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Some Applications of Cyclic Voltammetry to the Reactions and Properties of Ruthenium Ammine Complexes. Reduction Potentials and Rate Studies

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Formal reduction potentials (E_f) obtained by cyclic voltammetry in aqueous solution are reported for a series of pentaammineruthenium(III) complexes, $Ru(NH_3)_5L^{3+}$, and several tetraammine complexes $Ru(NH_3)_4L_2{}^{3+}$, where L is a substituted pyridine (py–X) or an organonitrile (R–CN). The nitrile complexes display more positive E_f values than do the pyridine complexes with π-unsaturated R groups giving the largest values. Among the pyridine complexes, electron-withdrawing substituents –X increase E_f, and this trend is attributed to a combination of π- and σ-bonding effects. The CV technique is also used to measure the rates of hydration and dehydration of the carbonyl group of N-coordinated 4-pyridinecarboxaldehyde and it is demonstrated that coordination to $Ru(NH_3)_5{}^{3+}$ slows the acid-catalyzed hydration path by several orders of magnitude.

Introduction

The chemistry of ruthenium(II) and ruthenium(III) ammine complexes has proved to be an exceedingly rich area of recent exploration.[2–16] Of particular importance is the feature that the Ru(II) and Ru(III) complexes are reasonably inert to substitution of coordinated ammonias and numerous other ligands; thus valid comparisons can be made for the reactions and properties of ligands under the influence of coordination to each of these metal ions. In broad generalities, it can be stated that the low-spin d^6 Ru(II) is an especially good π-back-bonding donor metal ion with unsaturated monodentate or bidentate ligands,[9,17–21] while the d^5 Ru(III) species is a good π acceptor,[8,22] owing to the vacancy in its t_{2g} d-orbital subshell. Thus, the sharply contrasting properties of the two oxidation states and their relative substitution inertness allows placing a ligand in one environment and rapidly switching it to a significantly different environment by a simple electron transfer. Cyclic voltammetry can be exploited as a way to measure the redox potentials of the Ru(III)/Ru(II) couple[23,24] influenced by various ligand fields and as a reasonably fast probe of the reactions which occur subsequent to the electron-transfer step.[25] Described here are some related cyclic voltammetry (CV) studies of such ruthenium–ammine complexes.

Experimental Section

Materials. The syntheses of the ruthenium complexes reported in this study have been reported previously.[8,17,18,21,26] Recrystallized *p*-toluenesulfonic acid (HpTs) was used as a supporting electrolyte. The potassium *p*-toluenesulfonate (KpTs) used as a supporting electrolyte was synthesized from HpTs by neutralizing with K_2CO_3 in hot (~100 °C) aqueous solution. A slight excess of potassium carbonate was added and the solution was maintained at 100 °C for 2 h to precipitate metal hydroxide impurities which were removed by filtration. The solution was adjusted to pH 5 with HpTs and then dried in a rotary evaporator to give the white KpTs powder which was dried under vacuum overnight.

Cyclic Voltammetry. The cyclic voltammetry of various Ru(II) and Ru(III) complexes was carried out with a Chemtrix polarographic time base (Type 201) and a polarographic amplifier (Type 300) in a Tektronix 564 storage oscilloscope. The current–potential curves were recorded on a Tektronix Model C-27 oscilloscope camera. The photographs were analyzed after compensating for the residual current–potential curves at the corresponding conditions. Several scan rates were employed to ensure that potentials measured were not a function of scan rate. The electrochemical cell used was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) as a reference electrode, and platinum wire as an auxiliary electrode. The SCE was connected to the cell solution through an H-type bridge which was filled with 50% saturated KpTs solution. The working electrode was either a platinum ball electrode (PBE) or a dropping mercury electrode (DME). The drop time of the DME was 30.6 s in water when the circuit was open. Each potential scan was initiated 20.0 s after the drop-fall where the growth rate of the electrode surface area was small. All of the electrochemical data were obtained in supporting electrolyte solutions of ionic strength 0.20 M at 25.0 °C prepared from HpTs and KpTs or acetic acid–potassium acetate buffer. All solutions were deaerated with argon prior to the electrochemical measurements.

Rate Studies. First-order rate constants for reactions occurring subsequent to an electron-transfer reaction at the electrode can be obtained from the CV curves according to the method of Nicholson and Shain.[25,27–29] Cyclic voltammograms were obtained for solutions containing $\sim 1 \times 10^{-3}$ mol of the ruthenium complexes at several acid concentrations for various scan speeds (calibrated against a time mark generator). The rate constants are obtained from the ratio of the peak currents of reverse scan to those of forward scan (corrected for residual currents) for the reversible wave according to theoretical relationships.

Results and Discussion

(1) Reduction Potentials. Formal reduction potentials measured by the CV technique are listed in Table I. For the species listed, reversible behavior was concluded based on peak to peak separations between the cathodic and anodic waves of 60–75 mV, close to the Nernstian value of 57 mV. For several complexes the formal potentials measured on the present apparatus can be compared to those measured via potentiometry, polarography, and cyclic voltammetry by Lin, Barclay, and Anson.[23] Our values for the pentaammineruthenium complexes of Cl^-, H_2O, NH_3, and pyridine are within the experimental uncertainty of their values. The new E_f value (Table I) for the benzonitrile complexes differs from that of Diamond, Tom, and Taube[12] by 25 mV but the difference is sufficiently close to be perhaps the result of the different experimental conditions. There are significant differences between the new values listed and previous ones measured by a potentiometric technique[24] for the pyridine, isonicotinamide, and methyl isonicotinate complexes. However, the consistency of our results when comparison can be made to those of Lim, Barclay, and Anson[23] and of Diamond, Tom, and Taube[12] adds credibility to the new values for these couples. In agreement with previous observations,[12,23,24] a π-unsaturated ligand, L, such as substituted pyridine (pyX) leads to substantially more positive reduction potentials for the $Ru(NH_3)_5L^{3+/2+}$ couples than when L is H_2O or NH_3. Electron-withdrawing substituents (X) increase E_f. The nitrile complexes as a group display more positive E_f values than the pyridines. For the $Ru(NH_3)_5RCN^{3+/2+}$ potentials, π-unsaturated R– groups increase E_f. A particularly interesting point is that a vinyl group has an effect comparable to a phenyl group.

One might rationalize the effect of changing L on the $Ru(NH_3)_5L^{3+/2+}$ couples on the basis of several ligand properties. For example, changes in L may affect the solvation of the respective complexes. A hydrophobic pendant group should disrupt structure of the first solvation sphere. Since tripositive complexes are more strongly solvated than the corresponding dipositive complexes, more positive E_f values might be expected for ligands having hydrocarbon pendant

Table I. Formal Reduction Potentials of Ru(III)/Ru(II) Couples in Aqueous Solution by Cyclic Voltammetry

Couple	$E_f{}^a$	Medium	Ref
Aromatic Heterocycle Complexes			
$Ru(NH_3)_5py\text{-}3,5\text{-}(CH_3)_2{}^{3+/2+}$	0.255	*b*	This work
$Ru(NH_3)_5py^{3+/2+}$	0.298	*b*	This work
	0.300	*b*	21
	0.305	*c*	23
	0.42	*d*	24
$Ru(NH_3)_5py\text{-}4\text{-}CH(OH)_2{}^{3+/2+}$	0.300	*b*	This work
$Ru(NH_3)_5py\text{-}4\text{-}Cl^{3+/2+}$	0.322	*b*	This work
$Ru(NH_3)_5py\text{-}3\text{-}CONH_2{}^{3+/2+}$	0.353	*b*	This work
$Ru(NH_3)_5py\text{-}3\text{-}Cl^{3+/2+}$	0.361	*b*	This work
$Ru(NH_3)_5py\text{-}4\text{-}CONH_2{}^{3+/2+}$	0.375	*b*	This work
	0.440	*d*	24
$Ru(NH_3)_5py\text{-}4\text{-}CO_2H^{3+/2+}$	0.382	*b*	This work
$Ru(NH_3)_5py\text{-}4\text{-}CO_2CH_3{}^{3+/2+}$	0.392	*b*	This work
	0.460	*d*	24
$Ru(NH_3)_5py\text{-}4\text{-}COCH_3{}^{3+/2+}$	0.392	*b*	This work
$Ru(NH_3)_5py\text{-}4\text{-}CF_3{}^{3+/2+}$	0.394	*b*	This work
$Ru(NH_3)_5py\text{-}4\text{-}CHO^{3+/2+}$	0.409	*b*	This work
$Ru(NH_3)_5py\text{-}3,5\text{-}Cl_2{}^{3+/2+}$	0.421	*b*	This work
$Ru(NH_3)_5pyr^{3+/2+}$	0.490	*e*	23
trans-$Ru(NH_3)_4(py)_2{}^{3+/2+}$	0.494	*b*	This work
cis-$Ru(NH_3)_4(py)_2{}^{3+/2+}$	0.505	*b*	This work
Organonitrile Complexes			
$Ru(NH_3)_5NCCH_3{}^{3+/2+}$	0.426	*b*	This work
$Ru(NH_3)_5NCCH_2CH_3{}^{3+/2+}$	0.420	*b*	This work
$Ru(NH_3)_5NCCH{=}CH_2{}^{3+/2+}$	0.512	*b*	This work
$Ru(NH_3)_5NCPh\text{-}4\text{-}CH_3{}^{3+/2+}$	0.475	*b*	This work
$Ru(NH_3)_5NCPh^{3+/2+}$	0.485	*b*	This work
	0.510	*f*	12
$Ru(NH_3)_5NCPh\text{-}4\text{-}Cl^{3+/2+}$	0.505	*b*	This work
$Ru(NH_3)_5NCPh\text{-}3\text{-}CN^{3+/2+}$	0.543	*b*	This work
$Ru(NH_3)_5NCPh\text{-}4\text{-}CN^{3+/2+}$	0.609	*b*	This work
cis-$Ru(NH_3)_4(NCPh)_2{}^{3+/2+}$	0.867	*b*	This work
Complexes of Other Ligands			
$Ru(NH_3)_6{}^{3+/2+}$	0.050	*b*	This work
	0.051	*g*	23
	0.060	*f*	12
$Ru(NH_3)_5H_2O^{3+/2+}$	0.067	*b*	This work
	0.066	*c*	23
$Ru(NH_3)_5Cl^{2+/+}$	−0.040	*b*	This work
	−0.042	*h*	23

[a] In volts vs. the NHE; all new values reported are ±0.010 V as obtained from reversible waves from cyclic voltammetry. [b] At 25 °C, complex is ~1×10^{-3} M in an aqueous solution of 0.10 M *p*-toluenesulfonic acid/0.10 M potassium *p*-toluenesulfonate. [c] Aqueous solution of 0.1 M CF_3CO_2H/0.1 M $CF_3CO_2{}^-Na^+$; by cyclic voltammetry. [d] Measured from the potential of an equimolar Ru(II)/Ru(III) solution at a platinum electrode vs. a silver wire in 1.00 M KCl/0.001 M HCl. [e] 1 M NaCl; pyr = pyrazine. [f] 0.1 M HCl. [g] 0.1 M $NaBF_4$. [h] 0.2 M CF_3CO_2Na.

groups. However, there is no indication that this interaction has a significant effect on the couples known. The E_f values for the acetonitrile and propionitrile complexes (Table I) are within experimental uncertainty while only minor differences are observed between the couples derived from the methylamine ($L = NH_2CH_3$, $E_f = 0.10$ V) and cyclohexylmethylamine ($L = NH_2CH_2C_6H_{11}$, $E_f = 0.12$ V) complexes.[12]

Both π- and σ-bonding interactions should have significant effects on E_f, although separation of such interactions is very difficult.[20] σ-Donor and π-donor ligands should stabilize Ru(III) relative to Ru(II). Complexes where L is a π-donor ligand such as Cl^- or OH^- [23] show more negative potentials than for L = NH_3 (which cannot π bond) or H_2O (which is a poor π donor). However, these π-donor ligands are negatively charged, another feature which should stabilize the Ru(III) oxidation state. A principal rationale for the much more positive E_f values for π-unsaturated ligands derives from the relative π-acceptor ability of L,[23] which is enhanced by electron-withdrawing substituents. However, it should be noted that electron-withdrawing substituents not only enhance π back-bonding but also decrease the σ-donor ability of the ligand (e.g., free ligand pK_a's of the pyridines listed range from 0.67 to 6.1).

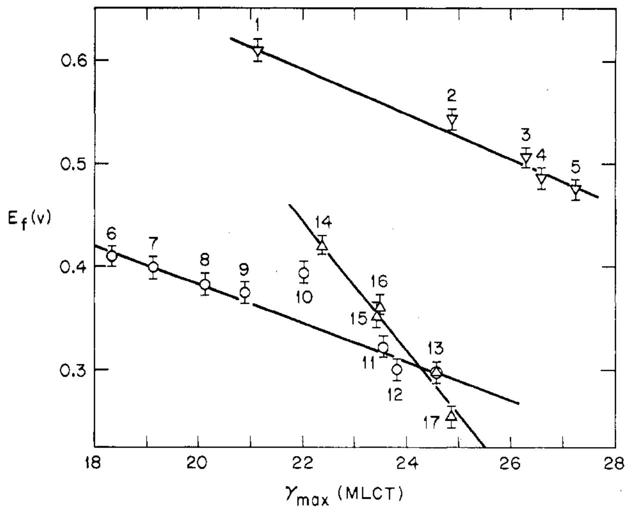
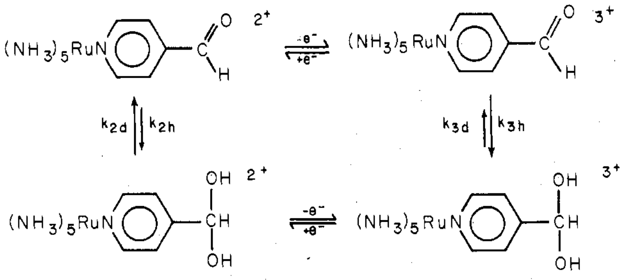


Figure 1. Plots of formal potential E_f of the $Ru(NH_3)_5L^{3+/2+}$ couples vs. the frequency of the metal-to-ligand charge-transfer band maxima for the $Ru(NH_3)_5L^{2+}$ complexes. △, L = substituted benzonitrile: 1, *p*-CN; 2, *m*-CN; 3, *p*-Cl; 4, H; 5, *p*-CH_3. ○, L = para-substituted pyridine: 6, *p*-CHO; 7, *p*-$COCH_3$; 8, *p*-CO_2H; 9, *p*-$CONH_2$; 10, *p*-CF_3; 11, *p*-Cl; 12, *p*-$CH(OH)_2$; 13, H. ▽, L = meta-substituted pyridines: 14, 3,5-Cl_2; 15, *m*-Cl; 16, *m*-$CONH_2$; 17, 3,5-$(CH_3)_2$.

The electronic spectrum of each $Ru^{II}(NH_3)_5L$ where L is a π-unsaturated ligand displays a metal to ligand charge-transfer (MLCT) absorption band.[3] Several years ago, Zwickel and Creutz[31] used the MLCT spectra to examine via a simple molecular orbital model the extent of π back-bonding between Ru(II) and pyridine ligands. Their interpretation suggested that the extent of π back-bonding is a function of the ligand substituents, owing primarily to perturbations of the lowest unoccupied pyridine π orbital (b_2 in C_{2v} symmetry). This orbital is particularly sensitive to para substituents, and it has been argued that the MLCT absorption band energy for various $Ru(NH_3)_5pyX^{2+}$ complexes is a function of its energy.[17] Hence, it is of interest to examine whether there exists a direct relationship between the stabilization of Ru(II) as indicated in the E_f values and the MLCT band energies. A linear relationship between E_f and ν_{max}(MLCT) has been suggested for substituted tris(bipyridine) complexes of several metals.[32] Plots of E_f vs. ν_{max}(MLCT) are approximately linear for the various benzonitrile derivatives and for those pyX complexes having para substituents (Figure 1). The major exception derives from the strongly electron-withdrawing 4-CF_3 substituent (pK_a of CF_3py is 2.6)[33] incapable of direct π interaction with the pyridine orbitals. Meta-substituted pyridine complexes do not fall on the same plot but appear to follow a separate line. Whether a linear correlation has significance is questionable; however, the failure of the meta and para substituents to respond to the same function suggests that the E_f values are responsive to features other than simply the energy of the acceptor orbital in the MLCT transition. The position of the 4-CF_3py complex suggests that the σ-donor ability of the ligand is also important. Thus, it is noteworthy that a plot of E_f vs. pK_a for the meta-substituted complexes is also linear and the 4-Cl and 4-CF_3 species fall close to this line while para substituents having π-unsaturated character do not.

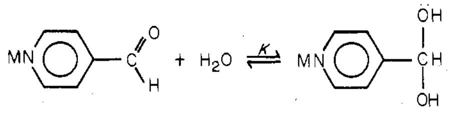
As demonstrated previously by the potentiometric technique,[24] bis complexes of unsaturated ligands, $Ru(NH_3)_4L_2{}^{3+}$, have larger formal reduction potentials than the corresponding

Scheme I



mono complexes. Interestingly, the cis and trans isomers display equivalent E_f values for the $Ru(NH_3)_4(py)_2^{3+/2+}$ couples. Since the pyridine rings of the cis complex can overlap with two of the metal dπ orbitals, the coincidence of E_f values would appear reasonable only if the planes of the two pyridine rings are perpendicular in the trans complex to allow similar interaction with two metal dπ orbitals. This conclusion contrasts with the argument of coplanarity for the trans complex pyridines based on consideration of the MLCT absorption band energies.[31]

(2) Rate Studies. A previous slow-scan CV study in this laboratory of $Ru(NH_3)_5(py\text{-}4\text{-}CHO)^{2+}$ gave irreversible behavior with peak separations of ~150 mV between the cathodic and anodic waves.[21] This behavior derives from the tendency of the aldehyde function to hydrate (eq 1). When



(1)

M is $Ru(NH_3)_5^{2+}$, the equilibrium is far to the left ($K_{II} < 0.1$),[17,21,34] but the opposite is noted when M is $Ru(NH_3)_5^{3+}$ ($K_{Ru(III)} > 10$).[34] The overall reaction is represented by Scheme I. Thus sufficiently rapid cyclic scans Ru(II) → Ru(III) → Ru(II) or Ru(III) → Ru(II) → Ru(III) should allow one to determine the E_f value for the aldehyde complex or hydrated analogue, respectively (Table I). Figure 2 illustrates the effect of scan speed on the CV of $Ru(NH_3)_5(py\text{-}4\text{-}CHO)^{2+}$ in 0.1 M HpTs. At 0.05 V s^{-1} single anodic and cathodic peaks are observed but with a separation of ~150 mV. At 0.5 V s^{-1} a single anodic peak but two cathodic peaks, one separated from the anodic peak by ~60 mV, are seen. At 5 V s^{-1} the reversible peak dominates the cathodic wave. Similar behavior was observed for the CV's of the Ru(III) form, prepared in solution by stoichiometric oxidation of the Ru(II) complex with cerium(IV). These results confirm the couples suggested by Scheme I.

The rate of the reaction subsequent to an electron-transfer step at the electrode may be determined by analysis of the CV curves. The decreased intensity of the cathodic peak of the reversible wave from the Ru(II) → Ru(III) → Ru(II) cycle is concluded to represent the relaxation of the ruthenium(III) aldehyde to the hydrate (Scheme I). The calculated rate constants (k_{obsd}) display a first-order dependence in acid concentration plus an acid-independent component, i.e.

$$k_{obsd} = k_{III}[H^+] + k_0 \qquad (2)$$

where $k_{III} = 14.9 \pm 1.4$ M^{-1} s^{-1} and $k_0 = 0.2 \pm 0.1$ s^{-1} at 25.0 °C. The relaxation rate is the sum of the forward and reverse rates; therefore

$$k_{obsd} = k_{3d} + k_{3h} \qquad (3)$$

However, equilibrium data indicate $k_{3h} >> k_{3d}$ in acidic solution, thus giving the relationship

$$k_{3h} \cong k_{III}[H^+] + k_0 \qquad (4)$$

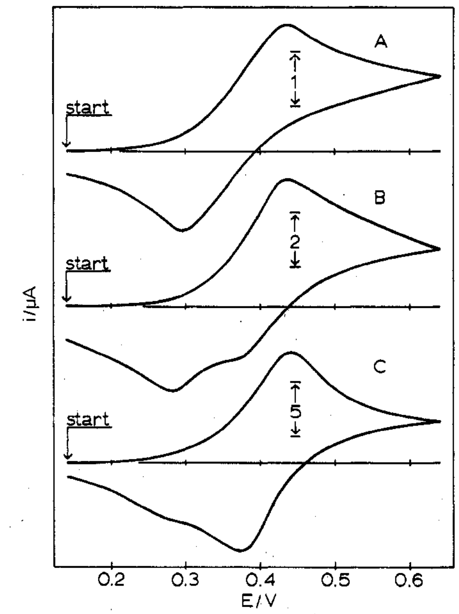


Figure 2. Cyclic voltammograms of $Ru(NH_3)_5py\text{-}4\text{-}CHO^{2+}$ in aqueous solution (pH 1.0; μ = 0.2 (HpTs/KpTs), 25 °C) at various scan speeds: A, 0.05 V s^{-1}; B, 0.5 V s^{-1}; C, 5.0 V s^{-1}.

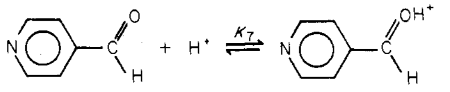
Similar treatment of the Ru(III) → Ru(II) → Ru(III) scan gives a rate constant k'_{obsd} for the relaxation of the ruthenium(II) 4-pyridinecarboxaldehyde complex initially in the hydrate form. The rate constant is first order in acid concentration with no clear indication of a nonzero intercept, i.e.

$$k'_{obsd} = k_{II}[H^+] \qquad (5)$$

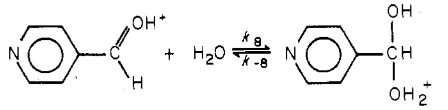
where $k_{II} = 45.7 \pm 1.8$ M^{-1} s^{-1} at 25.0 °C. Since $k_{2d} > 10k_{2h}$ in acidic solution (Scheme I), the following relationship holds

$$k_{2d} \cong k_{II}[H^+] \qquad (6)$$

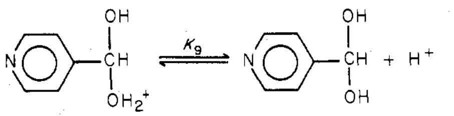
The second-order rate constant for the acid-catalyzed hydration of the free ligand (at 0 °C) is about 2 orders of magnitude faster[35] than k_{III} at 25 °C; however, this is consistent with the mechanism of eq 7–9. Since eq 7 and 9 are



(7)



(8)



(9)

simple proton-transfer steps in aqueous solution, they should be very rapid, leaving eq 8 as the probable rate-determining step. Therefore the hydration rate would depend on the basicity of the carbonyl group (K_7) and the rate of water attack (k_8) in the protonated carbonyl ($k_{III} = K_7k_8$). Coordination to Ru(III) would be expected to decrease K_7 but increase k_8. Ru(III) coordination has substantial effects on the basicity of ligands; however, it is probable that the positive charge on the protonated carbonyl would have the dominant role in accelerating H_2O attack and would attenuate the effect of Ru(III) on this step. In other words, Ru(III) coordination should decrease K_7 more than it accelerates k_8; hence, a k_{III}

value lower than observed for the free ligand would be expected. However, the acid-independent step noted for the free ligand (0.008 s^{-1} at 0 °C) may be accelerated somewhat by Ru(III) coordination.

Pocker and Meany[35] noted that metal ions such as Cu^{2+} had little catalytic effect on hydration of free 4-pyridinecarboxaldehyde but very large effects on the hydration of the ortho isomer. Consistent with this is our observation that a Ru(II) → Ru(III) → Ru(II) scan of $Ru(NH_3)_4$(2-pyridinecarboxaldehyde)$^{2+}$ leads to irreversible waves at even the fastest scans of our apparatus, implying that hydration is rapid ($k > 50$ s^{-1} at pH 1.0 and 4.7 at 25 °C). Similarly, dehydration of the ruthenium(II) 2-pyridinecarboxaldehyde hydrate was unmeasurable for Ru(III) → Ru(II) → Ru(III) scans implying a rate constant for relaxation in excess of 50 s^{-1} at these pH's. These results indicate that coordination to Ru(III) or Ru(II) greatly accelerates hydration or dehydration, respectively, of 2-pyridinecarboxaldehyde.

A previous stopped-flow kinetics study employed aqueous V^{2+} to reduce the ruthenium(III) hydrate complex (via an outer-sphere pathway) to the Ru(II) analogue thus allowing spectrophotometric observation of the relaxation to the aldehyde hydrate equilibrium.[34] The first-order rate constants measured were linearly dependent on $[H^+]$ with a value of k_{II} of 49.6 ± 1.5 M^{-1} s^{-1} at 25 °C. The agreement between the k_{II} values obtained by the electrochemical and stopped-flow methods is good. However, our data for the hydration of the Ru(III) complex are not consistent with the observation that small excesses of Ru(III) catalyzed the dehydration of the ruthenium(II) hydrate.[34] For the proposed explanation,[34] k_{3d} must be substantially larger than k_{2d}, a feature apparently inconsistent with our observations.

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Registry No. $Ru(NH_3)_5$py-3,5-$(CH_3)_2^{3+}$, 58560-84-2; $Ru(NH_3)_5$py-3,5-$(CH_3)_2^{2+}$, 58560-85-3; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5py^{2+}$, 21360-09-8; $Ru(NH_3)_5$py-4-$CH(OH)_2^{3+}$, 58580-98-6; $Ru(NH_3)_5$py-4-$CH(OH)_2^{2+}$, 19482-33-8; $Ru(NH_3)_5$py-4-Cl^{3+}, 58560-86-4; $Ru(NH_3)_5$py-4-Cl^{2+}, 58560-87-5; $Ru(NH_3)_5$py-3-$CONH_2^{3+}$, 50762-76-0; $Ru(NH_3)_5$py-3-$CONH_2^{2+}$, 19471-62-6; $Ru(NH_3)_5$py-3-Cl^{3+}, 58560-88-6; $Ru(NH_3)_5$py-3-Cl^{2+}, 19471-60-4; $Ru(NH_3)_5$py-4-$CONH_2^{3+}$, 46372-32-1; $Ru(NH_3)_5$py-4-$CONH_2^{2+}$, 19471-53-5; $Ru(NH_3)_5$py-4-CO_2H^{3+}, 58560-89-7; $Ru(NH_3)_5$py-4-CO_2H^{2+}, 58560-90-0; $Ru(NH_3)_5$py-4-$CO_2CH_3^{3+}$, 46479-04-3; $Ru(NH_3)_5$py-4-$CO_2CH_3^{2+}$, 19471-54-6; $Ru(NH_3)_5$py-4-$COCH_3^{3+}$, 58560-91-1; $Ru(NH_3)_5$py-4-$COCH_3^{2+}$, 52544-51-1; $Ru(NH_3)_5$py-4-CF_3^{3+}, 58560-92-2; $Ru(NH_3)_5$py-4-CF_3^{2+}, 52544-50-0; $Ru(NH_3)_5$py-4-CHO^{3+}, 35419-53-5; $Ru(NH_3)_5$py-4-CHO^{2+}, 19471-56-8; $Ru(NH_3)_5$py-3,5-Cl_2^{3+}, 58560-93-3; $Ru(NH_3)_5$py-3,5-Cl_2^{2+}, 52544-49-7; *trans*-$Ru(NH_3)_4py_2^{3+}$, 58560-94-4; *trans*-$Ru(NH_3)_4py_2^{2+}$, 46751-29-5; *cis*-$Ru(NH_3)_4py_2^{3+}$, 58560-95-5; *cis*-$Ru(NH_3)_4py_2^{2+}$, 46751-30-8; $Ru(NH_3)_5NCCH_3^{3+}$, 44819-54-7; $Ru(NH_3)_5NCCH_3^{2+}$, 26540-31-8; $Ru(NH_3)_5NCCH_2CH_3^{3+}$, 58560-96-6; $Ru(NH_3)_5NCCH_2CH_3^{2+}$, 58560-97-7; $Ru(NH_3)_5NCCH{=}CH_2^{3+}$, 44916-16-7; $Ru(NH_3)_5NCCH{=}CH_2^{2+}$, 44916-13-4; $Ru(NH_3)_5$NCPh-4-CH_3^{3+}, 58580-99-7; $Ru(NH_3)_5$NCPh-4-CH_3^{2+}, 58581-00-3; $Ru(NH_3)_5NCPh^{3+}$, 46343-59-3; $Ru(NH_3)_5NCPh^{2+}$, 31418-68-5; $Ru(NH_3)_5$NCPh-4-Cl^{3+}, 46458-95-1; $Ru(NH_3)_5$NCPh-4-Cl^{2+}, 58560-98-8; $Ru(NH_3)_5$NCPh-3-CN^{3+}, 46737-89-7; $Ru(NH_3)_5$NCPh-3-CN^{2+}, 46737-88-6; $Ru(NH_3)_5$NCPh-4-CN^{3+}, 58560-99-9; $Ru(NH_3)_5$NCPh-4-CN^{2+}, 46739-38-2; *cis*-$Ru(NH_3)_4(NCPh)_2^{3+}$, 58561-00-5; *cis*-$Ru(NH_3)_4(NCPh)_2^{2+}$, 47101-81-5; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_5H_2O^{3+}$, 25590-52-7; $Ru(NH_3)_5H_2O^{2+}$, 21393-88-4; $Ru(NH_3)_5Cl^{2+}$, 21560-19-0; $Ru(NH_3)_5Cl^{+}$, 29933-34-4.

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