k_{pz}, [pz], and [L] are known, k_L can be evaluated. A check on the kinetic analysis is provided by measuring the product distribution between the forms $(NH_3)_5Ru(pz)^{2+}$ and $(NH_3)_5RuL^{2+}$.

Results

Pyridine as Ligand. Two paths were observed for the formation of $(NH_3)_5Ru(py)^{2+}$, one involving py as a reactant and the other pyH^+, the complete rate law for the substitution reaction being

$$d[(NH_3)_5Ru(py)^{2+}]/dt = [(NH_3)_5RuOH_2^{2+}](k_{py}[py] + k_{pyH}[pyH^+]) \quad (1)$$

In Table I, data which bear mainly on the k_{py} path are presented. These were obtained in a buffer mixture with [py] = [pyH^+]. Under these conditions 97% of the total rate is carried by the k_{py} path; reaction takes place apparently without complication, and the final reading of the optical density is that expected from the initial concentration of Ru(II) and the value of ϵ reported.[19]

By doing experiments at low pH, the k_{py} path could be suppressed making possible the evaluation of k_{pyH}. The data at higher acidity are summarized in Table II.

Using the known values of K_{dis} for pyH^+ and the value of k_{py}, as determined by the data summarized in Table I, the contribution of the k_{py} path to the rate even at the lowest acidities used in getting the data of Table II is calculated to be very small (it affects the rate at pH 2.5 by no more than 3%). That it is small is borne out by the comparison of k_{obsd} at pH 2.5 and 2.1—the change in $[H^+]$ by a factor of 3 does not alter the rate significantly. In view of this comparison, the much diminished rate at still higher acidities is unexpected. On the face of it, the effect speaks for an interaction among Ru(II), H^+, and pyH^+, which depletes $(NH_3)_5RuOH_2^{2+}$ significantly. Lacking more complete information, we will not speculate further on the cause of the

(18) J. Stritar, Ph.D. Thesis, Stanford University, 1967.
(19) R. G. Gaunder and H. Taube, *Inorg. Chem.*, 9, 2627 (1970).

Table I. Substitution of Pyridine on Aquopentaammineruthenium(II)[a]

Temp, °C	[py], *M*	$10^2 k_{py}$, M^{-1} sec^{-1}
25.0	5.00	9.32 ± 0.17
15.0	10.00	3.39 ± 0.07
35.0	2.50	24.5 ± 0.9

[a] μ = 0.10 (LiCl); λ 408 nm; $[(NH_3)_5RuOH_2^{2+}] = 5.20 \times 10^{-5}$ *M*; [py] = [pyH$^+$]. Each entry is the mean of three.

Table II.[a] Reaction of Protonated Pyridine with Aquopentaammineruthenium(II)

Temp, °C	[pyH$^+$], *M*	pH[b]	$10^4 k_{obsd}$,[c] sec^{-1}
25.0	0.40	1.08	8.06
25.0	0.40	1.15	8.17
25.0	0.40	2.05	12.57
25.0	0.40	2.11	13.25
25.0	0.40	2.50	13.45
25.0	0.40	2.48	13.62
34.6	0.16	2.48	13.88
15.0	0.40	1.10	2.96
15.0	0.40	2.50	4.80

[a] μ = 0.50; λ 408 nm; [Ru(II)] = 8.0×10^{-5} *M* except in the first two experiments where it is 5.0×10^{-5} *M*. [b] pH measured at 25.0°. [c] Uncorrected for redox or free base paths.

behavior but will take the data at pH 2.1 and 2.5 after correction for an effect now to be discussed as defining k_{pyH}.

At high acidities, the amount of the pyridine substitution product formed is significantly less than is expected, in some cases by as much as 15%. We ascribe the deviation from the stoichiometry as expressed by eq 2 to reduction of pyH$^+$

$$(NH_3)_5RuOH_2^{2+} + pyH^+ = (NH_3)_5Ru(py)^{2+} + H_3O^+ \quad (2)$$

accompanying the substitution process. The Ru(III) produced by the parallel redox process accounts for the failure to observe the full absorbance expected if all the Ru(II) were converted to the Ru(II)-py complex. The situation here is also observed with 2,6-lutidine as the entering ligand, where it was shown that Ru(III) is formed (*vide infra*). When $(NH_3)_5RuOH_2^{2+}$ reacts with methylpyrazinium ion, the oxidation reaction is very prominent, consuming an even larger fraction of Ru(II) than in the pyH or 2,6-lutidine cases.[20]

Correcting for the side reaction at 25° and higher pH leads to $k_{pyH} = (3.12 \pm 0.15) \times 10^{-3}$ M^{-1} sec^{-1} compared to 3.2×10^{-3} M^{-1} sec^{-1} uncorrected. At 34.6 and 15.0°, the values of k_{pyH} are $(8.0 \pm 0.1) \times 10^{-3}$ and $(1.1 \pm 0.1) \times 10^{-3}$, respectively.

Data have been presented in the literature[4] for the reverse of reaction 2, by a path which at high acidity assumes the kinetic form $-d[(NH_3)_5Ru(py)^{2+}]/dt = k_{-pyH}[(NH_3)_5Ru(py)^{2+}][H^+]$. The value of k_{-pyH} compared with that for k_{pyH} leads to a value of the equilibrium constant of the reaction. Because the data reported in the literature featured an anomalous variation of rate with [H$^+$], which suggested a complex course for the reaction, we considered it prudent to reinvestigate the kinetics of the reverse of reaction 2, particularly because in studying the forward rate we found no counterpart to the "saturation" term

$$\frac{k[H^+][(NH_3)_5Ru(py)^{2+}]}{1 + a[H^+]}$$

which was indicated by the data of Ford, Kuempel, and Taube.[4]

Our data for the release of py from $(NH_3)_5Ru(py)^{2+}$ under the influence of acid are presented in Table III.

Our data were obtained at 400 nm where ε values for

(20) H. E. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, 94, 4039 (1972).

Table III. Acid-Induced Aquation of Pyridinepentaammineruthenium(II)

[H$^+$], *M*	$10^5[(NH_3)_5Ru(py)^{2+}]$, *M*	$10^5 k_{obsd}$, sec^{-1}
0.975[a]	10.15	6.25
0.975	9.14	6.11
0.975	9.01	6.16
0.975	8.97	5.79[b]
0.975	8.28	4.84[c]
0.487	8.99	3.60
0.482	10.62	2.80[c]
0.342	9.06	2.56
0.195	9.04	1.81
0.0487	8.90	0.684
0.0242	8.86	0.461
0.975[d]	8.86	5.78
0.975	8.61	5.99
0.975	7.86	5.94
0.860	8.87	5.33
0.731	8.77	4.43
0.487	8.41	3.38
0.244	8.76	2.04
0.750	10.58[e]	4.59[e]
1.00	7.50[f]	2.03[f]

[a] μ = 1.00 (NaCl-HCl) (B&A HCl); 25.0°; λ 400 nm; first isolation of $(NH_3)_5Ru(py)^{2+}$ by ion exchange–first eleven entries. [b] $[ClO_4^-]/Ru(II)] = 3.03$; see text. [c] Photoaquated solution containing $(NH_3)_4(H_2O)Ru(py)^{2+}$ using Titrisol HCl; see text. [d] J. T. Baker HCl; μ = 1.00; 25.0°; second isolation of $(NH_3)_5Ru(py)^{2+}$ by ion exchange–next seven entries. [e] *In situ* preparation of $(NH_3)_5Ru(py)^{2+}$; J. T. Baker HCl. [f] ClO_4^- salt dissolved in HCl.

$(NH_3)_5Ru(py)^{2+}$ and $(NH_3)_4(H_2O)Ru(py)^{2+}$ (the latter is an alternate but minor product) are almost the same. Some experiments featuring repetitive scans over the range of wavelength from 390 to 440 nm showed the values of k_{obsd} to vary no more than 2% over the range. The data are based on the first 20% or so of reaction where $(NH_3)_4(H_2O)Ru(py)^{2+}$ has not accumulated sufficiently for serious interference by the secondary and slower loss of py from this intermediate, and they are treated by assuming the theoretical product absorbance to be zero (Ru(II) species lacking py will have virtually zero absorbance at 400 nm).

Our rates are lower than those reported[4] by a factor of about 1.7 and show the saturation effect much less prominently. We found somewhat different results using a sample of $(NH_3)_5Ru(py)(ClO_4)_2$ (this was supplied through the courtesy of R. Magnuson) from those obtained using a preparation which had been separated by ion exchange or the species as prepared simply by adding py to $(NH_3)_5RuOH_2^{2+}$. It should be pointed out that Ford, *et al.*, used a perchlorate salt as the source of pyridine complex. Light does affect the reactivity but in the direction of decreasing the apparent rate of aquation, presumably owing to the intermediate formation of $(NH_3)_4(H_2O)Ru(py)^{2+}$.

A computer least-squares fit of the data of Table III for the high acid range, above 0.195 *M* HCl, yielded $(5.42 \pm 0.43) \times 10^{-5}$ M^{-1} sec^{-1} for the specific rate of the reverse of reaction 2 at 25°.

On correcting the value of k_{-pyH} to $\mu = 0.50$, to correspond to the conditions for substitution, it becomes 3.6×10^{-5} M^{-1} sec^{-1}. Combining this with k_{pyH} and taking account also of the proton association constant for pyridine ($pK_a = 5.45$ at $\mu = 0.50$[21]) the equilibrium constant for the reaction

$$(NH_3)_5RuOH_2^{2+} + py = (NH_3)_5Ru(py)^{2+} + H_2O \quad (3)$$

is calculated as $(2.4 \pm 0.3) \times 10^7$ at $\mu = 0.50$ and at 25°.

The formal reduction potential of the $(NH_3)_5Ru(py)^{3+,2+}$

(21) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17 (1964).

couple was measured as 0.35 V at $\mu = 1.00$ (KCl) and at 25°.

Ammonia as Ligand. The product $(NH_3)_6Ru^{2+}$ does not show absorption usefully different from that of the reactants $(NH_3)_5RuOH_2^{2+} + NH_3$ to make it feasible to follow the formation of the hexaammine directly, and thus we resorted to the competition method using pyrazine as the "indicator" reactant.

In measuring the formation constant and operating under the necessity of having the solution oxygen free, there is difficulty with the volatility of ammonia. Errors from this source were minimized by following the procedure to be described.

A solution was prepared containing pyrazine and NH_4Cl (0.10 M, $\mu = 0.10$) and was degassed by a stream of Ar. A separate solution of degassed NaOH was prepared, a measured amount was injected into the pz-NH_4Cl mixture, and, immediately thereafter, a solution of $(NH_3)_5RuOH_2^{2+}$ was injected. Allowing only enough time for mixing, a spectrophotometric cell was filled from the mixing chamber, avoiding gas space in the cell. The progress of the reaction was followed at 472 nm, which is a maximum for the species $(NH_3)_5Ru(pz)^{2+}$.

The concentration of NH_3 in the solution was calculated from the concentration of NH_4Cl originally used, making allowance for dilution on making up the final reaction mixture and using the measured value of pH to define the ratio of NH_3 to NH_4^+. The proton association equilibrium constant was evaluated by interpolation of Rorabacher's data[22] as $10^{9.263}$.

Four determinations of the rate of formation of the hexaammine complex were made yielding an average value of $(5.5 \pm 0.6) \times 10^{-2}$ M^{-1} sec^{-1} for the specific rate of reaction at 25°, the range of values being about 10%. By using the product distribution data, the specific rate was determined as 5.2×10^{-2} M^{-1} sec^{-1}, with the reproducibility by this method being somewhat less than that based on the reaction rates.

In the published work on the aquation of $(NH_3)_6Ru^{2+}$, only the path first order in $[H^+]$ was observed. The corresponding reaction for the formation of the hexaammine complex cannot be observed and thus the path in question is useless for evaluating the equilibrium constant of reaction 4. By

$$(NH_3)_5RuOH_2^{2+} + NH_3 = (NH_3)_6Ru^{2+} + H_2O \quad (4)$$

working at high pH we have succeeded in measuring the rate of aquation of $(NH_3)_6Ru^{2+}$, unassisted by H^+; these measurements together with those on the rate of formation, just described, make it possible to calculate the equilibrium constant for reaction 4.

Aquation of $(NH_3)_6Ru^{2+}$ was followed using isonicotinamide to react with $(NH_3)_5RuOH_2^{2+}$ as it forms. The isonicotinamide also serves as a buffer, and it has sufficient capacity (*cf.* Table V) to moderate the effect on pH of the release of NH_3. For these experiments, $(NH_3)_6Ru^{2+}$ was generated from $(NH_3)_6Ru^{3+}$ using V_{aq}^{2+} as reductant. With $[Ru(III)] = [V^{2+}] = 2 \times 10^{-4}$ M, the reduction is more than 90% complete in 15 min. Since the half-time for loss of NH_3 is 1.2×10^3 min, little error is introduced by allowing 30 min to elapse before the absorbance data are used. According to Newton's measurements,[23] the V^{3+}-VOV^{4+} equilibrium under our conditions is established with a half-life of 15 sec, and thus no complications caused by vanadium species undergoing change are expected after 30 min.

(22) D. B. Rorabacher, *Inorg. Chem.*, 5, 1891 (1966).
(23) T. W. Newton and F. B. Baker, *Inorg. Chem.*, 3, 569 (1964).

Table IV. Aquation of $(NH_3)_6Ru^{2+}$ [a]

[isoam], M	pH	10^6k, sec^{-1} Obsd	Cor[b]
0.050	4.25	9.54	9.47
0.100	3.85	9.24	9.06
0.100	4.27	9.56	9.49
0.205	5.35	0.09	9.09
			Av 9.28 ± 0.20

[a] $[(NH_3)_6Ru^{2+}] = [V^{2+}] = 2.00 \times 10^{-4}$ M; 25°; $\mu = 0.10$. [b] Corrected for the H^+-assisted contribution.

Table V. Reaction of Pyrazine with $(NH_3)_5RuOH_2^{2+}$ [a]

Temp, °C	10^2[pz], M	10^2k_{pz},[c,d] M^{-1} sec^{-1}
35.0	1.00	14.7 ± 0.1 (3)
30.0	1.00	9.1 (1)
25.0	1.00	5.61 ± 0.05 (3)[b]
25.0	2.00	5.52 (1)
15.0	3.00	1.93 ± 0.03 (2)
5.0	10.0	0.60 (1)
5.3	100.0	0.65 (1)

[a] $\mu = 0.10$ (LiCl), λ 472 nm; $[Ru(II)] = 5.0 \times 10^{-5}$ M; Ru(II) prepared by Zn(Hg) reduction of Ru(III). [b] An experiment at $\mu = 0.50$ (LiCl) did not show a significantly different rate. [c] Figures in parentheses denote the number of replicates. [d] $\Delta H^{\ddagger} = 17.5 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = 5.7 \pm 0.9$ cal mol^{-1} deg^{-1}.

To avoid corrections for the formation of higher order complexes of isonicotinamide, data covering only 10% of the reaction were used. The extinction coefficient of the isonicotinamide complex as determined in this study (*vide infra*) served to convert the absorbance data to concentrations of the isonicotinamide complex formed and thus a measure of the concentration of $(NH_3)_5RuOH_2^{2+}$ which is produced as an intermediate was provided. The rate of formation of the isonicotinamide complex was shown to be independent of the concentration of isonicotinamide. Even at the lowest concentration of the base used, the half-life for the conversion of the intermediate $(NH_3)_5RuOH_2^{2+}$ to the isonicotinamide complex was about 500 times less than that for the formation of the aquo complex from $(NH_3)_6Ru^{2+}$.

The data on the loss of NH_3 from $(NH_3)_6Ru^{2+}$ are summarized in Table IV.

The specific rates forward and reverse as determined in this work lead to the value of the equilibrium constant of reaction 4 as $(5.5 \times 10^{-2})/(9.3 \times 10^{-6}) = 0.59 \times 10^4$ at 25° and $\mu = 0.10$. To make this value commensurate with that for a reaction such as (3), it must be multiplied by the statistical factor of 6, yielding $(3.5 \pm 1.3) \times 10^4$.

Pyrazine as Ligand. The data on the reaction of $(NH_3)_5RuOH_2^{2+}$ with pz to form the pz complex are shown in Table V.

The experiments in Table V were obtained using Zn(Hg) to reduce Ru(III) to Ru(II). Some experiments were also done using Cr(II), in excess, for the reduction. The mean of 12 determinations at 25° gave 5.77×10^{-2} M^{-1} sec^{-1} for the specific rate of reaction, the agreement with the values of Table V being equally good at 35°. The experiments with Cr^{2+} as reductant were done at $[H^+] = 1.5 \times 10^{-4}$ M and the comparison with those of Table V shows that $[H^+]$ is not a significant variable in the concentration range covered by the experiments. Some interference is expected from the products formed when pyrazine is reduced by Cr^{2+}, but this was apparently not a serious complication in our experiments.

Measurements were made also for ionic media different from those specified in Table V. In 0.50 M LiCl and in

0.10 M NH_4Cl, k at 25° was found to be 5.64×10^{-2} and 5.49×10^{-2} M^{-1} sec^{-1}, respectively.

The extinction coefficient of the species $(NH_3)_5Ru(pz)^{2+}$ was determined at 472 nm in 0.10 M LiCl at 5.0, 15.0, 25.0, and 35.0° as 1.28×10^4, 1.34×10^4, 1.34×10^4, and 1.35×10^4.

Isonicotinamide as Ligand. Preliminary data on the rate of reaction at *ca.* 24° of isonicotinamide with aquopentaammine were obtained by Armor.[11] We have extended the measurements to improve precision and to investigate the variation of rate with pH and with the concentration of the ligand. Our data, which we restricted to a single temperature (25°) are summarized in Table VI. They support a rate law of the form

$$d[complex]/dt = [(NH_3)_5RuOH_2^{2+}](k_{isoam}[isoam] + k_{isoamH}[isoamH^+]) \quad (5)$$

The formation of $(NH_3)_5Ru(isoam)^{2+}$ by the reaction of the aquo complex with $isoamH^+$ is complicated by a redox process, as is the reaction of the aquo complex with pyridine. Under the experimental conditions this was always small. A correction for the redox reaction was made using data on the product distribution. It was found that the reduction involves the aquo ion and $isoamH^+$ and is not a significant process for the isoam complex acting on $isoamH^+$. In this context it is appropriate to mention that the isoamide complex is reduced by Zn(Hg) in 1.0 M H^+ to a species which shows the absorption characteristics of the 4-carbinol-pyridine complex.[7]

Our investigation of the interaction of $(NH_3)_5RuOH_2^{2+}$ with isonicotinamide led to a revision of the published extinction coefficient[15] of the isonicotinamide complex. The exact value of this property was a matter of consequence for analytical purposes in some of the systems under study. Our results on the extinction coefficient, together with the results of other measurements, as well as the values for other complexes of interest in this work are summarized in Table XIII, at the end of the Results.

An effort was made to determine the rate of the proton-assisted removal of isoam from the pentaammineruthenium(II) complex so as to evaluate the equilibrium constant for the formation of the isoam complex. The direct spectrophotometric method, focusing on the charge-transfer band for the isoam complex, was found not to be adequate for determining the rate of isoam loss because other reactions besides that of interest contribute to the changes in extinction. Efforts were made to determine the isoam released by cation-exchange methods, using the π-π^* transition to determine the isoam in the eluent solution. Reaction was allowed to proceed to only 10% to minimize complications by secondary reactions. Precision was rather poor. Blank corrections were made conservatively and the value of 1.0×10^8 estimated for the association constant of isoam with $(NH_3)_5RuOH_2^{2+}$ from the aquation data and those for the forward reaction is to be regarded as a lower limit.

3-Picoline as Ligand. The data for the reaction of the free base 3-picoline are summarized in Table VII and the study in this system was limited to this path.

Numerous data on this reaction were accumulated, though not by design, in the early phase of the study of the 2,6-lutidine reaction. A persistent impurity remained in the 2,6-lutidine, which by gas chromatography, as well as by its kinetic behavior, we take to be 3-picoline. The ratio of 3-picoline to 2,6-lutidine in the sample which was used in our experiments was 7.3×10^{-3}. Analysis of the data for the impure sample allowing for competition between 2,6-lutidine and 3-picoline for Ru(II) led to $k = 9.7 \times 10^{-2}$ M^{-1} sec^{-1}, which can be compared to 9.1×10^{-2} M^{-1} sec^{-1} using the direct method.

Table VI. Substitution by Isonicotinamide[a]

μ	pH	10^2[isoam], M	[isoamH$^+$], M	k,[b] M^{-1} sec^{-1}
0.10 (LiCl)	3.45	1.00	1.00	0.105 ± 0.003[c]
0.50 (LiCl)	3.45	1.00	1.00	0.106
0.10 (NaCl)	3.50	1.00	1.00	0.103
0.50 (LiCl)	1.0		10.0	3.59×10^{-3} [d]
0.50 (HCl)	1.08	0.16	40.0	4.28×10^{-3} [e]
0.50 (LiCl)	2.58	1.20	10.0	2.8×10^{-3} [d]

[a] λ 478 nm; $[(NH_3)_5RuOH_2^{2+}] = 6.50 \times 10^{-5}$ M; 25.0°. [b] $k_{isoam} = 0.105$ M^{-1} sec^{-1}, $k_{isoamH} = 3.6 \times 10^{-3}$ M^{-1} sec^{-1}. [c] Mean of four. [d] Corrected for parallel redox reaction and free-base path. [e] Contains redox impurity other than $isoamH^+$.

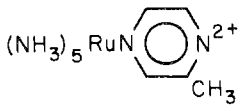
Table VII. Reaction of 3-Picoline with $(NH_3)_5RuOH_2^{2+}$[a]

Temp, °C	10^2[3-pic], M	10^2[3-picH$^+$], M	$10^2k_{3\text{-pic}}$,[b] M^{-1} sec^{-1}
35.0	0.281	1.00	22.6 ± 0.5 (2)
25.0	1.00	1.00	9.1 ± 0.3 (3)
25.0	0.281	1.00	8.5 (1)
15.0	3.00	3.00	3.15 ± 0.2 (3)

[a] $\mu = 0.10$ (LiCl); λ 404 nm; [Ru(II)] = 5.00×10^{-5} M; Ru(II) prepared using Zn(Hg) as reductant. [b] Figures in parentheses are the number of replicate experiments.

2-Picoline and 2-Methylpyrazine as Ligands. In one experiment with the concentrations of 2-picoline, 2-picolinium ion, and $(NH_3)_5RuOH_2^{2+}$ as 1.0×10^{-4}, 1.05×10^{-3} and 9.5×10^{-4} M, a peak at 375 nm slowly developed eventually shifting toward 370 nm. The shift is presumably caused by the onset of secondary reactions. To bring the reaction to an earlier terminus, thus avoiding secondary reactions, it seemed advisable to follow the rate by the competition method. A solution was prepared 0.10 M in 2-picoline, 0.10 M in 2-picolinium ion, 1×10^{-4} M in pyridine, and 6.65×10^{-4} M in $(NH_3)_5RuOH_2^{2+}$. Peaks developed at both 375 and 408 nm, the latter being characteristic of the pyridine complex. The specific rate of reaction of 2-picoline with $(NH_3)_5RuOH_2^{2+}$ was determined by this method as approximately 3×10^{-3} M^{-1} sec^{-1} at 25.0°.

The results with 2-picoline prompted investigation of the 2-methylpyrazine system where internal competition for the sterically hindered and unhindered ends of the molecule could be studied. Based on a −4-nm shift in λ_{max} for meta methyl ring substitution and −33-nm shift for ortho methyl substitution on pyridine, determined in this work, one would expect the product spectrum for 2-methylpyrazine reacting with $(NH_3)_5RuOH_2^{2+}$ to have maxima at 468 and 429–439 nm for coordination at the unhindered end and hindered end of the molecule, respectively. A single maximum at 467 nm was observed suggesting that the unhindered end reacts at a rate advantage so great that at most a few per cent of the alternative product is formed. This result is in agreement with the 30-fold reduction in rate of substitution found for 2-picoline relative to pyridine. The specific rate of formation of



was observed to be 5.0×10^{-2} M^{-1} sec^{-1}.

2,6-Lutidine as Ligand. When ultrapure 2,6-lutidine was added to a solution of $(NH_3)_5RuOH_2^{2+}$, no charge-transfer

absorption was observed in the region including the visible and extending to the cutoff in the uv imposed by the free ligand. An effort was made to detect the existence of an inner-sphere complex and to measure the rate of complex formation with 2,6-lutidine by the competition method using pyrazine as the indicator ligand. The relevant data are summarized in Table VIII. The data have been treated in accordance with the mechanism consisting of equations 6-8.

$$(NH_3)_5RuOH_2^{2+} + lu \rightarrow (NH_3)_5RuOH_2^{2+}\cdot lu \quad (K_{OS} \text{ rapid equil}) \quad (6)$$

$$(NH_3)_5RuOH_2^{2+} + lu \rightarrow \text{colorless products} \quad (7)$$

$$(NH_3)_5RuOH_2^{2+} + pz \rightarrow (NH_3)_5Ru(pz)^{2+} + H_2O \quad (k_{pz}) \quad (8)$$

Equilibrium 6 accounts for the fact that when 2,6-lutidine is added to a mixture of $(NH_3)_5RuOH_2^{2+}$ and pyrazine, the half-life for the formation of the pyrazinium complex increases rather than decreases (*cf.* Appendix). Reaction 7 accounts for the fact that in mixtures containing both bases, not all of the Ru(II) appears as the pyrazinium complex.

According to this mechanism, k_{obsd} takes the form

$$\frac{1}{1 + K_{OS}[lu]}(k_{pz}[pz] + k_7[lu])$$

leading to

$$\frac{k_{pz}[pz]}{Z} = 1 + K_{OS}[lu] \quad (9)$$

where

$$Z = k_{obsd} - \frac{k_7[lu]}{1 + K_{OS}[lu]}$$

The data on product analysis indicated for k_7 the value $4.3 \times 10^{-5}\ M^{-1}\ sec^{-1}$. This in turn leads to K_{OS}(at 25°) = 0.33 on plotting the data according to eq 9. K_{OS} was first estimated and its true value was sought by repeated approximations until linear agreement was achieved. Only three reiterations were necessary. At other temperatures, the parameter K_{OS} was evaluated from data solely at 1.00 *M* lu, the highest value of ligand concentration used in our studies, leading to values of 0.31 at 20° and 0.26 at 34.5°.

It is, of course, by no means certain the K_{OS} really represents outer-sphere association of Ru(II) with the ligand lu, and conceivably we are dealing with a medium effect. Our interpretation is bolstered by the work of Toma and Malin,[20] who found evidence for strong outer-sphere association between $(NH_3)_5RuOH_2^{2+}$ and *p*-$NC_4H_4NCH_3^+$.

Even at 1.00 *M* lu and with [pz] at 1.0×10^{-2} *M*, the difference between $[Ru(II)]_0$ and $[Ru^{II}\text{-pz}]_\infty$ is not large—*e.g.*, 5.00×10^{-5} *M* for $[Ru(II)]_0$ compared to 4.65×10^{-5} *M* for the pyrazine complex (mean of four experiments at 25°). If the difference is attributed to the formation of the complex, this comparison shows at once that its formation is very slow compared to that of the pz complex, even with this great disparity in concentrations. The experiments to be outlined show that at most only *ca.* 50% of the defect (0.35×10^{-5} out of 5.00×10^{-5}) can be attributed to the inner-sphere complex of lu with Ru(II) and that allowance must be made for the formation of Ru(III) in the system. By using Eu^{2+} to reduce Ru(III) to Ru(II) and waiting for the full development of absorption due to $(NH_3)_5Ru(pz)^{2+}$, from 35 to 75% of the "missing" Ru(II) was uncovered. The balance of the "missing" ruthenium, say 50% on the average, is attributable to $(NH_3)_5Ru(lu)^{2+}$, but even this must be considered to be an upper limit because still other forms of ruthenium may contribute to the products. In any case, the value for k_7 of $4.3 \times 10^{-5}\ M^{-1}\ sec^{-1}$ at 25° is to be regarded as a generous upper limit for k_{lu}, the specific rate of the formation of an inner-sphere complex, the actual value at most being only half as great.

Table VIII.[a] Competition Studies for $(NH_3)_5RuOH_2^{2+}$ in Solutions Containing both 2,6-Lutidine and Pyrazine

[lu],[a] *M*	$10^4 k_{obsd}$, sec^{-1}	Z[b]	$k_{pz}[pz]/Z$
0.00	2.82	2.82	1.000
0.25	2.75	2.65	1.063
0.50	2.59	2.40	1.175
0.50	2.57	2.38	1.185
0.50	2.69	2.50	1.129
1.00	2.66	2.23	1.265
1.00	2.51	2.18	1.292
1.00	4.69	4.36	1.291
1.00	4.46	4.13	1.365
1.00	4.58	4.25	1.325

[a] At 25°; $\mu = 0.50$; $[Ru(II)] = 5.00 \times 10^{-5}$ *M*; $[pz] = 5.00 \times 10^{-3}$ *M*, except in last three experiments where it is 1.00×10^{-2} *M*. [b] See accompanying text for definition of *Z*.

The observations just described arouse the suspicion that no direct inner-sphere union of $(NH_3)_5RuOH_2^{2+}$ with lu takes place. The experiments to be described indicate that such a combination does in fact form in solutions of the kind which have been dealt with.

To 10 ml of a solution prepared by dissolving 0.100 g of $(NH_3)_5RuCl_3$ and adding enough AgO_2CCF_3 to remove free chloride, an equal volume of ultrapure lu was added. The solution was purged of O_2 by a stream of Ar; Zn-Hg chips were added and the solution was left in a sealed vessel for 24 hr, protected from light. The product solution was charged on the top of a cation-exchange column shielded from light, and cationic species were eluted with solutions of sodium chloride, of successively increasing strength. The different fractions were examined spectrophotometrically.

The results are summarized in Table IX. The species showing strong absorption at ~260-265 nm presumably owes this band to lu, contained in species of ionic charge 2+ or 3+. The bands show fine structure not characteristic of lu or luH^+, and this rules out the possibility, remote in any case, that on increasing the concentration of NaCl, lu trapped on the resin continues to be eluted. The results are of qualitative rather than quantitative significance—concentrations of the various species were not determined—but do show that lu enters into substitution-inert binding with Ru(II).

The blue-green species, which we represent as $[(NH_3)_3RuCl_3Ru(NH_3)_3]^{2+}$ on the basis of information supplied by Stritar,[24] appeared to be the major product. The formation of such species places some limitations on the study of a complex such as $(NH_3)_5Ru(lu)^{2+}$, which forms extremely slowly. The complications from the side reaction in question become even more severe at higher concentrations of Ru(II).

Nitriles as Ligands. According to reports by Allen and Ford,[6] CH_3CN reacts with $(NH_3)_5RuOH_2^{2+}$ several times more rapidly than does a ligand such as pyridine. This feature and the added one that CH_3CN is miscible with water in all proportions prompted us to turn to this ligand for the purpose of ascertaining whether departures from linearity in the rate as a function of [ligand] could be observed. If reaction proceeds *via* an SN1 mechanism, at sufficiently high concentration of the ligand, the rate will become independent of this variable.

(24) J. A. Stritar, private communication. The species of this type are well described in the literature: R. E. Mercer and P. E. Dumas, *Inorg. Chem.*, 10, 2755 (1971).

Table IX. Ion Exchange of 2,6-Lutidine Reaction Products with Aquopentaammineruthenium(II)

Color	λ_{max}, nm	[NaCl] in eluting soln, M	Assignment of species
Colorless	263	0.00–0.10	2,6-Lutidine and 2,6-lutidinium ion
Blue-green	297	0.20	$(NH_3)_3RuCl_3Ru(NH_3)_3^{2+}$
Colorless	265–260	0.20	$(NH_3)_5Ru(lu)^{2+}$
Red	505	0.50	?
Colorless	260	0.50–1.00	$(NH_3)_5Ru(lu)^{3+}$

Our data on this system are summarized in Table X. The experiment at highest concentration of ligand, far from showing a decrease in the second-order specific rate, actually shows an increase. General medium effects apparently obscure whatever effect might be felt from rate saturation.

In the hope of providing more effective competition for the presumed intermediate we turned to cyanoacetate as the entering ligand, relying on the negative charge to provide for more efficient competition for an intermediate than is the case for the neutral ligand, CH_3CN. Only a few experiments were done, these being reported in Table XI.

The specific rate for the reaction of $CNCH_2CO_2^-$ with $(NH_3)_5RuOH_2^{2+}$, though higher than that for CH_3CN, is not so much greater as to offer promise of leading to an estimation of the "saturation" rate. In this system, both partners are charged; as a result, effects due to changes in the medium will be relatively large, and small deviations in the rate from being first order in [ligand] will not be interpretable without ambiguity.

Imidazole as Ligand. Visual experiments suffice to show that imidazole reacts with $(NH_3)_5RuOH_2^{2+}$. When a solution of the Ru(II) complex is added to 0.01 M imidazole–0.01 M imidazolium ion, the faint yellow color of $(NH_3)_5RuOH_2^{2+}$ gradually fades. It was shown by titration that Ru(II) is conserved in the course of the reaction leading to the color change described.

The rate at which imidazole converts $(NH_3)_5RuOH_2^{2+}$ to a complex was measured directly and also by using pyrazine as a competition reagent. In contrast to most of the heterocyclic ligands reported on thus far, the ruthenium(II)–imidazole complex does not absorb in the visible region of the spectrum and for the direct measurement of the rate of the reaction, the wavelength selected was 280 nm. The kinetic data on the reaction are summarized in Table XII.

The specific rates by the direct and competition methods are in reasonable though not perfect agreement. The data based on the competition experiments yield for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the values 16.5 ± 0.5 kcal mol^{-1} and −6.5 ± 2 cal mol^{-1} deg^{-1}.

The value of pK for imidazolium ion is 7.0, and thus at a pH of less than 5, the ion rather than the free base is the dominant form of the ligand. In a series of experiments with [imzH$^+$] at 9.9 × 10^{-2} M, [Ru(II)] = 2.00 × 10^{-4} M, μ = 0.10, T = 25.0°, and pH 5.1, 3.0, and 2.0, the first order specific rate for the consumption of $(NH_3)_5RuOH_2^{2+}$ was calculated to be 2.78 × 10^{-3}, 2.67 × 10^{-3}, and 2.68 × 10^{-3} M^{-1} sec^{-1}, respectively. The protonated form is less reactive than the free base by a factor of only about 70.

The state of protonation of the imidazole complex is a matter of some importance. An investigation of the absorption spectrum shows that it is independent of pH over the range of 3 to in excess of 7. Over this range, the spectrum features a double maximum on the near-uv region: 255 nm (ϵ 2.52 × 10^3 M^{-1} cm^{-1}), 280 nm (ϵ 2.51 × 10^3 M^{-1} cm^{-1}). At pH 7.9, absorption is significantly enhanced at <260 nm, though the spectrum at longer wavelengths is little altered. Whatever the state of protonation of the coordinated ligand, it is unchanged over a wide range of pH. Nmr measurements show that in the complex as described, Ru(II) is bound to N. It seems reasonable to suppose that the binding site is the same as that occupied by the proton in the imidazolium ion and, on this basis, also reasonable to suppose that the Ru(II) complex over the pH range specified exists as a dipositive ion. This conclusion, tentative on the basis of the evidence adduced here, has been confirmed in subsequent work. The shift in spectrum at pH >9 can be understood as arising from partial deprotonation of the coordinated ligand.

Table X. Substitution of Acetonitrile on $(NH_3)_5RuOH_2^{2+}$ [a]

Temp, °C	10^2[CH_3CN], M	$10^2 k_{CH_3CN}$, [b] M^{-1} sec^{-1}
25.0	0.185	29.5 ± 1 (4)
25.0	0.370	30.1 ± 1 (3)
25.0	263.5	34.0 ± 0.7 [c] (1)
34.7	0.148	75.1 ± 1 (3)
15.0	0.370	11.6 ± 0.2 (2)
5.4	2.22	4.27 ± 0.1 (3)

[a] μ = 0.10 LiCl; λ 229 nm; [Ru(II)] = 5.00 × 10^{-5} M. [b] Figures in parentheses represent the number of experiments. [c] Stopped-flow experiment.

Table XI. Reaction of Cyanoacetate Ion with $(NH_3)_5RuOH_2^{2+}$

Temp, °C	10^2[ligand], M	10^2[LiCl], M	k, M^{-1} sec^{-1}	Method
25.0	9.89	0.11	1.21	Flow [a]
25.0	0.100	9.90	1.04	*b*
32.9	9.89	0.11	2.37	Flow [a]

[a] μ = 0.10; λ 231 nm; [Ru(II)] = 6.5 × 10^{-5} M. [b] μ = 0.10, λ 229 nm, [Ru(II)] = 5.0 × 10^{-5} M.

Experiments were done to measure the reduction potential for the $(NH_3)_5Ru(imz)^{3+,2+}$ couple. The formal redox potential (pH 5, μ = 1.0 (NaCl)) at 25° was measured as 0.17 V.

Substitution of NCS$^-$ on $(NH_3)_5RuOH_2^{2+}$. Armor[25] has characterized the linkage isomers for NCS$^-$ bound to $(NH_3)_5Ru^{III}$. That $(NH_3)_5Ru^{II}$ binds NCS$^-$ was shown by oxidizing a solution (using $(NH_3)_5Ru(imz)^{3+}$ as oxidant) containing NCS$^-$ and $(NH_3)_5RuOH_2^{2+}$. The color of the Ru(III) complex is produced on a time scale much shorter than that required for substitution by NCS$^-$ on $(NH_3)_5RuOH_2^{3+}$.[26] In competition experiments done by adding $(NH_3)_5RuOH_2^{2+}$ to a mixture of NCS$^-$ and pz, it was found that only a part of the Ru(II) is converted to the pyrazine complex. The competition experiments do not take a simple course, at least in using a spectrophotometric method for following rates, and departures from pseudo-first-order behavior appear soon after the reactions are under way. Initial rate measurements point to a value of *ca.* 4 M^{-1} sec^{-1} for the specific rate at which NCS$^-$ converts $(NH_3)_5RuOH_2^{2+}$ to a complex. After the initial phase of the reaction which is quite rapid, slow growth in the formation of $(NH_3)_5Ru(pz)^{2+}$ continues, and this may be due to the dissociation of the Ru^{II}–NCS$^-$ complex followed by the aquo ion then being converted to the pyrazine complex.

Summary of Spectra. For ready reference, absorption maxima and extinction coefficients for the complexes dealt with in this study are summarized in Table XIII.[19,27-30]

(25) J. N. Armor, private communication.
(26) C. Kuehn, private communication.
(27) C. Creutz, Ph.D. Thesis, Stanford University, 1970.
(28) M. Abe and H. Taube, unpublished observations.
(29) J. Armor, private communication.
(30) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 9, 227 (1970).

Table XII. Reaction of Imidazole with $(NH_3)_5RuOH_2^{2+}$ [a]

Temp, °C	10^4[Ru(II)], M	10^2[pz], M	10^2[imz], M	$10^4 k_{obsd}$, sec^{-1}	k_{imz}, M^{-1} sec^{-1}
25.0	0.50	1.00	0.500	15.2	0.192 (1)
25.0	1.50	1.00	1.00	25.4	0.198 (1)
25.0	1.50	1.00	0.75	19.8	0.190 (1)
25.0	1.50	1.00	*d*		0.201 ± 0.014 (5)[c]
25.0	2.00	0.00	1.00	22.7 ± 0.2	0.227 ± 0.002 (2)[b]
15.0	1.50	1.00	0.500	5.47 ± 0.2	0.0704 ± 0.003 (4)
5.0	1.50	3.00	1.50	5.58 ± 0.1	0.0254 ± 0.0005 (2)
5.0	1.50	3.00	1.50		0.0254 ± 0.0018 (2)[c]

[a] $\mu = 0.10$ (LiCl); [imz] = [imzH$^+$]; λ 472 nm except as denoted by *b*; figures in parentheses denote the number of replicate experiments. [b] Direct rate measurement; λ 280 nm. [c] Done making use of data on product composition and the known value of k_{pz}. [d] Above three runs and two others at 5.00×10^{-3} and 1.00×10^{-2} M imz with Cr(II) present to reduce $(NH_3)_5RuCl_3$; [Cr(II)]/[Ru(III)] = 3.10.

Table XIII. Spectral Properties of Pentaammineruthenium(II) Complexes

Complex	λ,[b] nm	ε, M^{-1} cm^{-1}	Ionic medium	Ref[a]
$(NH_3)_5Ru(pz)^{2+}$	472	1.34×10^4	0.10 M LiCl	
	470	1.33×10^4	BF_4^- salt in H_2O	27
$(NH_3)_5Ru(py)^{2+}$	408	7.77×10^3	0.10 M LiCl	
$(NH_3)_5Ru(3\text{-pic})^{2+}$	404	7.92×10^3	0.10 M LiCl	
$(NH_3)_5Ru(2\text{-pic})^{2+}$	~370	~2.0×10^4	0.10 M 2-pic·HCl	
$(NH_3)_5Ru(2\text{-mepz})^{2+}$	468	1.36×10^4	0.10 M LiCl	
$(NH_3)_5Ru(isoam)^{2+}$	478	1.19×10^4	0.10–0.50 M LiCl or NaCl	
		1.14×10^4	0.10 M LiCl as ClO_4^- salt	
		1.05×10^4	0.10 M $HClO_4$	19
		1.10×10^4	1.00 M $HClO_4$	28
		1.17×10^4	0.001 M HCl	29
$(NH_3)_5Ru(NCCH_3)^{2+}$	229	1.53×10^4	0.10 M LiCl	
	229	1.55×10^4	ClO_4^- salt in H_2O	30
$(NH_3)_5Ru(NCCH_2CO_2)^+$	231	1.53×10^4	0.10 M LiCl	
$(NH_3)_5Ru(lu)^{2+}$	260		0.50 M NaCl	
$(NH_3)_5Ru(imz)^{2+}$	255	2.52×10^3	0.10 M LiCl	
	280	2.51×10^3	0.10 M LiCl	

[a] Present work unless otherwise indicated. [b] Precision of values of ε are ±0.03 unit when they are greater than 10^4, ±0.05 unit when they are of the order of 10^3; for 2-picoline, ±0.1, maximum error at 50% confidence limit.

Table XIV. Summary of the Kinetic Data on Complex Formation[a] with $(NH_3)_5RuOH_2^{2+}$

Ligand	k_L,[c] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	Ref[b]
Pyridine	9.3×10^{-2}	16.9 ± 0.3	−6.6 ± 1.1	
Pyridine	9.1×10^{-2}	15.3 ± 0.2	−12 ± 1	6
Pyridinium ion	3.1×10^{-3}	16.9	−13	
Ammonia	5.5×10^{-2}			
Pyrazine	5.6×10^{-2}	17.5 ± 0.2	−5.7 ± 1	
Isonicotinamide	10.5×10^{-2}			
Isonicotinamide (protonated)	3.6×10^{-3}			
3-Picoline	9.1×10^{-2}	16.9 ± 0.7	−6.7 ± 2.4	
2-Picoline	~3×10^{-3}			
3-Methylpyrazine	5.0×10^{-2}			
2,6-Lutidine	<4.3×10^{-5}			
Acetonitrile	30.2×10^{-2}	16.1 ± 0.4	−6.9 ± 1.4	
Acetonitrile	26.2×10^{-2}	16.2 ± 0.6	−7 ± 2	6
Cyanoacetate ion	1.2	15	−8	
Imidazole	2.0×10^{-1}	16.5 ± 0.5	−6.5 ± 2	
Imidazolium ion	2.7×10^{-3}			
NCS^-	4.0			
N_2	7.1×10^{-2}	18.3 ± 0.3	−2.4 ± 1	15
N_2O	7.2×10^{-2}	17.6 ± 0.7	−5 ± 2	3
CO	~12×10^{-2}			31

[a] At 25° and $\mu = 0.10$ for present work. [b] Present work unless otherwise indicated. [c] Precision of measured rate constants ±5%; see text, with the exception of 2,6-lutidine (50%) and 2-picoline (10%).

Discussion

The kinetic data obtained in this study are summarized in Table XIV.[3,6,15,31] The data show that for a wide variety of neutral unhindered ligands the rates of substitution on $(NH_3)_5RuOH_2^{2+}$ vary only over a very small range, from 0.05 to 0.30 M^{-1} sec^{-1} at 25°. The activation parameters are likewise rather uniform for the class of ligands under discussion. These observations are consistent with the view that activation for substitution is largely a bond-breaking process and that a dissociative mechanism operates. Arguments supporting the view that a square-pyramidal intermediate is involved in the stepwise substitution of pyridine on either cis or trans diaquoruthenium(II) have been advanced by Ford and Sutton.[32]

On the basis of an SN1 mechanism

$$(NH_3)_5RuOH_2^{2+} \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} (NH_3)_5Ru^{2+} + H_2O \quad (10)$$

$$(NH_3)_5Ru^{2+} + L \xrightarrow{k_{11}} (NH_3)_5RuL^{2+} \quad (11)$$

the rate law for the reaction becomes

$$d[Ru^{II}L]/dt = \frac{k_{10}k_{11}[L][RuOH_2^{2+}]}{k_{-10}[H_2O] + k_{11}[L]} \quad (12)$$

where we must suppose that under our conditions $k_{-10}[H_2O] \gg k_{11}[L]$. The activation energy corresponding to k_{-10} and k_{11} is in all likelihood much the same and thus the activation energy for the reactions, *ca.* 17 kcal mol^{-1}, comes close to measuring the activation energy for step 10.

Efforts were made in the course of this research to reach saturation rates, *i.e.*, to arrange conditions so that $k_{11}[L]$ would become significant compared to $k_{-10}[H_2O]$, which would make it possible to determine k_{10}. These efforts were unsuccessful. This is not surprising if the intermediate is very unstable and reacts extremely rapidly. In solutions dilute enough to keep general solvent effects constant, the solvent is much more abundant than solute and thus $k_{-10}[H_2O]$ is expected to be much greater than $k_{11}[L]$ unless some very special effects are operating.

An estimate of k_{10} can be made by assuming that the ratio of the specific rate of water exchange compared to that for substitution in other dipositive ions is the same as it is for $(NH_3)_5RuOH_2^{2+}$. Nickel(II), with pyridine as entering group, serves for the purposes of comparison. The ratio of the specific rate for water exchange[33] (sec^{-1}) compared to the specific rate of formation of the pyridine complex[34] (M^{-1} sec^{-1}) is 5, but when the latter is expressed in terms of replacement of coordinated water, rather than conversion of $Ni(H_2O)_6^{2+}$ to $(H_2O)_5Ni(py)^{2+}$, the ratio be-

(31) D. E. Harrison, Ph.D. Thesis, Stanford University, 1968.

(32) P. C. Ford and C. Sutton, *Inorg. Chem.*, 8, 1544 (1967).

(33) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

(34) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).

comes 30. Applying this ratio to the specific rate measured for py replacing H_2O in $(NH_3)_5RuH_2O^{2+}$, k_{10} is estimated as 2.7 sec^{-1}. Thus the rate of water loss is 40 times slower than the slowest first row 2+ ion vanadium(II).[35]

For most of the neutral ligands, the rates are so nearly alike that a very highly refined theory would be required to account for the small differences which do exist. The only large rate effect exposed by the data on the neutral ligands is that due to steric hindrance. The rates of substitution for pyridine, 2-methylpyridine, and 2,6-dimethylpyridine are in the ratio $1:3 \times 10^{-2}:<5 \times 10^{-4}$. Placing a negative charge on the ligand does increase the rates significantly, by a factor of 4 for cyanoacetate compared to acetonitrile.

The role played by the proton in the substitution process merits comment. According to the mechanism comprising eq 10 and 11, when $k_{-10}[H_2O] \gg k_{11}[L]$ –and this condition is met by all the systems studied–the intermediate is in equilibrium with $(NH_3)_5RuOH_2^{2+}$ and the solvent. Thus, although protons probably labilize H_2O, just as they do NH_3 or py in the coordination sphere of Ru(II), this cannot increase the rate of reaction by the path under discussion. In explaining the assistance by protons in releasing NH_3 or py from the coordination sphere or Ru(II), the suggestion has been made[4] that the proton acts by adding to a pair of πd electrons, thus forming a seven-coordinated intermediate which is more labile than the octahedral πd^6 system. Pursuing this suggestion and applying it to the reverse reaction, the mechanism for the process corresponding to the rate term $k[Ru(II)][pyH^+]$ becomes

$$pyH^+ \rightleftarrows py + H^+ \quad (13)$$

$$(NH_3)_5RuOH_2^{2+} + H^+ \rightleftarrows (NH_3)_5Ru(H_2O)H^{3+} \quad (14)$$

$$(NH_3)_5Ru(H_2O)H^{3+} \rightleftarrows (NH_3)_5RuH^{3+} + H_2O \quad (15)$$

$$(NH_3)_5RuH^{3+} + py \rightleftarrows (NH_3)_5Ru(py)H^{3+} \quad (16)$$

$$(NH_3)_5Ru(py)H^{3+} \rightarrow (NH_3)_5Ru(py)^{2+} + H^+ \quad (17)$$

Reactions 13–16 have been represented as rapid equilibria.

Since reactions 13–16 are rapid equilibria preceding the rate-determining step, the succession of events leading to the accumulation of the atoms needed for the activated complex cannot be specified from the kinetic data alone. A detailed mechanism has however been written to make explicit the proposal that species of coordination number 7, $(NH_3)_5Ru(H_2O)H^{3+}$ and $(NH_3)_5Ru(py)H^{3+}$, are being postulated as intermediates. The rate law is the same whether reaction 16 or 17 is written as being rate determining.

The mechanism does not provide an obvious explanation of a very striking feature of the data, namely, that the specific rates for the reactions of pyH^+, $isoamH^+$, and $imzH^+$ are so nearly alike–thus 3.1×10^{-3}, 3.6×10^{-3}, and 2.7×10^{-3} M^{-1} sec^{-1}. Since the data are sparse, the uniformity of the values can still be ascribed to coincidence. It appears in fact that the pattern is not general for nitrogen bases. Equilibrium data combined with the known rate[4] for the loss of NH_3 from $Ru(NH_3)_6^{3+}$ under the influence of H^+ ($k = 1.3 \times 10^{-3}$ M^{-1} sec^{-1}) leads to an estimate of the specific rate for the reaction

$$(NH_3)_5RuOH_2^{2+} + NH_4^+ = (NH_3)_6Ru^{2+} + H^+ + H_2O$$

as of the order of 10^{-9} M^{-1} sec^{-1}, markedly different from the values just cited. It is still possible however, that the reactions with ligands featuring an unsaturated nitrogen atom form a separate class.

In earlier work, it was proposed that the rate law for the acid-promoted release of py from $(NH_3)_5Ru(py)^{2+}$ has the form

$$k_{obsd} = k_{-1}[H^+] + \frac{k_{-2}[H^+]}{1 + a[H^+]}$$

In the present study, the second term of the rate law was found to be less prominent than in the earlier. The irreproducibility already makes it doubtful that the term is real and the following analysis confirms the suspicion that it is an artifact.

If reaction 18

$$(NH_3)_5RuOH_2^{2+} + pyH^+ = (NH_3)_5Ru(py)^{2+} + H^+ + H_2O \quad (18)$$

in the reverse direction is governed by the rate law above, then the rate law for the forward reaction must take the form

$$d[(NH_3)_5Ru(py)^{2+}]/dt = [(NH_3)_5RuOH_2^{2+}][pyH^+]\left(k_1 + \frac{k_2}{1 + a[H^+]}\right)$$

and

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}}$$

Taking the second term to be real, k_{-2} and a can be evaluated from the data on the reverse reaction as 1.6×10^{-4} M^{-1} sec^{-1} and 21.3 M^{-1}, respectively. Using now the known value of K_{eq}, k_2 is calculated as being 9.6×10^{-3} $M^{-1}sec^{-1}$. Taking account of the range of $[H^+]$ covered by our studies, the smallest contribution the k_2 path could make to k_{pyH} is 3.7×10^{-3} M^{-1} sec^{-1}, which is larger than the value of the specific rate observed. In addition the kinetic data on the forward reaction give no hint of a term corresponding to saturation effect on $[H^+]$.

The origin of the residual apparent saturation effect is obscure. It may be caused by the slight difference in ϵ for $(NH_3)_5Ru(py)^{2+}$ and $(NH_3)_4(H_2O)Ru(py)^{2+}$. More likely, it is caused by some aspects of the kinetic behavior which are not yet understood. This suspicion is strengthened by the fact that deviations from the rate law

$$d[(NH_3)_5Ru(py)^{2+}]/dt = k[(NH_3)_5RuOH_2^{2+}][pyH^+]$$

were recorded at the highest concentrations of acid (it should be noted that they were not of the form expected for a "saturation" term).

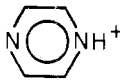
The values of the equilibrium constants for the association of py and NH_3 with Ru(II) make it possible to estimate the extra stability gained in the Ru(II)-py interaction from the fact that py is a π acid. The equilibrium constants governing the association for py and NH_3 are 2.4×10^7 and 3.5×10^4, respectively, at 25°, making allowance for the statistical factor. (The equilibrium described by reactions 3 and 4 should be approximately independent of ionic strength from $\mu = 0.10$ to $\mu = 0.50$.) In the absence of back-bonding, the affinity of NH_3 for a dispositive metal ion is expected to be greater than that of py. In fact, for the ions Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} the ratios of the formation constants for the ammine complex compared to the pyridine complex are 5, 7, 8, 30, 6, and 17, respectively, the geometric mean being 10. Ligand field effects also must be taken into account, but since the ligand field strengths of NH_3 and py in the absence of back-bonding are nearly the same, no large correction needs to be applied. Therefore the extra stabilization of the Ru(II)-py interaction arising from back-bonding is measured by the factor $10K_{(NH_3)_5Ru(py)}/K_{(NH_3)_6Ru}$ or 7×10^3. This converts to ~5.0 kcal mol^{-1} as a free energy quantity.

(35) M. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

An estimate can also be made by comparing the values of E° for the $(NH_3)_5RuNH_3^{3+,2+}$ and $(NH_3)_5Ru(py)^{3+,2+}$ couples. If it is assumed that back-bonding is insignificant in Ru(III) and that the differences between the affinities of NH_3 and py in respect to σ-bond interactions on Ru(II) and Ru(III) cancel (this is approximately true–*vide infra*), then the change in E° for the two couples on replacing NH_3 by py reflects the stabilization of Ru(II) by py due to back-bonding. This then leads to an estimate of 5.8 kcal mol^{-1} as the contribution to the free energy of association ascribable to back-bonding.

The stabilization of the Ru(II)-py bond by back-bonding calculated by Zwickel and Creutz on the basis of their theoretical treatment is 3.4 kcal mol^{-1}.[36] Considering the approximate nature of the experimental and theoretical approaches, the agreement between the three methods is satisfactory. The approximate value of 5 kcal mol^{-1} does of course not measure the strength of the π bond. Owing to the interaction between the σ and π components of the bond, only the total effect of allowing back-bonding to enter can be estimated by the two experimentally based methods which have been used.

It is interesting that the affinity of the ligands NH_3, pyridine, and isonicotinamide for Ru(II) increase in the order given, which is just the reverse of the order of their affinity for H^+. In this context it should be noted that the 100-fold increase[7] in basicity to H^+ of pyrazine when it associates with Ru(II) implies that the ion



has a 100-fold greater affinity for Ru(II) than does

Apparently, the greater back-bonding interaction for the ion compared to that for the neutral base again more than compensates for the diminished σ-bond basicity for the ion compared to the base.

Now that the equilibrium constants for the association of NH_3 and of py with $(NH_3)_5RuOH_2^{2+}$ and the values of E° for the couples $(NH_3)_5RuOH_2^{3+,2+}$, $(NH_3)_6Ru^{3+,2+}$, and $(NH_3)_5Ru(py)^{3+,2+}$ (0.16,[16] 0.10,[16] 0.35,[37] respectively[38]) are known, the values of the equilibrium constants for the reactions

$$(NH_3)_5RuOH_2^{3+} + py = (NH_3)_5Ru(py)^{3+} + H_2O \quad (19)$$

$$(NH_3)_5RuOH_2^{3+} + NH_3 = (NH_3)_6Ru^{3+} + H_2O \quad (20)$$

can be calculated. They are 1.5×10^4 and 6.1×10^4 for reactions 19 and 20, respectively. Again, for the purposes of comparison, the latter must be multiplied by a statistical factor of 6. For dipositive ions which lack the capacity to enter into back-bonding interactions, the affinity ratio for NH_3 compared to py is *ca.* 10; for Ru(III), it is seen to be 25, with the NH_3 again showing the stronger affinity. Data on the affinity of relatively strong bases such as NH_3 or py for tripositive transition metal ions are difficult to obtain by direct measurement, and few such data exist.

A point relating to the spectra of the complexes is worthy of special mention. It concerns the strong shift in the πd-π^* absorption band to shorter wavelengths attendant on methyl substitution in the 2 and 6 positions. For pyridine, 2-methylpyridine, and 2,6-dimethylpyridine, these bands are at 408, 370, and <260 nm, respectively. The effect of methyl substitution in this series appears to be too large to be ascribed to the electron-releasing properties of the methyl groups–note that for the 4-methylpyridine λ_{max} lies at 398 nm compared to 408 nm for py[7]–and a direct steric effect on the energy of the absorption band is indicated though not proven by the data. If the N-Ru bond distance is substantially greater for the hindered ligand than for pyridine, the greater charge separation in the excited state Ru^{3+},L^- would call for a greater expenditure of energy to form it.

Registry No. $(NH_3)_5Ru(pz)^{2+}$, 19471-65-9; $(NH_3)_5Ru(py)^{2+}$, 21360-09-8; $(NH_3)_5Ru(3\text{-pic})^{2+}$, 19471-57-9; $(NH_3)_5Ru(2\text{-pic})^{2+}$, 39003-88-8; $(NH_3)_5Ru(2\text{-mepz})^{2+}$, 39003-89-9; $(NH_3)_5Ru(isoam)^{2+}$, 19471-62-6; $(NH_3)_5Ru(NCCH_3)^{2+}$, 26540-31-8; $(NH_3)_5Ru(NCCH_2CO_2)^+$, 39003-92-4; $(NH_3)_5Ru(lu)^{2+}$, 39003-93-5; $(NH_3)_5Ru(imz)^{2+}$, 39003-94-6; $(NH_3)_5RuOH_2^{2+}$, 21393-88-4; $(NH_3)_3RuCl_3Ru(NH_3)_3^{2+}$, 39003-96-8; CH_3CN, 75-05-8; py, 110-86-1; 2-pic, 109-06-8; 3-pic, 108-99-6.

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Appendix

Competitive Pseudo-First-Order Reactions

Let

$$[pz], [L] \gg [M]$$

Assume

$$M + L \xrightarrow{k_L} ML \quad (A1)$$

$$M + pz \xrightarrow{k_{pz}} Mpz \quad (A2)$$

At $t = \infty$

$$[Mpz]_\infty = \frac{k_{pz}[pz][M]_0}{k_{pz}[pz] + k_L[L]} \quad (A3)$$

$$d[Mpz]/dt = k_{pz}[pz][M]_t \quad (A4)$$

and at $t = t$

$$[Mpz]_t = \frac{k_{pz}[pz]\{[M]_0 - [M]_t\}}{k_{pz}[pz] + k_L[L]} \quad (A5)$$

Solving for (5) and substitution in (4) gives

$$d[Mpz]/dt = k_{pz}[pz][M]_0 - [Mpz]_t(k_{pz}[pz] + k_L[L]) \quad (A6)$$

and (3) into (6) yields

$$d[Mpz]/dt = \{k_{pz}[pz] + k_L[L]\}\{[Mpz]_\infty - [Mpz]_t\} \quad (A7)$$

The specific rate k_{obsd} is defined as $d[Mpz]/dt([Mpz]_\infty - [Mpz]_t)$ as is given by $k_{pz}[pz] + k_L[L]$ for the appearance of Mpz.

(36) A referee has observed that any theory that would calculate a stabilization energy between 0 and 10 kcal mol^{-1} would be in "good" agreement with the experimental value.

(37) Present study.

(38) The values do not agree exactly with those reported by H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 11, 1460 (1972), but are referred to uniform conditions, different from those obtaining in the studies of Barclay and Anson. Those quoted for the aquopentaammine and hexaammine couples purport to apply at $\mu = 0$. That for the pyridine-pentaammine is based on the hexaammine as reference couple. It does involve the assumption that the change in E for the two couples as a function of ionic strength will be the same.